A THESIS

PRESENTED TO

THE FACULTY OF SCIENCE ,

THE UNIVERSITY OF BIRMINGHAM .

OCTOBER , 1939

For the Degree of

PHILOSOPHIAE DOCTOR

By

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The author wishes to express his sincere thanks to Dr.E.G.Cox for valuable advice and assistance, and for helpful criticism throughout these investigations.

To Sir G.T.Morgan and Professor W.Wardlaw he recognises his indebtedness and records his gratitude for the crystal specimens supplied for the purpose of this work.

For granting the facilities for the work the author is deeply grateful to Professor W.N.Haworth and the University of Birmingham Authorities.

A

CONTRIBUTION TO THE STEREOCHEMISTRY OF QUADRICOVALENT METALS.

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PART ONE.

EXPERIMENTAL METHODS AND TECHNIQUE.

CRYSTALLOGRAPHIC EXAMINATION.

Preliminary Examination.

It is useful before proceeding to the investigation of a crystalline substance by X-ray methods to carry out a preliminary examination of it under the microscope. More often than not, the polarising microscope is used, firstly as an ordinary microscope and subsequently in its special capacity.

This first examination provides the investigator with much valuable information and he often obtains facts which act as an excellent guide to the lines which he shall adapt when he begins the goniometric observations, and these coupled with the general ideas gained previously provide a first class ground on which to build the more detailed X-ray investigation.

At the outset one sees immediately whether or not there is one or more forms of crystal. Furthermore, the presence of foreign substances is instantly discernible. At this point the investigator can decide whether re-crystallisation is necessary - whether the specimen is good enough for goniometric measurements to be carried out upon it.

It is generally recognised that many crystals belonging to the different crystal systems have a particular appearance when viewed under the microscope, and though this is not always the case yet it is a fact of fundamental importance and such appearances often occur. Besides, an early knowledge of the system to which the crystal belongs is exceedingly helpful.

Again it often happens that certain prominent faces are easily distinguishable and by their orientation together with that of other less prominent ones the investigator can obtain information with regard to the elements of symmetry in the crystal. The zones which occur can often be judged with a fair degree of accuracy, and one can form a good idea of the disposition of the principal axes, a gain of great usefulness in subsequent goniometric examination.

At this early stage in the examination of the crystals suitable specimens are picked out for later use in the X-ray photography.

Examination in polarised light reveals whether the crystals belong to the isotropic or anisotropic class, whether they are uniaxial or biaxial, such information being obtained from the interference figures and extinction directions.

The optical examination of the crystals used in the present work was carried out on a Swift-Dick polarising microscope.

GONIOMETRY.

It is well known that the measurement of interfacial angles is of great value in providing a means of establishing the authenticity of the specimen under consideration. Furthermore when crystals of the same substance differ widely as regards habit a knowledge of the value of interfacial angles enables one quickly to obtain the relative disposition of the crystallographic axes.

In the present work goniometric measurements were made on the ester of Roussin's salt for the purpose of checking the results obtained against those formulated by O.Pavel (50) . But in the instance of Tripyridyl zinc chloride full goniometric measurements were taken which subsequently served as data both for the stereographic projections and the crystal drawings. The results obtained over a wide range of crystals showed good agreement,for the crystals were well developed, particularly so as regards the second form.

The apparatus employed was the Unicam photo-goniometer, the telescope being fixed at right angles to the illuminating beam which passed through the aperture which normally admitted the X-ray beam.

The crystal is mounted and set in the following manner.

It is attached to a fine fibre of glass either by means of seccotine or soft red wax, the fibre being mounted on a mass of plasticine fixed on the crystal holder, a hollow ebonite cylinder which tapers at the upper end. This is

fixed on to a pair of goniometer arcs at right angles to each other, and thus angular adjustment is possible in directions parallel to these. The arcs are fixed to a spindle which is mounted on a turntable graduated in minutes of arc. By means of the arcs any adjustments necessary to bring some crystallographic axis into coincidence with the axis of rotation can be made. An accurate centring of the crystal can also be carried out by means of a double cross slide arrangement fitted with centring screws.

The method adppted for setting the crystal depends on the crystal itself.

When it possesses several well formed faces in a zone, a preliminary approximate adjustment is first made by eye. The turntable is rotated so that one of the arcs is parallel to the telescope. The crystal is then set up so that one of the faces is parallel to this particular arc. It is then adjusted approximately perpendicular. The crystal is then viewed through the telescope and the disposition of the edge of a face in the zone in respect to the cross-wires observed. The turntable is then rotated through 180° and the new position noted. If the cross wire is not truly vertical the inclination of the crystal in the two positions will not be the same. The cross wire is then moved until it bisects the angle between the two positions of the crystal. An adjustment is then made on the crystal so that an edge parallel to the zone axis is parallel to the vertical cross wire. The turntable is then rotated through 90° and the

SAME procedure followed making adjustments on the second arc. The crystal is centred by means of the cross slide arrangement and centring screws. It is now in a position with the zone axis in coincidence with the axis of rotation of the instrument.

If the crystal faces are small but well developed it may be set by making use of the signal images obtained when the microscope is used as a telescope. Suppose the faces under observation are in the [c] zone. Two faces in this zone, (hk0) and ($\bar{h}\bar{k}$0) will send out reflections traversing the same path across the field of view only if they are parallel to the axis of rotation of the instrument. If several faces are observed the setting of the crystal in the vertical position can be done very accurately by making careful adjustments necessary to fulfil the conditions referred to.

In the measurement of angles, those angles between the normals to the faces are considered as the crystal angles rather than the angles of intersection of the faces. It is more convenient.

For the measurement of the angles the signal-image obtained when the microscope is used as a telescope is employed, and it is usual to work both with the telescope auxiliary lens in and out of position in order to make sure that the correct face is observed.

It has already been stated that several crystals were used. These furnished the data from which the mean

results shown in the experimental section were obtained.

SECTION II.

X-RAY TECHNIQUE.

X-ray PHOTOGRAPHY.

Powder photographs and Laue photographs were not used during this investigation.

The Rotating crystal method .

Here the necessary diffraction data are provided by oscillating or rotating a crystal in a beam of monochromatic x-rays. The interpretation of the resulting photograph involves certain geometrical considerations which assigns great power to this method , particularly in the instance of crystals possessing complex structures.

In the present work the diffraction pattern was registered on a photographic film contained in a cylindrical camera. In the camera itself a small lead stop is fitted so that it impedes the direct beam and so prevents general fogging of the film. The stop can be turned out of position for an instant so as to obtain a record of the central spot marking the position of the undeviated beam.

By this method two kinds of photograph can be obtained, firstly the complete rotation photograph, involving the turning of the crystal through a number of complete revolutions and secondly the oscillation photograph where the crystal is made to oscillate backwards and forwards with a constant angular speed throughout a definitely chosen angular range, usually 5°, 10°, 15°, or 20°. The oscillating movement is given to the spindle of the crystal holder which remains in contact with a heart shaped cam, so constructed that, turning with uniform speed it imparts to the

'rocking arm ' a uniform angular motion. This of course is imparted to the crystal itself. The range of oscillation can be set by referring to the graduated turntable on the instrument.

A small crystal is chosen whose dimensions are of the order 0.1 to 0.5 mm. If the crystal is too small the task of setting is difficult and tedious. On the other hand if it is too large, several factors are involved which make its use unsatisfactory. Such factors are the shape of the crystal, the non-homogeneity of the x-ray beam over a cross sectional area which is large, and the increased absorption.

Rotation photographs are usually taken with the axis of rotation of the crystal in coincidence with some principal crystallographic axis. The method of setting has already been outlined in the section on goniometry (page 3).

But often the faces are poorly defined, and again the axis of rotation amy not be a principal axis. In this event the crystal is set by means of x-rays. It is mounted with a pair of faces parallel to one of the arcs and centred. The turntable is then turned to such a position that one of the arcs is parallel to the direction of the beam. The crystal is then set to oscillate through a small range while a photograph is being taken. The crystal is then rotated through 180° and a second photograph recorded, this being registered on the same film. The range of oscillation adopted is such that the first orders of the face which is roughly parallel to the arc are recorded . Should this face prove not parrallel to the

axis of rotation, the two spots at the same distance from the central spot due to the undeviated beam, will be displaced vertically. This displacement is measured as also is the distance of the spot from the central spot. From these the angular displacement of the axis of the crystal in a plane which contains both the arc and the axis of rotation can be obtained. The crystal is then moved upon the arc in accordance with the result obtained. But it is impossible to differentiate between the spots and consequently , while the angular displacement can be calculated the same does not hold regarding the direction. The direction is chosen arbitrarily and a second series of photographs taken to ascertain whether the correct direction has been adopted. When this is settled, the crystal is rotated through 90° and the procedure repeated with the other arc.

During the present investigation rotation photographs were taken for the purpose of axis measurement. The length of primitive translation in the crystalline substance, in a direction ~~pral~~ parallel to the axis of rotation is obtained from the following equation :

$$L = n\lambda \operatorname{cosec} \tan^{-1} x/R$$

where n = number of layer line ; x its distance from the zero layer line ; R the radius of the camera ; λ the wavelength of radiation employed, the K_{α} radiation from copper, this being very convenient for it tends to give a well spread out pattern. The β lines are suppressed by using a nickel filter of 0.001 inch thickness.

The value of x was obtained as follows. The photograph is fixed firmly on to a piece of white paper. Over the film rests a piece of plate glass 4" X 1" X ¼", two V-shaped incisions having been made at the midpoint of each end, the apices being joined by a diamond scratch. This line is arranged so that it coincides with a layer line on the photograph. Pin pricks are then made at the apices of the V-shaped incisions. This procedure is repeated for every layer line and the distances between the pin pricks measured with the travelling microscope.

OSCILLATION PHOTOGRAPHS.

Sometimes the interpretation of rotation photographs results in certain ambiguities. Consequently the rotation photograph is supplemented by oscillation photographs. Often in the case of crystals of complex structure the diffracted beams have some overlap on the layer lines and it is difficult to assign indices with certainty. But the oscillation photograph has a more limited range of possible diffractions which leads to a correct evaluation of the indices. Furthermore the oscillation photograph is useful in bringing out weak spots which might be overlooked in the rotation photograph, because in the former the possibility exists of greatly increased intensity of the diffraction spots which are not so intensely recorded on the rotation photograph.

Thus in the determination of the space-groups it is imperative to know the indices of the planes responsible for the diffraction pattern. Oscillation photographs of 10°, 15°

with an overlap of 5° were usually used during this investigation.

When making the oscillation photograph the motion of the crystal is confined to a turning to and fro through a fixed small arc, therefore any spots which appear on the film can only come from the planes in the crystal which pass through the correct position as the crystal moves within the fixed arc. To determine these planes it is essential to know the orientation of the crystal with regard to the x-ray beam. The reading on the scale can be taken and the orientation of the crystal with respect to the direction of the beam is quickly determined at any phase of the rotation.

When the orientation of the crystal is known it is not difficult to determine by graphical methods what planes will pass through a diffracting position during an oscillation of known range. In order to interpret the oscillation photographs use is made of the conception of the reciprocal net.

The Reciprocal Lattice .

The conception of the reciprocal lattice was first put forward by P.P.Ewald (44) . But the method used for indexing the spots on oscillation photographs is that described by J.D.Bernal (45).

Any set of planes of spacing d can be represented by a single point at a distance x from the origin , such that

$$dx = \text{constant} = k \ .$$

Consequently the orders of a plane whose spacing is d_1 will appear as points along a straight line at distances

$\frac{k}{d_1}$, $\frac{2k}{d_2}$, ...$\frac{nk}{d_n}$

If this idea is extended to two dimensions, all the planes in a given zone will be represented by a series of points lying in a plane, the distance of each point from the origin being related to the spacing of the plane whose index it bears from the relationship indicated previously.

The constant k is chosen equal to λ , the wavelength of the x-radiation employed, and according to Bernal the distance of any point from the origin will be $\frac{\lambda}{d} = 2\sin\theta = \xi$.
Again, by extending these principles to three dimensions the whole conception of the reciprocal lattice is obtained, including every set of planes.

The position of a point in the reciprocal lattice is expressed in terms of cylindrical co-ordinates ξ ζ and ω , the axes of the co-ordinate system being chosen to coincide with the axis of rotation of the crystal. Thus the origin of co-ordinates lies at the centre of the crystal and coincides with the origin of the reciprocal lattice. ξ is the coordinate which measures the radial distance of the point, ζ measures its distance above or below the equatorial plane perpendicular to the axis of rotation, ω measures the angle of rotation of the crystal and is indeterminate in the case of a complete rotation.

The problem of relating these coordinates ξ and ζ in the reciprocal lattice to the coordinates of the spots corresponding to the point on the film has been worked out by J.D.Bernal. Equations have been deduced but their use

would prove very laborious and consequently graphical methods are employed. Charts have been prepared for reading values of ξ and ζ from the photograph. These are laid over the photograph and the values of ξ and ζ corresponding to all the diffraction spots can be read off directly.

It has been shown by P.P.Ewald (44) that diffraction can only take place when the point in the reciprocal lattice representing the plane in question intersects the surface of the sphere of diffraction. (The reciprocal lattice is regarded as stationary while the x-ray beam and the sphere of diffraction revolves about the axis of rotation in the opposite sense).

The solid figure cut out in space by the surface of the sphere is a torus and all the points in the reciprocal lattice which can diffract during a complete rotation lie in it. But in the oscillation photograph the x-ray beam moves only through a small angle with regard to the stationary lattice. Consequently the solid figure cut out by the spherical surface consists of two cup-shaped solids whose interiors contain all points of the reciprocal lattice which can diffract within the limits laid down by the oscillation.

In the interpretation of oscillation photographs the layer lines are considered separately. Consequently on the equatorial plane of the limiting sphere, the surface of the sphere of diffraction has swept out two lune-shaped portions and all the lattice points lying within these lunes have passed through the position of diffraction.

They will be recorded on the zero layer line in the photograph.

For the analysis of the photographs the reciprocal nets are drawn for each zone axis under consideration . The net is the two-dimensional conceeption already referred to. The scale employed is $1\xi = 10$ cms , and circles increasing in radius by 0.5 cm. from 1 cm. to 18 cms. are constructed with their centres at the origin. These serve as a scale for measuring the ξ values. From theoretical considerations the maximum value of ξ is 2.0 . But spots beyond 1.8 merge into the general background of the film. The lunes used to obtain the indices of the planes which can theoretically give rise to spots on the photograph are drawn on tracing cloth or celluloid and placed over the reciprocal net in such a position that the central line indicates the course of the beam. The circles on the lunes are sections cut off from the cup-shaped solid figures by the plane of the net. Hence all the points which appear between the circles are those which represent planes which can , from theoretical considerations, give rise to the diffraction pattern on the layer line under consideration.

A table is then drawn up for each photograph. This shows the planes which theoretically could give rise to spots, their ξ values are also added and compared with those of the spots on the zero layer line of the photograph. These vales are obtained from J.D.Bernal's Chart II which has been reduced to the correct size. In the instance of spots not occurring on the zero layer line lunes of appropriate

radius have to be used. Futhermore , if the crystals are other than orthogonal, the origin must be moved.

This procedure is adopted for every photograph in the zone under consideration. Ultimately one can obtain a list of planes which could have given rise to diffraction spots but have not done so. The absence of these spots may be due to interference within the molecule or to interference between molecules because of symmetry relations. When such is the case the indices of the missing planes obey some law and from this the space group can be deduced.

The set of oscillation photographs taken was usually such as to cover 180.°

MEASUREMENT OF ABSOLUTE INTENSITIES .

This was carried out using the (400) Rocksalt reflection as the standard of measurement, its value being 0.38×10^{-4}.

The film is first exposed for the Rocksalt reflection . The Rocksalt is then replaced by the crystal under consideration and the line due to the first order of planes,(001) in the case of the ester of Roussin's salt, registered on the same film. An accurate knowledge of the exposure assigned to each is essential, and fluctuations in the tube must be eliminated. This is done by heating the filament from a large capacity accumulator. These factors are of fundamental importance if the spectra are to be directly comparable. Both crystals are oscillated with the same speed about a position at which the reflections take place.

The exposures are governed by means of a penny-in-the slot watt hour meter adjusted so that one shilling passing through the meter signifies one kilowatt hour.

The spectra registered should possess approximately the same density in order to reduce errors in photometry to a minimum. This is done by altering the intensity of the x-ray beam by means of aluminium screens placed between the tube and the slit system of the camera; in this work the Pye Universal X-ray photogoniometer was employed. The screens have previously been assigned a factor which indicates the amount by which the intensity is cut down.

The crystal is set up with the extended face

parallel to the axis of rotation and centred so that the axis lies in the plane of the face and as near as possible in the middle of it. In the instrument used the arcs carrying the crystal are interchangeable with another set on which the Rock salt is mounted. This set is different from the first. It is fitted with an auxiliary centring device so that the Rock salt can be adjusted about the (400) face without interfering with the previously set crystal. The x-ray beam enters the camera through a vertical slit whose width can be varied. Consequently the spectra obtained are vertical lines : it is usual to use a slit of 0.20 mm. width.

An exposure is first made for the Rock salt while the crystal is oscillated through a five degree range . The camera is then carefully removed, the Rock salt complete with its arcs is lifted off and replaced by the arcs carrying the crystal. The camera is then replaced, the aluminium screen inserted between the slit system and the camera, when the exposure is registered for the crystal. Duplicate or triplicate exposures are usually made so as to obtain a mean figure for the values of the intensities.

Measurement of the intensities of the spectra.

These were made by means of the Photo-Electric Micro-photometer, an illustration of which is shown in Fig. 1, which is accompanied by a diagrammatic representation of the optical arrangement , Fig. 2. From opposite sides of the straight filament gas filled lamp B , two beams of light are symmetrically reflected by two prisms M M mounted on each

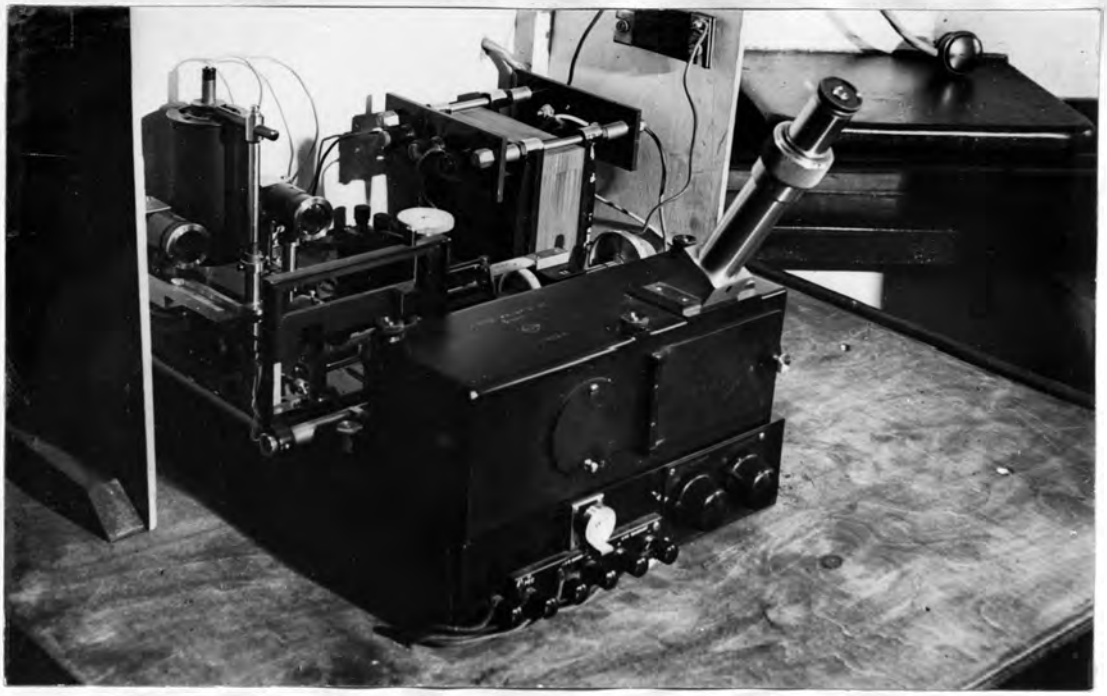


Fig 1.

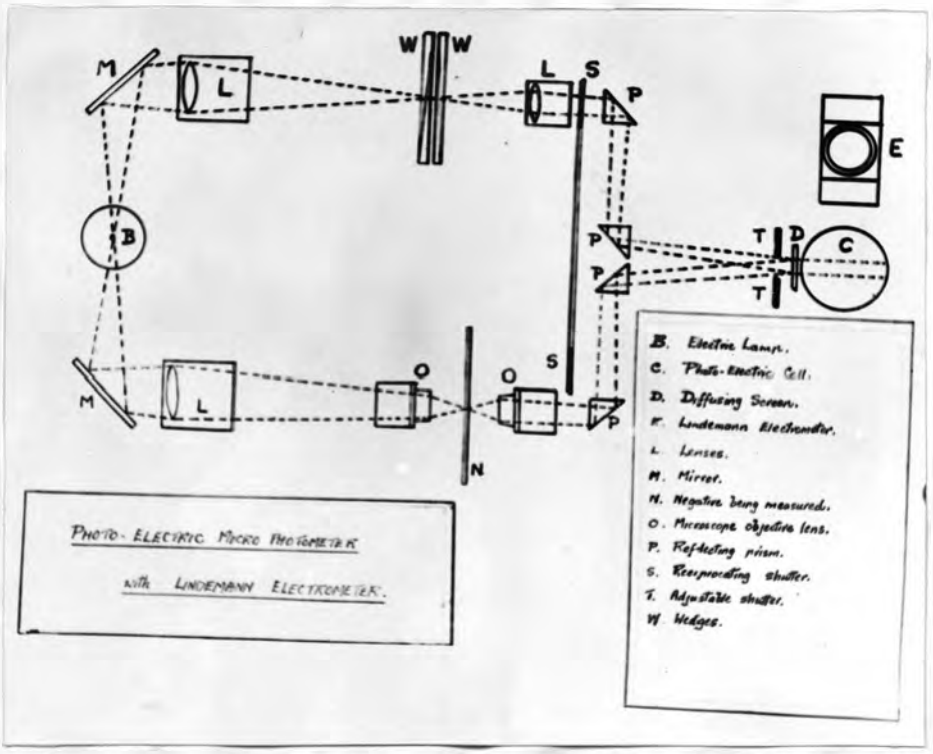

M
L
W
W
L
S
P
E
B
T
D
C
P
P
T
M
L
O
O
S
P
N
B. Electric Lamps.
C. Photo-electric Cell.
D. Diffusing Screen.
E. Lindemann Electrometer.
L. Lenses.
M. Mirrors.
N. Negative being measured.
O. Microscope objective lens.
P. Reflecting prism.
S. Reciprocating shutter.
T. Adjustable shutter.
W. Wedges.
PHOTO-ELECTRIC MICRO PHOTOMETER
WITH LINDEMANN ELECTROMETER.

Fig 2.

side of the lamp . They then pass through different optical systems on to the slit T which is situated in front of the photo-electric cell. One beam passes through a condenser L, and a microscope objective O_1 which forms an image I of the filament on the surface of a photographic film mounted at N. A second objective, O_2, identical with O_1 and two reflecting prisms P form a magnified image I in the plane of the adjustable shutter T. The second beam passes through a condenser similar to L, but adjusted to form an image of the filament in a plane half way between the two wedges W . A lens L_3 and two reflecting prisms form an image in the plane of the slit T, coincident with the image from the first beam. At the point where the two beams have the same diameter a reciprocating shutter S is mounted, and the positions of the two beams are so arranged that manipulation of the shutter opens up the path of the one beam at the same rate as it closes that of the other. The plate N, carrying the photograph to be measured, is mounted on a mechanical stage having a micrometer movement in the direction of its length and a screw movement across its width. The wedges W have a lateral micrometer movement which can result in a density change of three. The photo-electric current is measured by means of an alcohol-xylol resistance and a Lindeman electrometer. The position of the electrometer needle is observed through a microscope mounted in a light- tight box which covers the prisms P and the slit T and upon which the reciprocating shutter S is mounted.

The photograph is mounted at N and adjusted so that,

Mic. Reading.	Wedge reading
28.28	1169
28.29	do
28.30	do
28.31	do
28.32	do
28.33	do
28.34	do
28.35	do
28.36	do
28.37	1160
28.38	do
28.39	do
28.40	do
28.41	do
28.42	do
28.43	do
28.44	1172
28.45	1180
	20993
28.46	1180
28.47	1195
28.48	1210
28.49	1225
28.50	1237
28.51	1237
28.52	1247
28.53	1255
28.54	1255
28.55	1255
28.56	1265
28.57	1278
28.58	1278
28.59	1278
28.60	1278
28.61	1278
28.62	1265
28.63	1265

Micr. reading	Wedge reading.
28.64	1255
28.65	1245
28.66	12.32
28.67	1232
28.68	1232
28.69	1232
28.70	1218
28.71	1218
28.72	1212
28.73	1200
28.74	1200
28.75	1190
28.76	1180
	38225
28.77	1170
28.78	do
28.79	do
28.80	do
28.81	do
28.82	do
28.83	do
28.84	do
28.85	do
	10540

upon turning the micrometer screw the line to be measured passes through the image of the lamp filament. As the line passes through the image at N, its image will travel across the slit T , excluding some of the light, so causing a deflection of the needle of the electrometer. The photograph is moved at intervals of 0.01 mm. and at each point the wedges are adjusted so that when the shutter is manipulated no movement is registered by the electrometer needle. Measurements were made at distances of 0.25mm. on either side of the line so as to determine the density of the background.

The photometer wedge readings were tabulated against the micrometer readings which recorded the position of the line. The table facing this page shows the results obtained for (005) of the ester of Roussin's salt.

It will be noticed that the peak lies at 28.58 with a value of 1278 on the wedge. This value diminishes gradually both before and after 28.58 until the values of 28.45 and 28.76 are reached. Hence the peak region extends from 28.45 to 28.76 and includes the line and the background. From these figures until the beginning and the end of the readings the background value is observed.

Hence :-

18 background readings = 20993

9 ditto = 10540

27 ditto = 31533

But peak plus 31 background readings = 38225

Therefore 31 background readings $= \frac{31533 \times 31}{27}$

$= 36210$

Therefore Peak 38225 -36210 = 2015

This value is then compared with the Rock salt value obtained in a similar manner, and from the same photograph. The ratio Ester : Rock salt is then calculated after making the necessary correction for the aluminium screen (if one has been used) . In this case no screen was used for the ester but a 10.19 X screen was employed when registering the Rock salt line. The Rock salt value proved to be 7496 and with the screen correction 7496 X 10.19 .

Hence the ratio Ester ; Rock salt equals 2015 : 7496 X 10.19

equals 0.0264 .

When this is multiplied by 0.38×10^{-4} the absolute intensity value (ρ) is obtained. In this case 1.003×10^{-6}.

From these absolute intensity values, the structure amplitudes can be calculated but their sign is not determined.

The integrated reflection from a crystal face is given by the formula

$$\rho = \frac{Q}{2\mu} = \frac{N^2 \times e^4 \times \lambda^3}{4\mu m^2 c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot F^2$$

where Q = integrated intensity, $N = 1/V$, volume of unit cell in c.c. $\frac{1+\cos^2 2\theta}{\sin 2\theta}$ = Lorentz polarisation factor (L) ,

θ = the glancing angle

$\frac{e^4 \lambda^3}{m^2 c^4} = 28.93 \times 10^{-50}$ for $Cu_{K\alpha}$ radiation

μ = linear absorption coefficient , F = structure amplitude.

then $\rho = \frac{N^2 e^4 \lambda^3}{4\mu m^2 c^4} . L . F^2$

and since $N = 1/V$ and $e^4\lambda^3 / m^2 c^4 = 28.93 \times 10^{-50}$

we have $\rho = \frac{L F^2 \times 28.93 \times 10^{-50}}{4\mu V^2}$

$\therefore F^2 = 4\mu V^2 / L \times 28.93 \times 10^{-50} = \rho / L . 4\mu V^2 / 28.93 \times 10^{-50} = \rho / L . k$

where $k = 4\mu V^2 / 28.93 \times 10^{-50}$

But $\mu = 227.8$ and $V = 636.5 \times 10^{-24}$ c.c.

$$k = \frac{4 \times 227.8 \times 636.5^2 \times 10^{-48}}{28.93 \times 10^{-50}} \quad \frac{4 \times 227.8 \times 636.5^2 \times 10^2}{28.93} = 1.276 \times 10^9$$

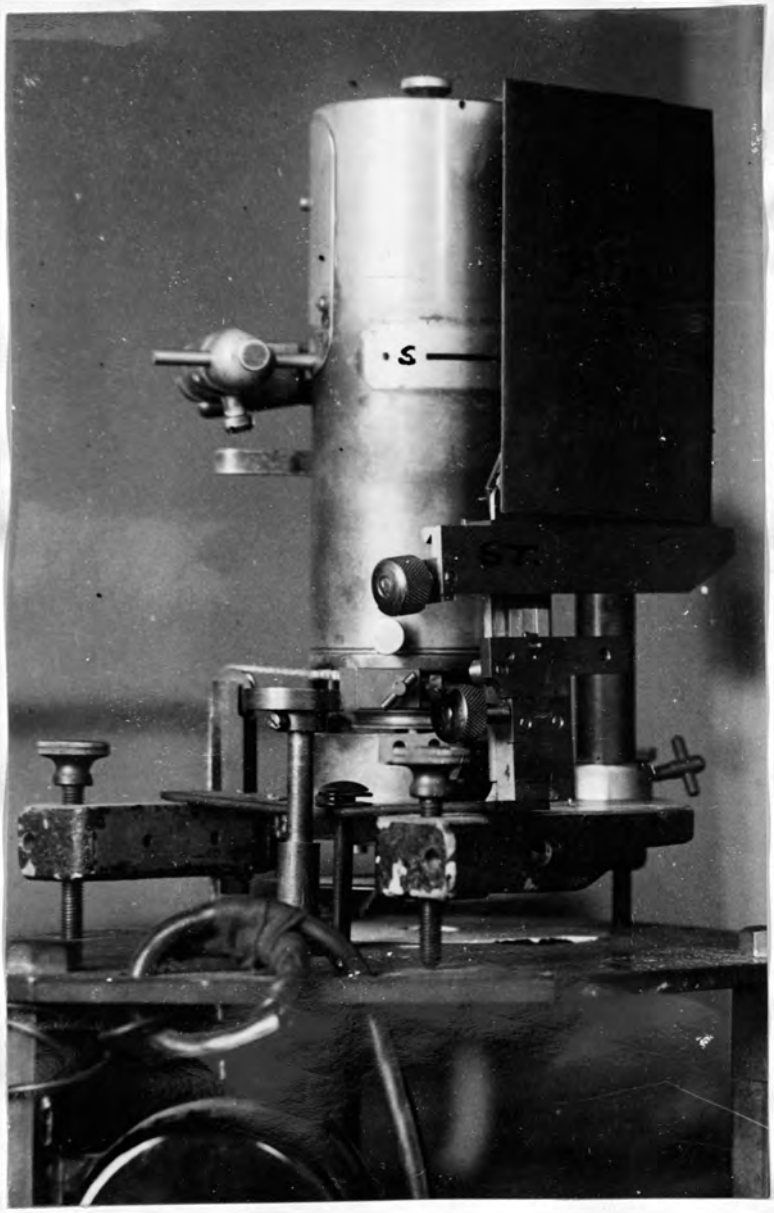
$\therefore \quad F^2 = 1.276 \times 10^9 \times \rho / L$

But $\rho = 1.003 \times 10^{-6}$ and $L = 1.15$

$$F^2 = \frac{1.276 \times 10^9 \times 1.003 \times 10^{-6}}{1.15}$$

$$F = \pm 10 \sqrt{\frac{12.76}{1.15}}$$

$$= \pm \underline{33.32}$$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MEASUREMENT OF RELATIVE INTENSITIES .

Relative intensities were measured for the spots occurring on the zero layer line of the [c] axis oscillation photographs registered for Tripyridyl zinc chloride , the results being used for preparing the Patterson projection.

The measurement was carried out by eye estimation by comparison with standard calibration photographs previously prepared and to be described below. The scale used was an arbitrary one, and this is sufficient to enable one to make comparisons among the peaks themselves . This will be referred to later in the discussion of the Patterson synthesis.

THE CALIBRATION PHOTOGRAPHS .

These are prepared by registering oscillation photographs over a small angular range of five degrees, using the same crystals, the same films , and the same conditions of development as were employed when registering the original [c] axis oscillation photographs.

The oscillation photographs were first examined and a spot selected which had such an intensity that one could estimate that when given about one-fifth the normal exposure it would still show a measurable intensity. Such a spot proved to be (020) when identified on Bernal's Chart II. Reference was then made to the [C] axis reciprocal net and the position found at which the (020) reflection would flash out. The crystal was set up and an oscillation photograph about this position over a five degree range was registered in a special way.

The Sauter camera was used after removing the zero layer line cover, which is a strip of metal covering a slit S , through which all the zero layer line reflections can pass. Behind this was arranged a plate holder P containing two films. It could be given a vertical movement by means of a travelling stage ST to which it was attached. In this way several spots could be separately registered by moving the stage after each exposure. Thus on the same film a series of spots one below the other were registered on the same film .

By trial and error it was found that 12 minutes was a suitable exposure to give. After registering the spot an aluminium screen was inserted between the camera and the film, the stage raised $\frac{1}{4}$ inch and another exposure registered. This procedure was repeated for 9 different screens in all, their values being 1.41X ; 1.93X ; 2.40X 4.47X ; 10.19X ; and 20.10X; 28.40X ; 37.40X and 100.86X . The percentage intensity was then calculated on the basis that the spot registered without screen possessed 100% intensity. Expressed as percentages the ten recorded spots were 100 ; 71 ; 52 ; 41.5 ; 22.5 ; 10 ; 5 ; 3.5 ; 2.5 ; and 1 % . The plate holder was then returned toits original position and then moved laterally and the whole process repeated giving seven minutes exposure instead of the previous twelve . The values assigned to these spots were each 7/12 of the corresponding spot in the first series. Thus were obtained two films with 18 spots each possessing an assigned intensity value. The films were

bound up in the form of lantern slides. By comparing one or other of the calibration records with a complete set of oscillation photographs an intensity value can be assigned to every spot which has been registered.

During the preparation of these photographs strict attention was paid to development. Each photograph was timed for five minutes in Ilford developer, the film being agitated throughout the development. Ilfex Blue Base films were used, these being the same as those employed during the recording of the original [c] axis oscillation photographs.

THE PATTERSON SYNTHESIS .

Although the Fourier synthesis affords an excellent means of representing the electron density throughout a structure as projected in any plane therein, in practice its direct application to a complicated structure is a matter of great difficulty. While intensity measurements supply the magnitudes of all the terms of the Fourier synthesis no information is afforded as regards signs. These can only be obtained when positions of most of the atoms in the structure have been found by other means. It has been shown by A.L.Patterson (46) that if a Fourier synthesis is made, using the intensities of the x-ray reflections as coefficients of the corresponding terms in the synthesis, the resultant diagram is such that the vectors joining the origin to each of the peaks represent the interatomic distances in the structure.

In the general case the Patterson series is of the form $P_{(xyz)} = \sum_h \sum_k \sum_l |F^2_{hkl}| \cos 2\pi(hx + ky + lz)$

In order to be manageable this is usually reduced to a two-dimensional series

$$P'_{(xy0)} = \sum_h \sum_k |F_{hk0}|^2 \cos 2\pi(hx + ky)$$

in which the F's of only one zone are used.

The general term F^2 includes the following individual terms

F_{hkl} , $F_{\bar{h}kl}$, $F_{h\bar{k}l}$, $F_{hk\bar{l}}$, $F_{\bar{h}\bar{k}l}$, $F_{h\bar{k}\bar{l}}$, $F_{\bar{h}k\bar{l}}$, $F_{\bar{h}\bar{k}\bar{l}}$.

In the case of Tripyridyl zinc chloride the projection was made upon the (001) plane and consequently l equals 0 when the above eight terms are reduced to

F_{hk0} ; $F_{\bar{h}k0}$; $F_{h\bar{k}0}$; $F_{\bar{h}\bar{k}0}$.

The general term can therefore be expressed as :-

1. $\Sigma|F_{hk0}|\ \cos 2\pi(hx+ky)$

2. $\Sigma|F_{\bar{h}k0}|\ \cos 2\pi(-hx\ ky)$

3. $\Sigma|F_{h\bar{k}0}|\ \cos 2\pi(hx-ky)$

4. $\Sigma|F_{\bar{h}\bar{k}0}|\ \cos 2\pi(-hx-ky)$

And since $\cos\theta = \cos(-\theta)$ we can write

1. $\Sigma|F_{hk0}|^2\ \cos 2\pi(hx+ky)$

2. $\Sigma|F_{\bar{h}k0}|^2\ \cos 2\pi(hx-ky)$

3. $\Sigma|F_{h\bar{k}0}|^2\ \cos 2\pi(hx-ky)$

4. $\Sigma|F_{\bar{h}\bar{k}0}|^2\ \cos 2\pi(hx\ ky)$

The relationship existing between these four terms depends upon the space group assigned to the substance. In the instance of tripyridyl zinc chloride (I) the space group is C_{2h}^6 or C_s^4 . When (h+k) is even and l is even the following relationships hold,

$$F_{hk0} = F_{\bar{h}k0} = F_{h\bar{k}0} = F_{\bar{h}\bar{k}0}$$

$$\therefore P'_{xy0} = 2\Sigma\Big[F^2_{hk0}\cos 2\pi(hx+ky) + F^2_{hk0}\cos 2\pi(hx-ky) + F^2_{hk0}\cos 2\pi(hx-ky) + F^2_{hk0}\cos 2\pi(hx+ky)$$

$$= 2\sum_{0}^{H}\sum_{0}^{K}\Big[F^2_{hk0}\ \cos 2\pi(hx+ky) + \cos 2\pi(hx-ky)\Big]$$

$$\therefore P'_{xy0} = 2\sum_{0}^{H}\sum_{0}^{K} F^2_{hk0}\ [\cos 2\pi hx\cos 2\pi ky - \sin 2\ hx\sin 2\pi ky + \cos 2\pi hx\cos 2\pi ky + \sin 2\pi hx\sin 2\pi ky]$$

$$= 2\sum_{0}^{H}\sum_{0}^{K} |F_{hk0}|^2\ 2\cos 2\pi hx\cos 2\pi ky$$

$$4\sum_{0}^{H}\sum_{0}^{K} |F_{hk0}|^2\ \cos 2\pi hx\cos 2\pi ky$$

This expression can be written

$$P'_{xy0} = \sum_{H}^{0} F^2_{hk0}\cos 2\pi hx \sum_{0}^{K}\cos 2\pi ky$$

Since the planes(0k0) and (h00) can only occur twice the values of F^2 used in the summation are half those obtained

experimentally. F^2_{ooo} if included would be divided by 4. To evaluate this function the strips designed by Beevers and Lipson were used. The portion of the expression $\sum_{o}^{H} F^2_{hKO} \cos 2\pi hx$ was first evaluated the values of F^2 being taken from the summary table (Appendix, p. xiii)

Selecting a strip at random it appears :

11 C 18 | 11, $\bar{3}$, $\bar{9}$, 9, 3, $\bar{11}$, 3, 9, $\bar{9}$, $\bar{3}$, 11, $\bar{3}$, $\bar{9}$, 9, 3, $\bar{11}$,

The first number 11, indicates F^2 , C $\cos 2\pi$, 18 the appropriate h or k or l value. The above strip gives $F^2 \cos 2\pi hx$ equal to 9 , where x is the fractional coordinate, 4/60ths.

To evaluate the expression $\sum_{o}^{H} F^2_{hKO} \cos 2\pi hx$ one proceeds in the following manner.

k is kept constant while the summation is done for all values of H and values of x from 1 to 15 sixtieths, the F values being abstracted from the table (Appedix p.xiii). In the present work , in the case of tripyridyl zinc chloride the values of h are 2, 4, 6 , 8, 10, 12, 14, 16.

It is useful to extract from tha main table a subsidiary one , e.g. k equals 0

F	34	4	6	30	37	1	1	0
h	2	4	6	8	10	12	14	16

From the set of cosine strips we remove the required values i.e. 34 from h=2 ; 4 from h=4 ; 30 from h=8 and so on. These are arranged beneath each other and the vertical columns so produced are added for each sixtieth of the appropriate coordinate, viz., x in the present case. The strips applicable to the foregoing subsidiary table have the appearance shown below :

34	C	2	34	33	31	28	23	17	11	4	$\bar{4}$	$\bar{11}$	$\bar{17}$	$\bar{23}$	$\bar{28}$	$\bar{31}$	$\bar{33}$	$\bar{34}$
4	C	4	4	4	3	1	0	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	0	1	3	4	4
6	C	6	6	5	2	$\bar{2}$	$\bar{5}$	$\bar{6}$	$\bar{5}$	$\bar{2}$	2	5	6	5	2	$\bar{2}$	$\bar{5}$	$\bar{6}$
30	C	8	30	20	$\bar{3}$	$\bar{24}$	$\bar{29}$	$\bar{15}$	9	27	27	9	$\bar{15}$	$\bar{29}$	$\bar{24}$	$\bar{3}$	20	30
37	C	10	37	$\bar{18}$	$\bar{18}$	$\bar{37}$	$\bar{18}$	18	37	18	$\bar{18}$	$\bar{37}$	$\bar{18}$	18	37	18	$\bar{18}$	$\bar{37}$
1	C	12	1	0	$\bar{1}$	$\bar{1}$	0	1	0	$\bar{1}$	$\bar{1}$	0	1	0	$\bar{1}$	$\bar{1}$	0	1
1	C	14	1	0	$\bar{1}$	0	1	0	$\bar{1}$	$\bar{1}$	1	1	0	$\bar{1}$	0	1	0	$\bar{1}$
Totals			113	80	13	$\bar{35}$	$\bar{28}$	13	48	41	3	$\bar{36}$	$\bar{45}$	$\bar{30}$	$\bar{13}$	$\bar{15}$	$\bar{32}$	$\bar{43}$

These figures at the foot of the vertical columns give the values of $\sum_{0}^{H} F^{2}_{hKO} \cos 2\pi hx$ for values of x from 0 to 15 sixtieths, when k equals 0 . The same procedure is adopted for values of k from 1 to 10 inclusive. Finally the whole table (Appendix xiv & xv) is evolved. The next stage is the calculation of $\sum_{0}^{H} F^{2}_{hKO} \cos 2\pi hx \sum_{0}^{K} \cos 2\pi ky$. The first term in the product, $\sum_{0}^{H} F^{2}_{hKO} \cos 2\pi hx$, has already been obtained (Appendix xiv & xv), and can be quickly abstracted for any value of x from 0 to 15 and k from 0 to 10 . A similar method is employed in effecting the final summation as was used in obtaining the first product. However, the strip now gives $A \cos 2\pi ky$, where A equals $\sum_{0}^{H} F^{2}_{hKO} \cos 2\pi hx$. From the strips are selected the ones shown in the table(Appendix xiv&xv) i.e.,

113 C 0 ; 80 C 1 ; 114 C 2 .....10 C 7

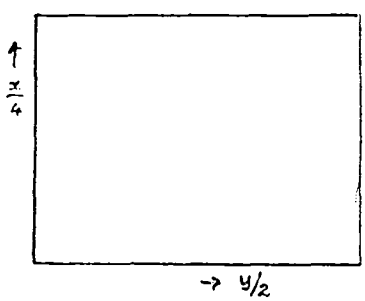
In the present instance the summation was done for values of y from 0 to 30 . The totals of the columns it will be noticed, only provide 16 values. The others, y from 16 to 30 are obtained as follows. Each strip ending in 0 is turned over and the summation done by working from left

to right omitting the end right hand column. In this manner the table (Appendix xvi, xvii, & xviii) was obtained which which gives the value of P'_{xyO} for values of x and y from 0 to 15 and 0 to 30 sixtieths respectively.

A series of curves, fifteen in all, were drawn for each value of x from 0 to 15, the ordinates being P for values of y between 0 and 30. These curves served as data for the plotting of the contours in the Patterson projection. Of these, the values chosen were 200 , 150, 100, 50, 0 . In the present case the portion of the unit cell over which these were drawn was $\frac{1}{2}y \times \frac{1}{4}x$. This was adequate for a full representation of the contours since the projection is symmetrical about the y axis and the origin is a centre of symmetry resulting from the operation of the symmetry b axis and the reflection plane perpendicular to it.

The projection was drawn on cms^2 paper ,the scale being $1cm = \frac{\frac{1}{2}[b]}{15}$ A.U. = 0.304 A.U.

The following procedure is adopted for the drawing of the contours. The rectangle represents the portion of the unit cell over which the projection is drawn. The length x/4 was divided into 15 sections each representing 1/60 of x. As regards the y axis 0.5cm. represents 1/60 of y.



The plotting of the 200 contour will be described, the same method being adopted for the others.

The curve $P'_{xyO} = f(y)$ for x equals 0 is examined and

the values of the y-intercepts on the [illegible] line $P'_{xyo} = 200$ read off. These are plotted on the line $x = 0$ on the projection . The curve $P'_{xyo} = f(y)$ for x equals 1 is then taken, the intercepts on the 200 line read off and plotted on the line x equals 1 on the projection. In a similar manner values of y are read off from the entire set of 15 curves and plotted on the appropriate lines x equals 1 to 15 on the projection.

The outlines of the 200 contours can then be drawn. In like manner are constructed the 150, 100, 50, and0 contours. The resulting Patterson projection for the whole (001) face is shown on page (54a).

PART TWO.

SOME STEREOCHEMICAL CONSIDERATIONS REGARDING 4-COVALENT METALS.

SOME STEREOCHEMICAL CONSIDERATIONS REGARDING 4-COVALENT METALS : A SHORT SURVEY .

Up to the present time no instance of a co-ordination compound has been cited which is in conflict with the generalisation that as regards 6-covalent compounds the configuration of the valencies is octahedral.

But the same remark cannot be applied to quadricovalent compounds for there is an abundance of evidence in favour both of a planar and of a tetrahedral disposition of valencies in these compounds : it is remarkable that until recent times planar configurations of valency had only been demonstrated among the metals of the transition periods, all other metals possessing a tetrahedral valency configuration.

However, instances of metals outside the transitional elements, some of which possess variable valency such as tin, lead (1) and thallium (2) have been shown by E.G.Cox, W.Wardlaw and A.J.Shorter to possess a planar distribution of their valemcies.

Furthermore in the case of 4-co-ordinated beryllium phthalocyanine investigated by R.P.Linstead and J.M.Robertson (3), and in the instance of tripyridyl zinc chloride (4) , a planar configuration has been demonstrated as regards beryllium and a four square co-ordinated structure is probable in the zinc derivative . In both these cases the valency configuration is apparently at variance with the generally accepted view concerning that property, viz., a

a tetrahedral disposition of valencies. But here as in other instances where experimental evidence is in conflict with previously accepted views, suitable explanations have been forthcoming . These will be dealt with later in this work.

Even the discovery of planar valency configurations among the elements already mentioned is comparatively recent. Prior to 1932, with the exception of platinum and palladium, no evidence for a planar configuration in 4-covalent compounds has been obtained. It may be mentioned that in 1920 R.H.Vernon (5) claimed to have isolated planar isomerides of dimethyltellurium iodide. This error remained unnoticed for some years until 1929 when H.D.K.Drew (6) proved that the isolated compounds were not cis-trans isomerides.

Therefore until recent times the available evidence based on classical methods of stereochemistry led to the general conclusion that the spatial distribution of the valencies of 4-covalent atoms was almost always tetrahedral. It is the purpose of this review to shew where deviations have occurred and to account for them as far as possible.

In 1931, L.Pauling (7) suggested that nickel in its 4-covalent state could have a planar configuration of valencies, his deductions being based upon wave-mechanical considerations. His statement that 4-covalent nickel should be planar and diamagnetic received support when S.Sugden (8) isolated two diamagnetic compounds of nickel with benzylmethylglyoxime. Since that date much evidence

has accrued as regards the planar configuration of nickel and by 1935 the planar nature of 4-covalent compounds of nickel, bivalent platinum and palladium was fully established.

In 1935, E.G.Cox (9) was led to the conclusion that copper might form 4-covalent compounds of planar configuration. Accordingly he investigated some cupric derivatives of β-diketones, viz., those of acetylacetone, benzoylacetone, diproprionylmethane and 3-chloro acetylacetone, and by means of space group considerations, optical properties and cell dimensions he definitely established that in the crystalline state these 4-covalent compounds of bivalent copper possess a planar valency configuration. Since then the same investigator has obtained further evidence of the planar configuration of that element. Because of the facts that the valency configuration both in nickel and in copper 4-covalent compounds may be planar, and that there is very little difference in radius of the two atoms, one might expect isomorphism to be exhibited in corresponding nickel compounds. This has been proved to be so as regards the methylethylglyoxime derivatives which were investigated by W.Wardlaw and his collaborators (10). In view of the results of the work of S.Sugden and H.J.Cavell (11) affording the deduction that the unsymmetrical glyoxime derivatives of nickel are planar, additional evidence is now added to the conclusion that 4-covalent copper may be planar in its bivalent compounds.

It has already been stated that the phthalocyanine

derivative of 4-covalent beryllium has been proved (3) to exhibit planar symmetry in its crystals. To this may be added the derivatives of manganese, iron, cobalt, nickel, copper and platinum.

Pauling's theory appears to be unable to furnish an explanation why the the beryllium atom, which normally possesses no d electrons, adopts a planar valency configuration. The general opinion is, however that the rigid planar character of the organic portion of the molecule forces its steric requirements upon the beryllium atom, thus compelling it to adopt a planar disposition of its valencies.

In the present work beryllium acetylacetone was investigated but without any conclusive result. The observations obtained by x-ray methods are recorded in the appendix, page xix.

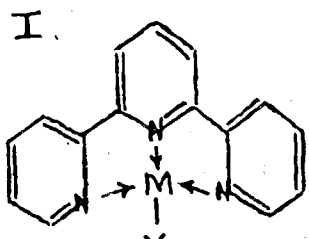
In striking contrast to the planar 4-covalent derivatives of bivalent copper, it has been proved thatsome 4-covalent cuprous compounds are tetrahedral ; similarly silver has been found to be planar when bivalent and tetrahedral in the univalent state, and gold tetrahedral in its univalent 4-co-ordinated compounds and planar when tervalent. This appears to be the first instance of a metal , in the tervalent state, with a planar valency configuration. It may be added that the planar configuration of tervalent gold has been recently confirmed (18) by the x-ray analysis of $CsAu_2Cl_2$ and $Cs_2AgAuCl_6$ whose structures contain square $[AuCl_4]'$ and linear $[AgCl_2]'$

and $AuCl_2'$ univalent anions. Recently the substance dipyridyl manganous chloride $MnCl_2.2C_5H_5N$ has been shown to be planar and isomorphous with the corresponding bivalent cobalt compound $CoCl_2.2C_5H_5N$ whose planar configuration has been indicated by E.G.Cox and his collaborators (12).

Im the instance of manganese M.J.Buerger (13) claims that the metals possesses a planar configuration in manganite $MnO(OH)$. But the accuracy of Buerger's work is a little doubtful. Actually the metal in manganite is surrounded by six oxygens, and according to Buerger, four in a plane are nearer than the other two, but it all depends on the accuracy of the distance measurements which was not very high. It might be mentioned, however, that manganese is tetrahedral in two valency states MnO_4'' and MnO_4' .

Finally in the instances of 2:2':2" tripyridyl derivatives of zinc, cadmium and mercury, isolated by Sir G.T.Morgan and F.H.Burstall (14) of the type (I)

I.



M = metal, Zn, Hg, Cd.
X = univalent acid radical.

the planar configuration of the metal is not excluded.

It seems reasonable to suppose that a theoretical explanation exists which indicates why in certain cases the configuration is tetrahedral and in others planar. L.Pauling (7) in 1931, applying wave-mechanical principles to the problem of covalent linkages, concluded that a tetrahedral configuration is to be expected firstly when only s and p electrons are involved, as exemplified

by carbon, and secondly when three d electrons take part, as is possible in the elements of the transition series. On the other hand, however, Pauling concludes that when only one d electron is involved in link formation the valency disposition will be planar, examples being afforded by bivalent nickel, platinum and palladium. Since the d electrons are mainly repsonsible for the magnetic moment of the atom, sharing of them should reduce this property. Consequently, bivalent nickel ,paramagnetic in its simple salts should become diamagnetic when it forms 4-covalent planar compounds.

Pauling's theory receives support by the magnetic evidence recorded for nickel. Although the significance of the magnetic evidence is not so great in the instances of platinum and palladium, all the simple salts of this diad being diamagnetic, yet the diamagnetic character of the planar compounds is in perfect accord with Pauling's hypothesis. However a discrepancy arises with regard to certain cupric compounds, those of the β -diketones, isolated by E.G.Cox and K.C.Webster (9) who have proved them to be planar. These compounds are paramagnetic and there is not a 3d level in the cupric ion. When the electron distribution of the nickel and copper atoms is examined it is seen that the difference between nickel and copper is not simply the addition of an electron in the nickel atom but a change in the number of electrons in the d level.

An interesting case of the application of Pauling's theory to explain experimental facts has recently occurred. It has been discovered (15) that square ICl_4 groups exist in the compound $KICl_4$. Since the theory of square co-ordination postulating sp^2d bonds is regarded as inapplicable in this case, it has been suggested that this is really an octahedral (d^2sp^3) co-ordination possessing two vacant positions.

Although Pauling's deductions have been criticised by W.Heisenberg (17) and others, yet the general opinion is that they are essentially correct. In the case of the transition elements, the results show that the metals in question may have, but not necessarily must have, a planar disposition of valencies. The veracity of this statement is indicated by the work of H.M.Powell and A.F.Wells (18) who have examined the salt Cs_3CoCl_5 , by x-ray analysis, and have found that the group $CoCl_4$" has a regular tetrahedral configuration, thereby proving that the transition element cobalt can actually be tetrahedral when covalent.

Another factor which may be of fundamental importance in influencing the spatial distribution of the valancies in 4-covalent compounds is the principal valency, and recent investigations have shown that a change in that property may influence the valency configuration. There are several instances. E.G.Cox and K.C.Webster (19) investigated the structure of trimethyl platinic chloride,

$Pt(Me)_3Cl$, by x-ray methods and found that the structure was non-planar. They incline to the view that it is most likely tetrahedral. Although platinum here is quadricovalent yet it is quadrivalent. This example is illustrative of the phenomenon of a change in valency configuration accompanying a change in principal valency of the metal under review. Furthermore in the nickel complex , nickel carbonyl, $Ni(CO)_4$, which is neutral, a tetrahedral configuration is exhibited. The principal valency of the nickel atom here is zero.

Again it has been found that some 4-covalent cuprous compounds are tetrahedral. Similarly silver has been shown to be planar in its bivalent state and tetrahedral when univalent. Prior to the year 1936 the only evidence regarding the configuration of either 4-covalent cuprous or argentous derivatives was that afforded by the work of F.Hein and H.Regler (20) who claimed, in 1935, to have brought about a partial resolution of an argentous derivative of 8-hydroxyquinoline. In 1936 these workers advanced further details of their investigation (21) and asserted that they had obtained evidence for the optical activity of their silver compound and it must therefore possess a tetrahedral valency for the silver atom. But they were unable to obtain the activity when the optically active acid was removed.

Since that date E.G.Cox and his collaborators (22) have examined by x-ray methods potassium cuprocyanide, the compounds tetrakis-thioacetamide cuprous and argentous

chlorides, isomorphous with it, and have demonstrated a tetrahedral distribution of valencies in each case. The same workers have also shown that bivalent silver (22) is 4-covalent and planar. Anx-ray examination of argentic derivatives of picolinic acid was made. In addition E.G.Cox and K.C.Webster (23) have shown that the ion $[AuBr_4]'$, present in potassium auribromide, $K[AuBr_4]2H_2O$, gold being tervalent, possesses a planar configuration. Furthermore it may be stated that the tetrahedral distribution of valencies in regard to 4-covalent cuprous copper has been demonstrated by F.G.Mann and his collaborators (24) in the molecule $[(C_2H_5)_3As \rightarrow CuI]_4$.

A change in structure with a change in valency has also been discovered among certain derivatives of tin, lead (25) and thallium (26). In 1900 W.J.Pope and S.J.Peachey prepared an optically active compound of tin (the bromocamphorsulphonate of methyl-ethyl-propyl tin)(26a) but until recently no experiments had been made to discover whether this tetrahedral disposition of valencies exhibited in stannic tin also holds for quadricovalent compounds of bivalent tin.

In potassium stannous chloride, $K_2[SnCl_4]2H_2O$ the four atoms of chlorine and the tin are coplanar, whereas in stannic iodide a tetrahedral disposition of the halogens is demonstrated, while in the case of plumbous lead in the thiourea derivative of plumbous chloride $[PbCl_2.2CS(NH_2)_2]$ the arrangement of addenda is planar, this being in sharp

contrast to the tetrahedral configuration displayed in quadrivalent lead compounds exemplified by tetraphenyl lead ($Pb(C_6H_5)_4$) .

As regards thallium, the complex salts $[Tl4CS(NH_2)_2]NO_3$ (or Cl) containing the univalent element are planar whereas in the thallic compound, the element being tervalent, a tetrahedral arrangement is considered most probable, e.g., dimethylthallium acetylacetonate.

The case of quadricovalent cobalt is somewhat enigmatical since both a tetrahedral and a planar distribution of its valencies has been demonstrated, thus showing that both types of spatial configuration can be manifested in unchelated derivatives of a bivalent metal. Briefly, of the two known forms of dipyridyl cobaltous chloride , $CoCl_2.2C_5H_5N$, henceforward styled as α and β forms, one, the α , has been shown by E.G.Cox and his collaborators (27) to be trans-planar, yet the structure of the β , supposed to be the 'cis' form, by analogy with the corresponding platinous compounds, remains uncertain. These facts coupled with the result of the investigation, by x-ray methods, of Cs_3CoCl_5, By H.M.Powell and A.F.Wells (28), who demonstrated the tetrahedral configuration, and the presence of the bivalent anion $CoCl_4$" therein shows that cobaltous cobalt may be an example of a metal in the same valency state exhibiting both a planar and atetrahedral configuration in its quadricovalent derivatives.

The only other instance of a metal exhibiting

both configurations in its quadricovalent compounds is beryllium. But in this case no actual parallelism can be drawn for the factors causing the divergence from the usual tetrahedral configuration are probably not the same, unless there is actually more tolerance in the distribution of valencies about 4-co-ordinate metal atoms than has hitherto been realised , then the parallelism is manifest.

So far it has been assumed that it is the central metallic atom which directs the spatial distribution of the co-ordinating units. But there are other factors which must be taken into consideration for the co-ordinating addenda may, on account of its size or rigidity, force its steric requirements upon the metal. This phenomenon is most evident among certain metallic phthalocyanines and other instances such as the tripyridyl derivatives of certain bivalent metals. These instances will be discussed in the next section of this work.

From this review the conclusion is reached that it is not possible, at the moment, to formulate any generalisation with regard to planar valency configurations. But it is evident that most of them occur in the bivalent state.

In times to come will the application of wave mechanics indicate why a change of principal valency results, in certain cases, in achange of valency configuration ? And will any distinction on theoretical grounds be discovered as regards the co-ordinate and covalent linkage ?

The stereochemistry of zinc has been deliberately omitted from this review since the purpose of this investigation as regards tripyridyl zinc chloride has been to determine whether the configurations of zinc and cadmium, whose tripyridyl compound is isomorphous with that of zinc, are planar as is indicated by the argument that the tripyridyl molecule is unable to encircle a tetrahedron without suffering considerable distortion. It therefore should force its steric requirements upon the zinc atom, i.e., tripyridyl zinc chloride should have a planar valency configuration.

The conclusions reached in regard to these compounds from the results of x-ray investigations will be developed in the sequel.

PART THREE.

THE STEREOCHEMISTRY OF ZINC.

THE STEREOCHEMISTRY OF ZINC .

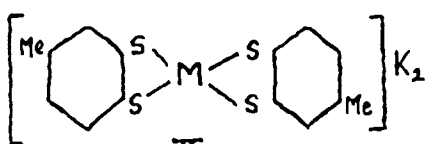
It is well known that Werner maintained that the tetrahedral valency configuration in quadricovalent compounds was not general and suggested that in the cases of the ammines of platinous and palladous chlorides, the valency distribution was planar. Furthermore he was of the opinion that the 4-covalent compounds of several other metals besides platinum and palladium might be planar. Since no other examples of planar configurations were forthcoming, these elements were regarded as unique and it was generally assumed that the usual configuration in 4-covalent compounds was tetrahedral.

During the course of their investigations many workers failed to prove that their compounds were actually 4-covalent. For example, many compounds contain two molecules of water and consequently the valency configuration might be octahedral. Again the compound might be dimeric, e.g., tripyridyl zinc chloride if dimeric could be assigned the formula $\left[Zn(tripy)_2\right]\left[ZnCl_4\right]$, a compound giving rise to two ions. In settling such problems the determination of molecular weights and conductivities have played an important part.

In 1922 the accepted view regarding the tetrahedral valency distribution in 4-covalent compounds received support by the results of the investigation of R.G.Dickinson (29) on the structure of the double cyanides $K_2\left[Zn(CN)_4\right]$, $K_2\left[Cd(CN)_4\right]$ and $K_2\left[Hg(CN)_4\right]$, by x-ray methods. These

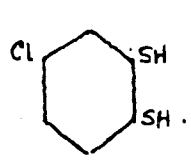
substances had been mentioned by Groth (30) as probably crystallising with cubic symmetry, and were found by Dickinson to be optically isotropic. He observed that $K_2[Zn(CN)_4]$ has a spinel-like structure,(31). each Zn being surrounded by 4 CN in a tetrahedron and each K by six CN in an octahedron. But the actual distances measured in 1922 must be accepted with reserve.

It may be added that the valency distribution of 4-covalent zinc has received attention recently as a results of the work of W.H.Mills and R.E.D.Clarke (32) who were of the opinion that benzene -1:2-dithiols might yield stable co-ordination derivatives of zinc, cadmium and mercury. They asserted that spirocyclic metallic compounds of that type would, if suitably substituted, provide a means of investigating the stereochemistry of the metals (in the 4-covalent state) from which they were derived. Accordingly they prepared o-dithiol benzenes containing an additional substituent group with the object of obtaining molecularly disymmetric metallic derivatives. They prepared the complex mercury , cadmium and zinc derivatives of toluene-3:4 dithiol of the type II and also obtained



II

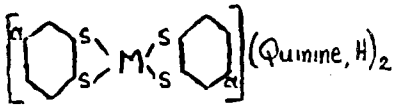
M = Zn, Cd, Hg.



III

complex derivatives of 1:chlorobenzene-3:4 dithiol III . Various alkaloid salts IV , were investigated but no evidence of their optical resolution could be obtained. Of these alkaloid salts

two forms α and β were obtained, the two forms being interconvertible. These investigators put forward two hypotheses to explain the observed facts of isomerism. Firstly it might have been due to a cis or trans arrangement of the unsymmetrically substituted phenylene groups, if the valencies of the central metallic atom had a uniplanar distribution. This they ruled out on account of the findings of R.G.Dickinson (29) which demand a tetrahedral valency disposition of the metallic atom. Besides, the isomerism would then be independent of the disymmetry of the base and should be shown also by the metallic salts of the complex. Secondly, if the four sulphur atoms in the complex anion were disposed tetrahedrally with regard to the metallic atom, the anion would be disymmetric giving rise to d- and l-enantiomorphous forms. Consequently it would give two quinine salts lB.lA and lB.dA. If one of these diastereoisomeric salts were more soluble inchloroform and the other in acetone, and if the anion underwent rapid autoracemisation in solution, phenomenon of the kind observed would result.



IV

M = Zn, Cd, Hg.

But in spite of the use of an apparatus particularly constructed to permit of the polarimetric examination of a substance within the space of 20 seconds from dissolution, no mutarotation could be detected even at -35 degrees C .

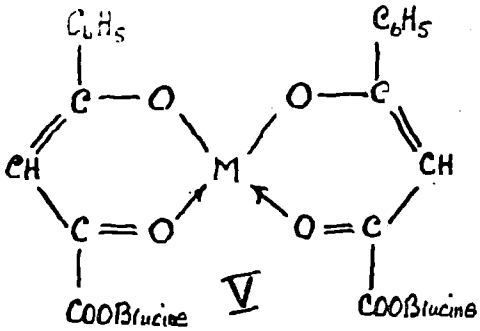
Even though no optical activity could be detected

and consequently the second hypothesis of the investigators not substantiated by experimental evidence, it seems reasonable to suppose that their deductions were correct and that the isomerism was due to the disymmetry of the spirocyclic complex.

Meanwhile in 1907, Tschugaeff (33) had suggested the possibility of the formation of closed ringsby co-ordinate links in the ease of metallic compounds of biuret and similar substances. This idea was subsequently developed by Werner who applied it to a great many compounds among which may be mentioned the metallic derivatives of acetylacetone. From 1913 onwards (Sir) G.T.Morgan and his collaborators applied the same ideas very extensively and the properties of the chelate group are now firmly established . The word "chelate" was introduced by G.T.Morgan.

However as regards the structure of the co-ordination compounds formed by such substances as β-diketones with bivalent metals, many investigators, following Werner, had assumed that such salts possessed a tetrahedral configuration of which the metallic atom was the centre. Such structures they argued, should give rise to the possibility of optical activity due to the normally bivalent metallic atom alone just as was the case with the octahedral structures of corresponding derivatives of normally tervalent metallic atoms, e.g., cobalt. In 1924, H.Burgess and T.M.Lowry(34) had shown this possibility by an investigation of the mutarotation of beryllium benzoylcamphor. But their findings

were somewhat indecisive on account of the presence of additional optical activity due to carbon. But in 1926, this hypothesis received support as a result of the investigations of W.H.Mills and R.A.Gotts (35) who resolved the beryllium, copper and zinc salts of benzoylpyruvic acid V.



V

M = Be, Cu, Zn.

The β-diketone itself is free from molecular disymmetry. The experiments of these workers furnished positive evidence of the tetrahedral disposition of the valencies of the normally bivalent metallic atom in the 4-co-ordinated state. Furthermore it may be remarked, they afforded evidence of the existence of a real linking between the metallic atom and the carbonyl oxygen atom of the β-diketone. (At this time the metallic derivatives of the β-diketones were sometimes represented as organo-metallic compounds in which the metal was linked to the inter-ketonic carbon atom).

From that time it was generally accepted that the valency configuration of zinc in its 4-covalent compounds was tetrahedral.

In 1935 a further contribution to the stereochemistry of 4-covalent metals was made and proved to be of great importance. It was the result of the work of J.M.Robertson (36) and R.P.Linstead and J.M.Robertson (37) on the metallic phthalocyanines. In that year, J.M.Robertson, as a result of x-ray investigations, concluded that in the

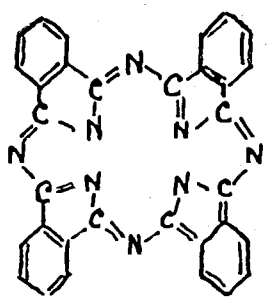
instances of nickel, copper and platinum phthalocyanines the metal atom and the four nitrogen atoms were coplanar. In the following year, the same investigator proved that the whole molecule of the metal-free phthalocyanine was planar to within a few hundredths of an Angstrom unit (38). Later in the same year R.P.Linstead and J.M.Robertson (39) conducted x-ray measurements upon single crystals of beryllium, manganese, iron and cobalt phthalocyanines and observed that these substances were closely isomorphous with phthalocyanine and its copper and nickel derivatives,

What significance has this work from the standpoint of general stereochemistry ? Do the results violate or do they confirm previously accepted views regarding the valency configurations of bivalent metals ? In what way does it apply to the stereochemistry of zinc?

Thefacts already indicated show that some bivalent metals , whose spatial distribution of valencies is generally accepted as tetrahedral can be planar, and that other bivalent metals which generally give rise to planar structures still retain that configuration in the phthalocyanine derivative. Again the monoclinic crystals of the zinc derivative are reported as distinctly similar to those discussed above and it therefore seems highly probable that the molecules of zinc phthalocyanine and of all other covalent metallic phthalocyanines will be planar.

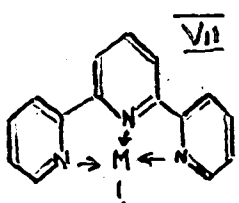
The reason for the deviations from the generally accepted views, where they occur, has already been referred

to and may pertinently be repeated here. The rigid planar structure of phthalocyanine, with its central 16-membered ring (VI) in all probability forces its steric requirements upon the metal with which it combines, thus compelling normally tetrahedrally disposed valencies to assume a planar configuration. This seems the only reason to hand at the present time, as regards zinc, the other factors which have hitherto led to a change in the spatial valency distribution, viz., Pauling's application of wave-mechanics to stereochemistry - in zinc the electrons of the d level are not taking part - and the change of principal valency causing modified valency configuration - zinc is exclusively bivalent - cannot apply.



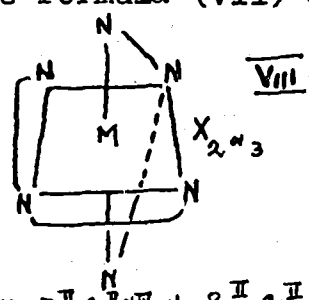
VI

In 1932 (Sir) G.T.Morgan and F.H.Burstall (40) isolated the triamine 2:2':2" tripyridyl and subsequently found that it formed a remarkable series of co-ordination compounds with metallic salts, the base acting as a tridentate group. Since that date these investigators have isolated two series of salts (41), one containing one molecule of the base having the formula (VII) and the other containing two molecules of the base of formula (VIII) Again in the same year (42) they prepared another



VII

M = Cu^{II}, Ag^{I}, Zn, Cd, Hg, Pt, Pd
X = univalent acid radical

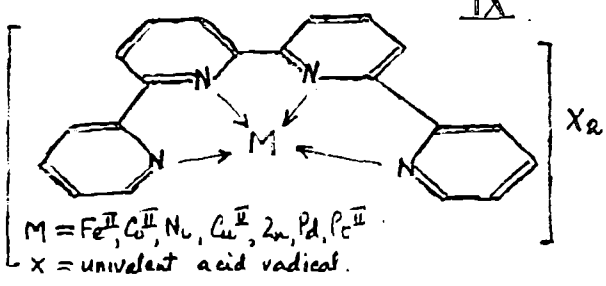


VIII

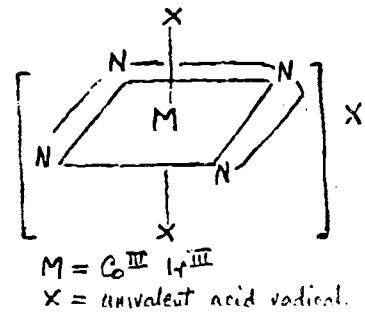
M = Fe^{II}, $Co^{II \text{ or } III}$, Ni, Ru^{II}, Os^{II}, Cr^{III}
X = univalent acid radical.

series of salts, two in number, using 2:2':2";2"' tetrapyridyl as a quadridentate group. These series comprised compounds of the type (IX), where the base is combined with bivalent metals, and fills all four positions in the co-ordination shell, and (X) when it is combined with tervalent metals.

IX



X



These investigators claim that owing to the configuration of the tripyridyl and tetrapyridyl molecules these are unable to encircle a tetrahedron without suffering considerable distortion. Consequently they incline to the view that the bases force their requirements on the metallic atom compelling it to adopt a planar configuration.

Finally it may be mentioned that C.R.Porter (43) has attempted the preparation of 4-covalent compounds whereby a metal, normally planar is constrained to take up a tetrahedral configuration by combination with a non-planar molecule. But the results appear to be inconclusive though the isolation of the cadmium and zinc compounds are in accord with the generally accepted view concerning the spatial valency distribution of those metals.

PART FOUR.

THE STRUCTURE OF TRIPYRIDYL ZINC CHLORIDE.

TRIPYRIDYL ZINC CHLORIDE .

Theoretical.

When dealing with the structure of tripyridyl zinc chloride several problems had to be considered . Some of them proved capable of solution in the early stages of the investigation whilst others remained until the last phases were complete.

The whole problem was approached, as has already been stated, with the purpose of establishing whether the zinc has subjected to the steric requirements of the tripyridyl molecule and has adopted a planar configuration.

At the outset no evidence was available to show that the compound was ionised, no conductivity measurements having been recorded in the paper by (Sir) G.T.Morgan and F.H.Burstall(4) . In view of this the possibility of a covalent structure was not excluded. On the other hand the zinc has not been proved 4-covalent. The possibility of a 6-covalent configuration was still open, a fact which would automatically make the molecule of tripyridyl zinc chloride dimeric. Again in view of resonance effects there existed the possibility of zinc being linked by two nitrogen atoms. Such a union would make the zinc compound covalent with the metallic atom either tetrahedral or planar.

Microscopic evidence led the author to conclude that in the sample supplied there existed two forms of monoclinic crystals, one appearing to belong to the domatic

class and the other to the prismatic. Subsequent goniometric measurements proved that the crystals were monoclinic and that there were actually two forms. These are hereinafter styled as I and II .

From investigation by x-rays and density determination it was found that there were four molecules to the unit cell and that the space groups of the two forms were C_s^4 or C_{2h}^6 for the first (I) and C_{2h}^5 for the second (II).

The first form seemed most useful for pursuing the investigation further, and data concerning this form was used for the development of the structure.

Discussion of the Space Groups.

C_{2h}^5 for the second form (II)

This space group has a glide plane parallel to the [a] -axis and the two-fold symmetry [b] -axis is a screw axis. It can be obtained with four asymmetric units of structure per unit cell. Since there are four molecules of tripyridyl zinc chloride per unit cell each of these must possess no symmetry. But in this cpace group there is the possibility of the association of asymmetric units of structure, but only through a symmetry centre. Consequently the compound in this form is probably monomeric because it is not possibl e to devise a dimeric form with a centre of symmetry unless zinc is square co-ordinated.

First Form (I) C_s^4

This space group can be obtained with four asymmetric units of structure per unit cell and no molecular

symmetry is permissible. Because there are four molecules of tripyridyl zinc chloride per unit cell, these are asymmetric if the substance is monomeric. But in the space group it is impossible to have two molecules each with a plane of symmetry. Consequently there cannot be two dimeric molecules and the compound is certainly monomeric.

C_{2h}^{5}

For this space group eight asymmetric units of structure are required. Since thereare four molecules per unit cell, each of these has an element of symmetry and the possibilities are either a centre or a two-fold symmetry axis. Since the substance is monomeric it cannot have a centre, hence, if the space group is C_{2h}^{5} the molecule must have a two-fold symmetry axis. These findings definitely exclude the possibility of a 6-covalent configuration.

Discussion of the Patterson Synthesis.

If the intensities used in the development of this synthesis had been measured on the absolute scale, the values of the inter atomic vectors P_{xyO} would have been proportional to the square of the atomic numbers in the case of like atoms and in the instance of unlike atoms, the product. Even so, theses values can be used for general comparison as regards the peaks themselves. The atomic numbers of Zn , Cl , and Cl' are 30 , 17 , and 18 respectively. Hence if absolute intensities had been used ,

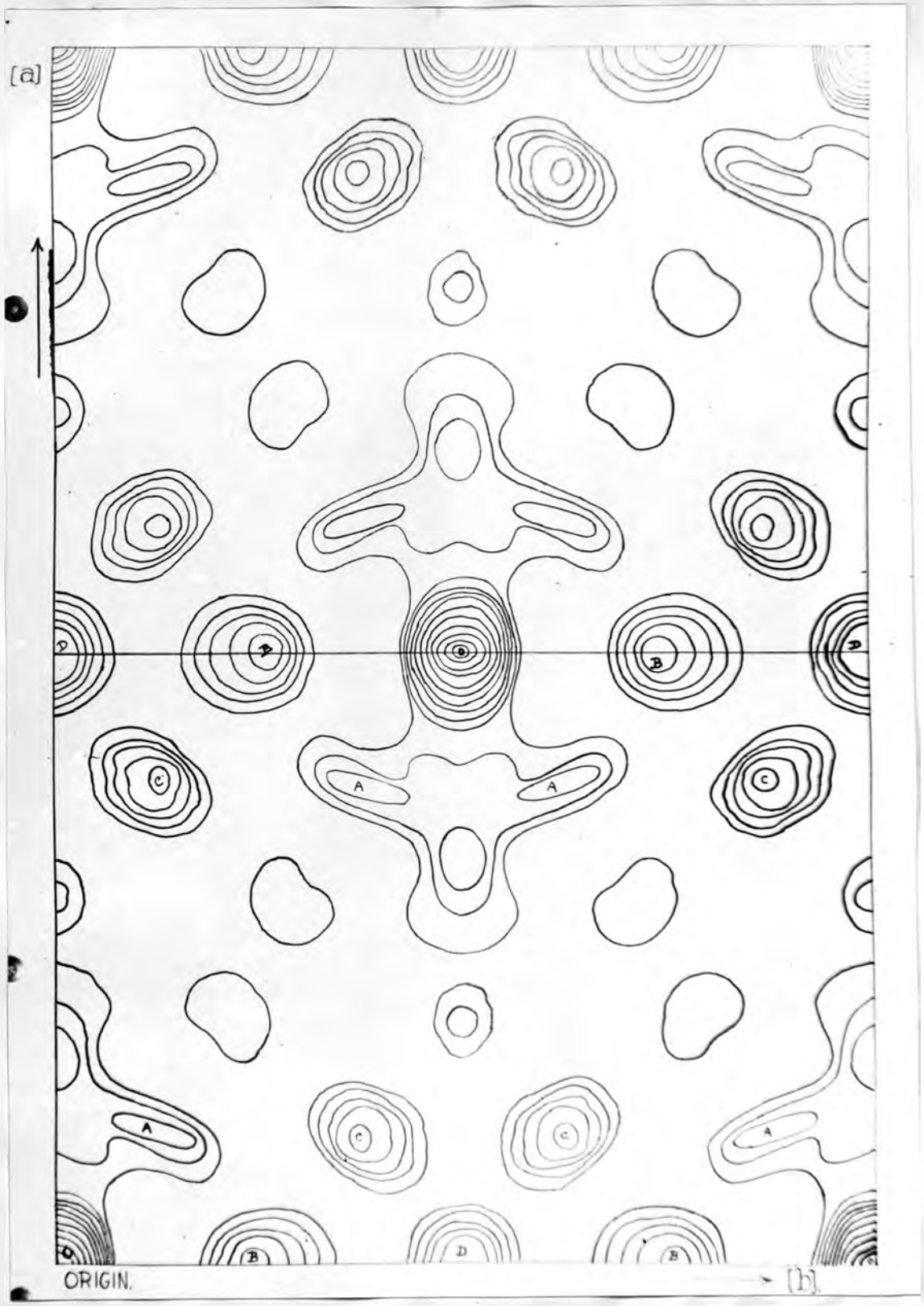


Fig. 1a

Zn - Zn peaks would be proportional to 900

Zn - Cl_1 .. .. .. to 500 - 540 , i.e. 520

Cl_1- Cl_{11} .. .. .. to 324 - 316 ,i.e. 310

all very roughly. Cl_1 denotes non-ionised chlorine and Cl_{11} ionised chlorine.

It may be noted that in contrast the Carbon -carbon peak is proportional to 36 , that is, 9 or 10 of these are required to equal one chlorine - chlorine peak.

It is clear that all important peaks appearing will be due to Zn - Zn or to the superimposing of the smaller ones upon each other, i.e., $Cl_1 - Cl_{11}$; $Zn - Cl_1$; $Zn - Cl_{11}$. The contour diagram facing this page shows one peak of 300, one of 100 and three of 200. From the values of the square of the atomic numbers and the products in the cases of unlike atoms, it will be seen that,

$$\text{One Zn-Zn peak} \equiv (Zn-Cl_1)+(Zn-Cl_{11}) \equiv (Cl_1-Cl_1)+(Cl_{11}-Cl_{11}) + (Cl_1-Cl_{11})$$

These relationships enabled an interatomic vector to be assigned to each peak.

Consideration in regard to the Space Group C_{2h}^6 .

There are four molecules to the unit cell and the space group can be obtained with eight asymmetric units of structure or four possessing two-fold symmetry. It has been pointed out previously that the molecule cannot have a centre of symmetry and that it must therefore have a two-fold symmetry axis. In the space group the special positions

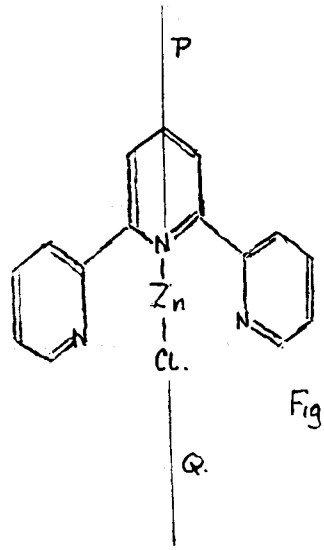


Fig. 2a.

are ,

(a) 000 , $00\frac{1}{2}$; (b) $0\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$; (c) $\frac{1}{4}\frac{1}{4}0$, $\frac{1}{4}\frac{1}{4}\frac{1}{2}$

(d) $\frac{1}{4}\frac{1}{4}\frac{1}{2}$, $\frac{3}{4}\frac{1}{4}0$, and symmetry axes passing through $0y\frac{1}{4}$, $0\bar{y}\frac{3}{4}$. Consequently if the zinc atom lies on a symmetry axis, there must be an atom at $0y\frac{1}{4}$ and by the operation of the glide plane another appears at $0\bar{y}\frac{3}{4}$. Since the cell is body centred the other two positions are $\frac{1}{2}$, $y+\frac{1}{2}$, $\frac{3}{4}$; $\frac{1}{2}$, $y-\frac{1}{2}$, $\frac{1}{4}$. Therefore in the Patterson the co-ordinates of the Zn-Zn vectors are ,

$(0,2y)$ $(\frac{1}{2},\frac{1}{2})$ $(\frac{1}{2},\frac{1}{2}-2y)$ $(\frac{1}{2},\frac{1}{2}+2y)$ $(0,2\bar{y})$ $(-\frac{1}{2},2y-\frac{1}{2})$ $(-\frac{1}{2},-\frac{1}{2}-2y)$

Exactly the same considerations apply to the non-ionised chlorine (y_1) while the co-ordinates of the Zn-Cl_1 peaks will be $(0,y_{Cl}-y_{Zn})$ $(0,y_{Cl}+y_{Zn})$ $(\frac{1}{2},\frac{1}{2}+y_{Cl}+y_{Zn})$ etc.

The ionised chlorine, presumably must lie at the other special positions, viz., at symmetry centres. Since there are no peaks in the Patterson projection at x equals $\frac{1}{4}$, the positions $\frac{1}{4}\frac{1}{4}0$ etc or $\frac{1}{4}\frac{1}{4}\frac{1}{2}$ etc. are inadmissible and therefore the Cl ions must lie at (000) etc or $(0\frac{1}{2}0)$ etc. Consequently all the Zn and Cl peaks must have x equals 0 and any other peaks present are due to carbon and nitrogen and will be small. But the projection shows large peaks at A and C which are probably due to Zn and Cl_1 and Cl_{11} . This is inconsistent with the space group. Again if the space group is C_{2h}^6, the line PQ (Fig.2) is parallel to the [b]-axis and the molecules will be parallel to each other. This will mean that some (h0l) plane will contain all the atoms or nearly so and will have a very high intensity. This has not been observed.

Also very high negative birefringence will be expected. In view of the Patterson considerations and some one (hOl) plane not having been observed as very intense and the negative birefringence, the space group C_{2h}^6 is excluded.

Consideration of the Space Group C_s^4 .

It was decided to interpret the peaks as follows :-

O due to all atoms being at zero distance from themselves and also $Cl_I - Cl_{II}$.

A due to $(Zn - Cl_I) + (Zn - Cl_{II})$

B due to $(Zn - Zn)$

C due to $(Zn - Cl_I) + (Zn - Cl_{II})$

D due to $(Cl_I - Cl_I) + (Cl_{II} - Cl_{II}) + (Cl_I - Cl_{II})$.

There are no special positions the general ones being ,

x,y,z ; $x,\bar{y},z\ \frac{1}{2}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$.

If an atom is placed at the point $x_1y_1z_1$, etc the co-ordinates of the Zn -Zn vectors will be ,

$(0,2y_1)$ $(0,2\bar{y}_1)$ $(\frac{1}{2},2y_1-\frac{1}{2})$ $(\frac{1}{2},-\frac{1}{2}-2y_1)$ $(\frac{1}{2},\frac{1}{2}+2y_1)$ $(\frac{1}{2},\frac{1}{2}-2y_1)$ $(\frac{1}{2},\frac{1}{2})$.

On the Patterson the Zn -Zn peaks lie at B ,

i.e., at (0,.24) ; (0,.76) ; ($\frac{1}{2}$,.24) ; ($\frac{1}{2}$, .76)

Equating with the Zn -Zn co-ordinates of vectors,

$0, 2y_1$ equals 0, .24

whence y_1 equals 0.12

And solving the remaining equations we get,

y_1 equals 0.12 ; 0.38 ; 0.62 ; 0.88 .

Hence the y co-ordinates of the zinc atoms are,

0.12 ; 0.38 ; 0.62 ; 0.88 .

By similar reasoning the Cl_1 - Cl_1 vectors will have co-ordinates,

($0,2y_2$) ($0,2\bar{y}_2$) ($\frac{1}{2}$, $2y_2-\frac{1}{2}$) ($-\frac{1}{2},\frac{1}{2}-2y_2$) ($\frac{1}{2}$, $\frac{1}{2}+2y_2$) ($\frac{1}{2},\frac{1}{2}-2y_2$) ($\frac{1}{2},\frac{1}{2}$) , these peaks being represented by D on the Patterson and occure at ($0,\frac{1}{2}$) ($\frac{1}{2},0$)

Equating we get,

$0,2y_2$ equals $0,\frac{1}{2}$

whence y_2 equals $\frac{1}{4}$.

From the solution of the remaining equations it is found that only two values are obtained, viz., y_2 equals $\frac{1}{4}$ or $\frac{3}{4}$. Therefore there are two atoms at y_2 equals $\frac{1}{4}$ and two at y_2 equals $\frac{3}{4}$. But this only accounts for a peak half as high as shown. It must therefore be due to the superimposition of Cl_{11} upon Cl_1 . Hence the co-ordinates of Cl_1 are the same as those of Cl_{11} .

Consideration of the Zn - Cl_1 peaks.

The zinc atoms are at ,

(x_1,y_1,z_1) ($x_1,\bar{y}_1,z+\frac{1}{2}$) ($\frac{1}{2}+x_1$, $\frac{1}{2}+y_1$, $\frac{1}{2}+z_1$) ($\frac{1}{2}+x_1,\frac{1}{2}-y_1$, z_1)

and the Cl_1 atoms are at,

(x_2,y_2,z_2) ($x_2,\bar{y}_2,z_2+\frac{1}{2}$) ($\frac{1}{2}+x_2,\frac{1}{2}+y_2,\frac{1}{2}+z_2$) ($\frac{1}{2}+x_2,\frac{1}{2}-y_2,z_2$)

Since there are no special,positions x_1 can be equated to zero. Hence substituting the y co-ordinates of Zn and Cl_1 as already found we get,

Zn atoms at, (0,.12,z_1) (0,.88,$z_1+\frac{1}{2}$)(.5,.62,$\frac{1}{2}+z_1$)

(.5,.38,z_1)

and chlorine atoms at,(x_2,.25,z_2) (x_2,.75,$z_2+\frac{1}{2}$)($\frac{1}{2}+x_2$,.75,$\frac{1}{2}+z_2$)

($\frac{1}{2}$ x_2, .25, z_2)

Therefore there are peaks at ,

(x_2, .13) (x_2, .63) ($\frac{1}{2}+x_2$, .63) ($\frac{1}{2}+x_2$, .13)

(x_2, $.\overline{63}$) (x_2, $.\overline{13}$) ($\frac{1}{2}+x_2$, $.\overline{13}$) ($\frac{1}{2}+x_2$, $.\overline{63}$)

(x_2, $.\overline{37}$) (x_2, .13) ($x_2-\frac{1}{2}$, $.\overline{37}$) ($x_2-\frac{1}{2}$,.13)

($x_2-\frac{1}{2}$, $.\overline{13}$) ($x_2-\frac{1}{2}$, .37) (x_2, .37) (x_2, .13)

Rewriting, clearing negative signs and sorting out like terms we have,

(x_2, .13) (x_2, .63) ($\frac{1}{2}+x_2$, .63) (x_2, .37) (x_2, .87)

($\frac{1}{2}+x_2$, .87) ($\frac{1}{2}+x_2$, .37) ($x_2-\frac{1}{2}$, .63) ($x_2-\frac{1}{2}$, .13)

($x_2-\frac{1}{2}$, .87) ($x_2-\frac{1}{2}$,.37) .

Now the co-ordinates of the zinc atoms are 0 , .12 , 0 and those of the Cl_1 atoms x_2 , .25 , z_2 . Hence from the position of the peaks on the projection ,

x_2 equals 0.103 and

$x_2+\frac{1}{2}$ equals 0.603

Thus all the peaks are accounted for. But they are only half as high as Zn - Zn , and consequently must be due to the superimposition of Cl_1 upon Cl_{11} . Therefore the x co-ordinates of Cl_1 and Cl_{11} are the same . That is to say there are,

Two chlorines at 0.103 and two at 0.603 .

Hence the x , y co-ordinates of the

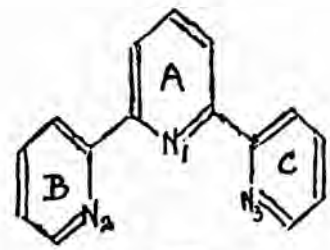
Zn atoms are (0, .12) (0, .88) (.5 , .62) (.5, .38)

Cl_1 and Cl_{11} are (.10, $\frac{1}{4}$) (.10, $\frac{3}{4}$) (.60, $\frac{1}{4}$) (.60 ,$\frac{3}{4}$)

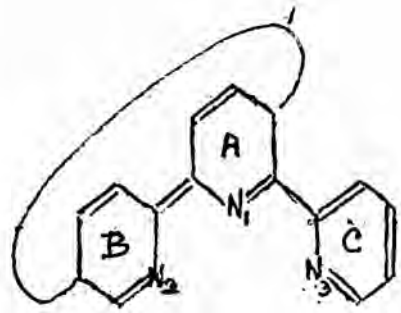
The question of resonance.

The older views on the stereochemistry of polynuclear aromatic molecules permitted free rotation of the parts abou t the single bonds. But today it has been found that those parts are kept in a planar configuration because of the conjugation between the rings. This confers some double bond properties on the single bonds. Furthermore for a considerable period it has been accepted that the nearest approach of atoms not held by in adjacent positions by covalent linkages is about 3.5 A.U. In some molecules there must be conflict between the tendency of groups to repel each other at distances less than 3.5 A.U. and the tendency to adopt a coplanar configuration. C.T.B.Clews and (Mrs)K.Londsdale (4) have shown that in the case of o-diphenylbenzene the ortho phenyl groups are probably inclined at approximately 50 degrees to the parent ring. Furthermore there is evidence that in the case of m-diphenylbenzene, there is a slight repulsion between the phenyl groups since examination of crystals of symmetrical triphenylbenzene showed that the three phenyl groups were apparently rotated approximately 16 degrees out of the plane of the nucleus. It therefore appears that in m-diphenyl benzene the inclination should not be greater than 16 degrees.

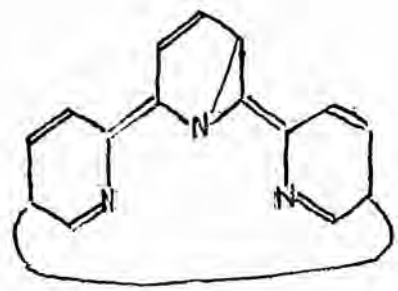
In view of this and the fact that N may be regarded as equivalent to CH in the nucleus, it seems reasonable to suppose that the tripyridyl molecule is approximately planar.



XI



XII



XIII

The possible states in which the molecule may exist in a state of resonance are shown in (XI) (XII) (XIII), and the forms XI and XII will be the main contributors since the energy of the third would be very high.

When the union of the molecule with zinc takes place there are some different possible configurations. Firstly the molecule could co-ordinate by three links to the zinc, affording [Zn(tripy)Cl]Cl. Again it could be attached by two linkages, one from N_1 and the other from N_3, the zinc atom thus retaining its usual tetrahedral configuration, and the chlorine atoms lying in a plane perpendicular to the A, B, Zn plane. This would afford the compound $[Zn(tripy)Cl_2]$, a covalent one. Placing this possibility under consideration it is seen that it must be excluded for the following reasons. The(Zn)-(N) distance equals 2.1 A.U. and consequently $N_1 - N_3$ equals 3.4 A.U. But in the molecule of tripyridyl the distance N_1-N_3 equals 4.8 A.U. Hence the nitrogens are too remote to form the union suggested above. Again the zinc may be supposed linked to N_1 and N_2 and the ring C rotating by repulsion to give the nearest of atoms a distance of at least 3.5 A.U. This is possible since N_1-N_2 equals 2.8 A.U. Such a union would give rise to two possibilities :

(a) the chlorine atoms could lie in a plane perpendicular to the A, B, Zn plane, if the Zn maintained a tetrahedral configuration. The compound would be covalent.

(b) If Zn adopted a planar configuration, coplanarity

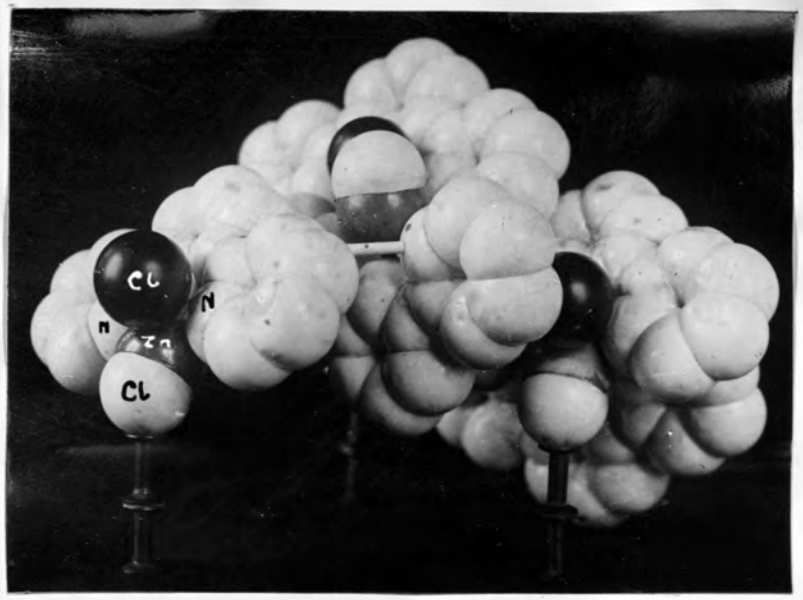
would exist between A,B, and $ZnCl_2$ and the compound would be covalent.

When these possibilities are analysed in view of the experimental facts ascertained during the present investigation it is found that the idea of a covalent configuration seems incredible since the substance is soluble in water. But caution must be observed here for the free nitrogen would confer a slight solubility on it. Secondly if the results of the Patterson are assumed, which afforded the co-ordinates of the Zn and Cl atoms, the molecule can be put into the cell. Since both chlorines have the same x , y co-ordinates, that is to say, the line Cl-Cl is parallel to [b] -axis, if the configuration is anything like tetrahedral, the A and B rings must be approximately parallel to (010) and lying in the (080) planes. The chlorine atoms lie in these planes. Hence the intensity of (080) should be very high. Actually this is rather weak.

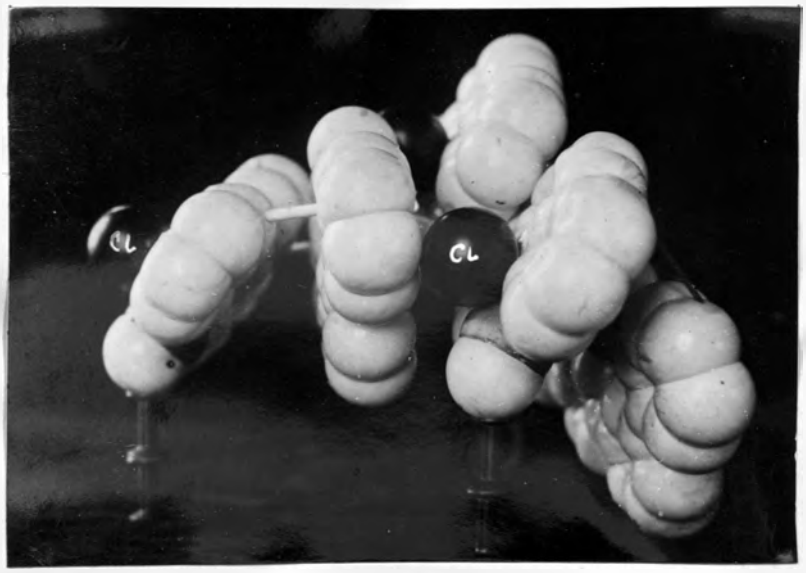
Again with such an arrangement the molecules are much too close together and actually overlap in alternate (080) planes ; Zn at y equals .12 , .38, .62 , .88 , the spacing of (040) is only 2.3 A.U.

Finally a planar configuration of A,B, and $ZnCl_2$ is impossible since the ring C would obstruct the chlorine. Consequently both possibilities are excluded.

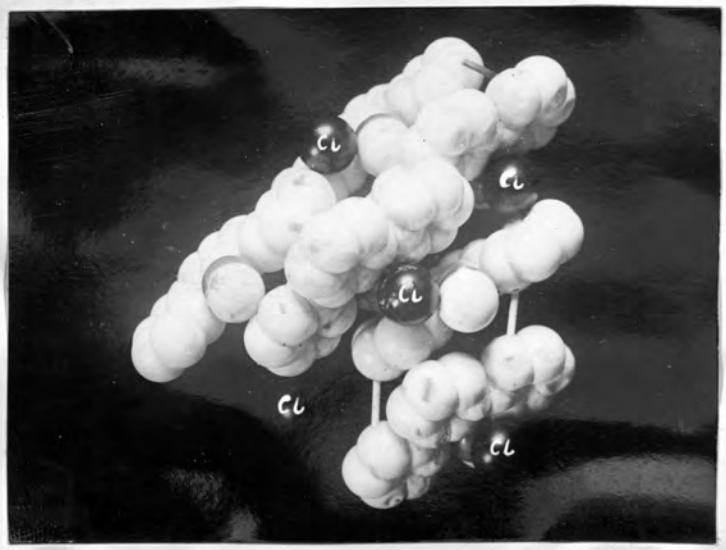
Hence from these considerations it seems reasonable to suppose that the most likely configuration is the ionised structure [Zn(tripy)Cl]Cl , with zinc adopting a planar configuration.



View along the [c] axis



View along the [101] axis.



View along the [b] axis.

The model of the unit cell.

It has been shown from space group considerations that the molecule cannot be dimeric and the possibility of the compound being covalent has also been excluded both from the result of the Patterson synthesis and from resonance considerations.

All the experimental evidence points to the fact that the co-ordination complex $[Zn(tripy)Cl]^+$ is planar.

The packing models of the molecule built up on this conclusion fit into the unit cell in such a position that the plane of the ion is parallel to the [101] axis , and inclined to the (010) face. The photographs, Figs. 3 , 4 , and 5 showed the appearance of the unit cell when viewed along the [c] -axis , the [101] -axis and the [b] -axis.

It is conceivable that a six-point system might have been arranged around the zinc atom had the molecule been parallel to the [b] -axis, Figs. 6 and 7

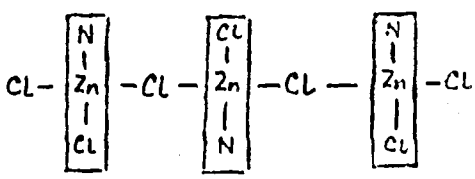


Fig. 6.
End view of cations.
Glide plane perp. to plane of paper.
Cations parallel to [b] axis.

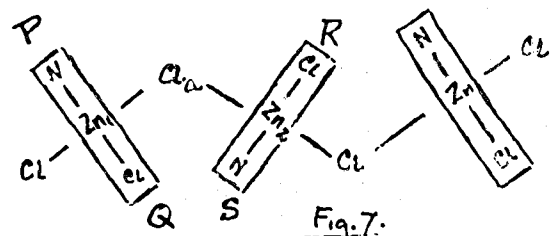


Fig. 7.
End view of cations. Glide plane as in 6.
Cations parallel to [101].

But it has been proved that the molecule is inclined to the [b] -axis. Consequently such a system cannot be arranged for the lines $Zn_1 - Cl_a$ and $Zn_2 - Cl_a$ cannot both be perpendicular to their respective planes, PQ and RS.

The optical measurements.

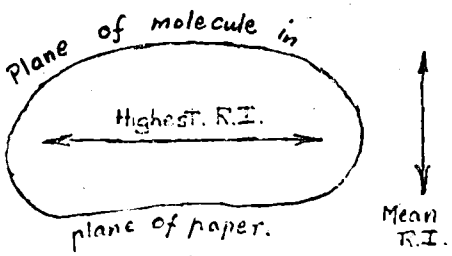


Fig. 8.

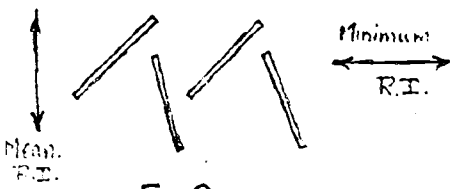


Fig. 9.

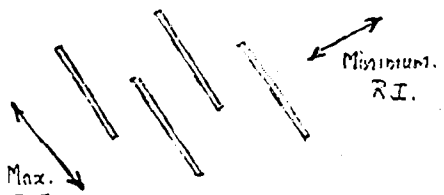


Fig. 10.

From theoretical considerations if the molecule is of the shape shown in Fig. 8 , then the refractive indices will be in the order shown, the direction of minimum refractive index being perpendicular to the plane of the paper . When the structure is viewed 'end on' the impression is illustrated in fig. 9, the directions of the refractive indices being indicated by arrows as before. Viewing the unit cell along the [b]-axis, the arrangement shown in Fig. 10 is observed.

The results of the optical measurements showed that the direction of minimum refractive index made an angle of approximately 53° with the [c]-axis, in the acute angle β , a direction approximately parallel to the $[10\bar{1}]$ axis. Therefore the length of the molecule which is parallel to the direction of maximum refractive index is roughly parallel to the [101] axis. This observation confirms the result previously obtained from x-ray investigation.

General conclusions.

In view of the results of this investigation it is concluded that the zinc atom has adopted a planar configuration having been compelled to do so by the steric requirements imposed upon it by the tripyridyl molecule.

Furthermore it may be stated that the same conclusions may be drawn as regards cadmium for axis measurements have been made for tripyridyl cadmium chloride, of which there is only one form, which has been found to be fully isomorphous with tripyridyl zinc chloride (I).

It seems reasonable to suppose, therefore, that the valency configuration of an atom may change from its usual form according to the nature of the co-ordinating addendum and it will be of interest to see whether future investigations will yield results as will make such a generalisation possible.

EXPERIMENTAL.

Optical Measurements.

These were made in sodium light using a Swift-Dick polarising microscope. The following results were obtained for the values of refractive index.

α equals 1.52 ; β equals 1.71 $\gamma \gg$ 1.72 .

The direction of minimum refractive index made an angle of 50° with the [c] -axis in the acute angle β , this direction being approximately parallel to the $[10\bar{1}]$ axis. The direction of the mean refractive index was parallel to the [b] -axis. Therefore the length of the molecule which is roughly parallel to is approximately parallel to the [101] axis.

GONIOMETRY FIRST FORM (I)

Several good crystals were examined , the following forms being observed,

$p\{011\}$; $\{m\{\bar{1}10\}$

The angles measured were,

	Observed.	Calc. from x-ray data.
$m : m_1$	66° 37′ ±4′	66° 44′
$p : p_1$	77° 43′ ±8′	78° 0′
$m : p$	46° 39′ ±4′	46° 46′

Angle β (calculated) 95° 56′

From the goniometric data the axial ratios were ,

$$a : b ; c = 1.531 : 1 : 1.248$$

and from x-ray results,

$$a : b : c = 1.525 : 1 : 1.242$$

The above results were used for preparing the stereographic

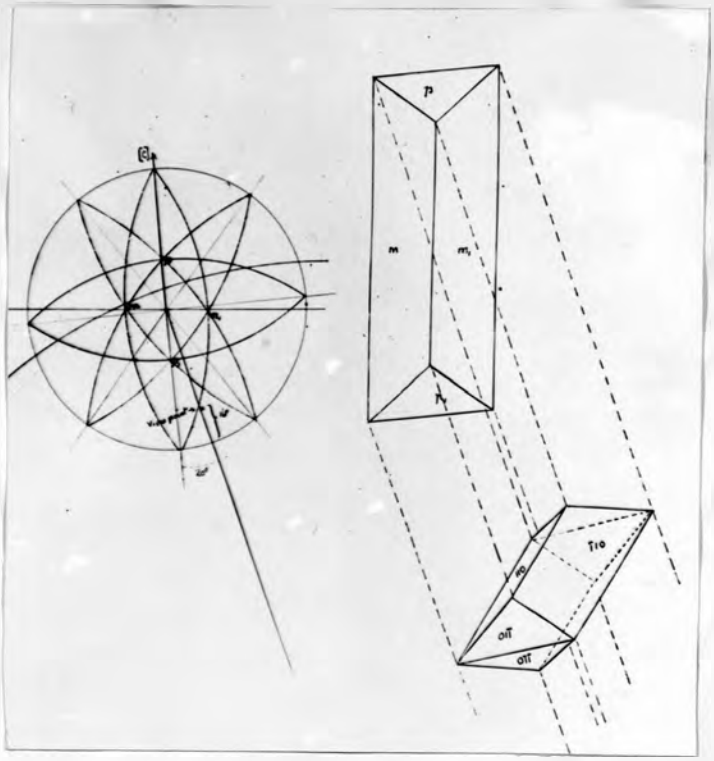


Fig. 11.

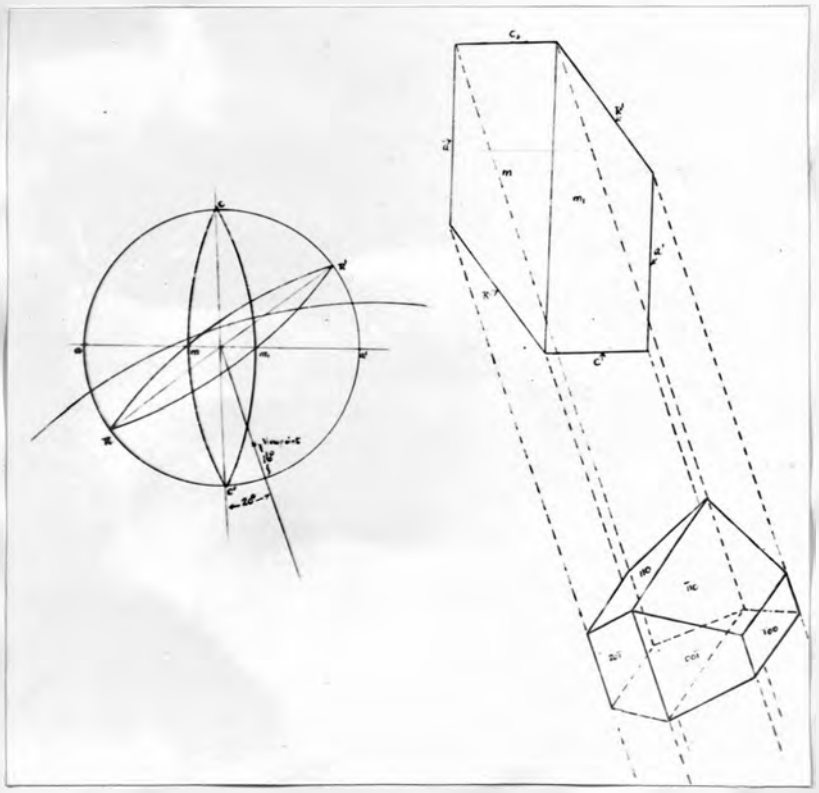


Fig. 12

projection and the crystal drawing ; Fig. 11

Second Form (II)

The forms observed were,

a $\{100\}$; c $\{001\}$; R $\{20\bar{1}\}$; m $\{110\}$

the angles measured being,

	Observed.	Calculated from x-ray data
m : m_1	53° 51′ ±15′	54° 48′
a : R	37° 27′ ±10′	37° 22′
a : c	86° 19′ 7′	86° 19′

Angle β (calc.) 93° 41′

The axial ratios calculated from goniometric results were,

a : b : c = 2.010 : 1 : 2.754

and from x-ray data,

a : b : c = 1.959 ; 1 : 1.334

The above results were used for preparing the stereographic projection and the crystal drawing, Fig. 12.

Density determination

The density of both forms was measured by the flotation method using carbon tetrachloride and methylene iodide.

Found , 1.72 g./cc. Calc. for Form I , 1.71 g./cc.

Found, 1.69 g./cc. Calc. for Form II, 1.70 g./cc.

Cell dimensions.

From rotation photographs taken about the three axes, the cell dimensions proved to be ,

[a] = 13.89 A.U. ; [b] = 9.11 A.U. ; [c] = 11.31 A.U. for (I)

and,

[a]=18.08 A.U. ; [b]=8.20 A.U. ; [c]=10.90 A.U. for (II).

From the volumes of the unit cell there proved to be four molecules per unit cell. For method of calculation see Appendix vi .

Space Groups.

First Form (I)

The analysis of [a] and of [b] oscillation photographs gave the following halvings,

{hkl} halved for(h + k + l) odd ,

and (h0l) halved for h and l odd.

These observations show that the cell is body-centred and that there is a glide plane parallel to [a] and to [c].

The space groups are,

I_a (C_s^4) or $I_{2/a}$ (C_{2h}^6)

Second Form (II)

The analysis of [a] and of [b] oscillation photographs showed that (h0l) was halved for h odd , and (0k0) halved for k odd. Since there were no general (hkl) halvings, the cell is simple. The halvings indicate a glide plane parallel to [a] and that the symmetry [b] is a screw axis.

The space group is $P_{2_1/a}$ (C_{2h}^5) .

Measurement of Relative Intensities

Two sets of [c] oscillation photographs were recorded for the purpose of intensity measurement, the first set, range 15° with 10° overlap being given an exposure

sufficient to produce spots at $\xi = 1.7$, and the second set, range 10° with 5° overlap, had one-fifth the exposure of the first. This procedure ensured that the spots which appeared blackest on the first set would only appear of measurable intensity on the second.

A spot of medium intensity (130) was chosen in the first set and given an arbitrary intensity value of 50 . This was then used to estimate the intensity of the spots on the photographs of the first set. The intensities of the second series was measured by comparison with a standard calibration film previously made. The preparation of this has already been referred to, page 22.

From the two sets of intensity measurements a mean ratio could be calculated for the two sets of films and thus an intensity value could be assigned to every spot which occurred on the zero layer line. The results of these measurements are shown in the table in the Appendix, page xi . From the values of $2\sin\theta$ for each spot, read off from Bernal's Chart II, the values of the Lorentz polarisation factor could be ~~re~~ obtained by reading it off from a Lorentz Factor curve previously drawn. Finally, F^2 (the structure amplitude) was found from the relationship,

$F^2 \propto$ Intensity / Lorentz factor (for zero layer line).

The values of F^2 were then multiplied by a factor of 1.23 so as to make the largest equal to 100. The values obtained are shown in the table in the appendix, pages xii and xiii.

These values were used for carrying out the Patterson synthesis which is described in the section on technique, page 25.

The Packing Models.

Five packing models of the molecule were made, the scale being 1 A.U. ≡ 1.19 cms. These were fitted into the unit cell constructed on the same scale, in orientations laid down by the space group symmetry , and those deduced from the consideration of the Patterson projection. Since the z co-ordinates were unknown the correct packing as regards these co-ordinates was effected by a method of trial and error. The position finally found was one such that the length of the molecule was parallel to the [101] axis. The appearance of the model from three view-points is shown in the photographs facing page 62.

P A R T F I V E .

T H E E T H Y L E S T E R O F
R O U S S I N ' S R E D S A L T .

THE ETHYL ESTER OF ROUSSIN'S RED SALT .

Introduction.

The compounds described in the literature as Roussin's salts have been known for a long time, having been discovered by J.Roussin in 1858 (48).
Although the properties which he described are in fairly close agreement with those observed by subsequent workers yet the formulae which he assigned to them were not accepted by those early workers. (49)

But in the literature we find that O.Pavel(50) draws attention to the widely discrepant results of those investigators and he himself suggests an improved method of preparation, ensuring a purer product.

Furthermore, three years later, in 1882, he describes (51) the preparation of the ethyl ester of the red salts, gives the results of goniometric measurements and suggests formulae both for this compound and the black and red salts, the formula of the latter being confirmed by L.Marchlewski and J.Sachs (52) by analysis and determination of molecular weight by the Beckmann boiling point method, while in 1895, a further confirmation of his results was afforded by the isolation of the ester by a new mode of preparation, and the confirmation of O.Pavel's proposed formula $[Fe(NO)_2SEt]_2$, by a determination of its molecular weight in benzene (53).

By 1905 the methods of preparation of Roussin's

salts and their derivatives were fully established and there was a close agreement among workers as regards the formulae assigned to these compounds, and since that date several new derivatives of both salts have been prepared.

From 1906 we find a period in the history of these compounds where chemists devoted their efforts chiefly to the elucidation of the constitution of these compounds. In 1906, W.Manchot and K.Zechentmayer,(54) investigated the absorbtion of nitric oxide by ferrous salts and concluded that the reaction resulted in the formation of a chemical compound containing Fe and NO in the proportion of 1 : 1, and put forward the hypothesis that such a reaction corresponded with the conversion of $Fe^{\bullet\bullet}$ to $Fe^{\bullet\bullet\bullet}$. But their conclusions were contradicted by V.Kohlschütter and M.Kutscheroff (55) yet were confirmed by G.von Hüfner (56)

However in the same year I. Bellucci and p. de Cesaris (57), from the results of experiments regarding the oxidation of Roussin's salts, concluded that most of the iron present was in the ferrous condition and furthermore, they inclined to the view that the sulphur atoms in the molecule existed in the form of sulphide and were probably combined with the iron.

But L.Cambi (58) went a stage further and suggested that the compounds were complexes of sulphides and hyponitrites and claims to have demonstrated the

presence of hyponitrous acid as a decomposition product when silver nitrate reacts with the black Roussin's salt. Further investigations led him to conclude that the iron was present in the ferrous state and that they do not contain the residue of hyponitrous acid ON:NO , but contain a univalent group NO capable of functioning in two ways , firstly giving hyponitrous acid and secondly of yielding nitric oxide under the action of various oxidising agents.

In 1926 an entirely new view was put forward by W.Manchot (59) who assigned a constitution wherein the Fe was univalent, the NO being regarded as neutral without effect on the valency of the iron.

But L.Cambi and L.Szego (60) entirely disagreed, stating that the compounds containing the group .S.Fe.N_2O_2 afforded absorption spectra which showed certain analogies to those of ferric compounds such as $Fe(N_2O_2\ Ph)_3$, adding that there was no justification at all for the hypothesis that they contained univalent iron. Furthermore he definitely rejected the conception of nitrosyl groups being present as neutral addenda (61)

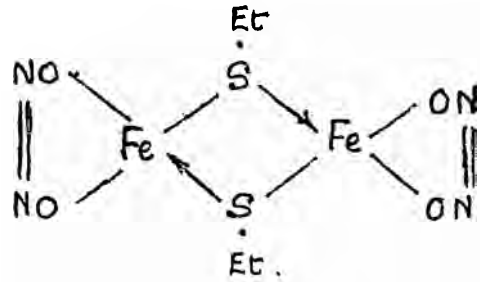
However L.Cambi received support from H.Reihlen and A.von Friedelsheim (62) who formulated the ester of Roussin's salt as a compound containing bivalent iron and stated that this formula accounts for the fact that it cannot be obtained from hyponitrites (I) He also asserted that on Manchot's view the formation of the

ester would involve the reduction of bivalent iron to the univalent state by the ethyl mercaptan used in the method of preparation by Hofmann and Weide.

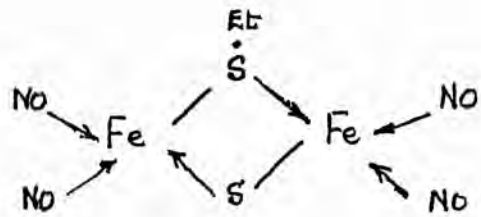
Continuing their investigations Manchot and his collaborators (63) compared the sulphur nitric oxide compounds of Fe ,Ni, Co with the hyponitrites and reached the conclusion that the sulphur nitric oxide compounds do not contain a hyponitrite grouping, and that nitric oxide is attached as a neutral molecule. In a theoretical discussion regarding the structure of these on the basis of Sidgwick's co-ordination theory, they state that a compound such as $[Fe(NO)_2SEt]_2$, has the NO groups attached to the iron atom by co-ordinate linkages and that the SEt groups are attached by a normal covalency.

Even so, L.Cambi(64) still maintained that in Roussin's salt iron is present in the tervalent state for from the measurements of magnetic susceptibility of the red salt he concluded that the bimolecular formula is correct, one iron atom being $Fe^{\bullet\bullet}$ and the other $Fe^{\bullet\bullet\bullet}$ and three of the NO groups being present as univalent radicals and the fourth as a molecule.

From this historical survey of Roussin's salts it seems that their structure is very complicated and still somewhat obscure. On the basis of the Sidgwick co-ordination theory the ester may be formulated firstly as a derivative of hyponitrous acid(I) and secondly



I.



II

as a derivative of univalent iron (II)

THEORETICAL

It has already been pointed out that the structure of Roussin's salt which belong to the class of nitrosyls is still somewhat obscure. The two structures which have been considered for them are firstly that they are compounds analogous to carbonyls where the nitrosyl group is functioning as a neutral addendum and secondly that they are derivatives of nitrous acid. The chief grounds for the maintenance of the hyponitrite structure are that during their chemical reactions the nitrosyls occasionally afford hyponitrous acid, secondly the usual valency of the metal is maintained, and lastly the ambiguous evidence of absorption spectra. However there exists a great deal of evidence against such a supposition. These compounds are prepared from nitric oxide and cannot be obtained by using hyponitrites in place of it. Added may be the fact that when acids decompose nitrosyl compounds nitric oxide is produced while the acid decomposition of hyponitrites affords nitrous oxide. Again the formation of iron nitrosyl compounds from ferrous salts would be a case of oxidation if the nitrosyls were ferric compounds. Again the hyponitrite view would modify the usually accepted formula for the nitroprussides which contain one nitrosyl group to one metallic atom : the formula would require doubling.

But there is no justification for this.

As far as the second view is concerned, viz., the conception of nitric oxide co-ordinately attached to the iron atom accords better with the experimental facts. If such a formula be accepted the analogy between the nirosyls and carbonyls is at once drawn. Even so there is every reason to suppose that these compounds are closely analogous. In their preparation and properties the similarity is shown ; they are derived from the same metals and the direct action of nitric acid oxide affords them just as carbonyls are produced by the direct action of carbon monoxide. It therefore seems reasonable to suppose that in the nitrosyl compounds each NO group is separately attached to the metal atom. This great similarity at once suggests an extension of the analogy to the structure of the nitrosyls and the carbonyls, and demands the presence of a triple bond between the nitrogen and the oxygen giving (M-N≡O) just as exists between the carbon and the oxygen in carbon monoxide (M -C≡O) ,a fact which has been proved from Raman spectrum considerations (65) . But there is one very important difference between nitric oxide and carbon monoxide, the electronic arrangements are not the same. Nitrogen possesses an excess of one electron over carbon, a dissimilarity which should bear on the electronic configuration of nitrosyl compounds.

The fact that the $[NO]^{+}$ ion can exist in electro-

valent compounds such as nitrosyl perchlorate $ClO_4[NO]$,(66) nitrosyl sulphate, $SO_4H[NO]$ (67) and nitrosyl fluoborate, $BF_4[NO]$ (68) , has an important bearing on the hypothesis regarding the linking of the NO groups to the metal atom in nitrosyl compounds.

N.V.Sidgwick and R.W.Bailey (69) suggest that the link between the NO group and the metal atom consists of two shared electrons, and in addition another electron is transferred to the metal, whose E.A.N. is consequently increased by three. It may be noted that this idea had already been indicated (70) but the mechanism of the linkage was not advanced. The structures which Sidgwick and Bailey suggested were $[:N:::O:]^+$, $N \equiv \overset{+}{O}$, $\bar{M} - \overset{+}{N} \equiv \overset{+}{O}$.

This hypothesis receives support in the cases of some nitrosyl and carbonyl compounds of copper which are of the type Cu(CO)Br, copper being cuprous, while the nirosyl derivatives are derived from cupric copper, e.g., $Cu(NO)SO_4$.

This difference is explained by the view that the No group donates an additional electron.

This theory satisfactorily explains the observed facts. When it is applied to most nitrosyl compounds a formulation results in which the inert gas rule is not violated. Besides, this remark can be said to include the complex molecules of Roussin's salts.

Again the theory apparently explains the

structure advanced by WmManchot regarding the ester of Roussin's red salt $[Fe(NO)_2SEt]_2$. It has already been stated that Manchot considers the Fe to be in the univalent state. This conception is arrived at by considering only the 'principal' valency of the atom in the sense expressed by Werner and not considering the more passive type of chemical affinity shown in the co-ordinate link with the NO groups. However this assumption is obviated by considering the co-ordination of the NO in the manner just indicated, Moreover the analogy between the nitrosyls and the carbonyls is thereby brought out, the electron having been transferred, the E.A.N. of the metal atom is raised by one unit, and the NO co-ordinates on as the $(NO)^+$ group.

The purpose of the present investigation carried out in regard to the ester of Roussin's salt was to examine crystals, by x-ray methods, and to obtain such evidence as would enable one or other of the proposed formulae to be assigned to it.

It has been pointed out previously that two formulae have been proposed, viz., the hyponitrite and the nitrosyl formula. In view of the analogy which clearly exists between the carbonyls and the nitrosyls , the author inclines to the view that it will be expedient to apply the results firstly to the nitrosyl formula.

Mention has already been made of the fact that O.Pavel (50) prepared the ester and performed certain

Goniometric measurements. He states (71) that he obtained two kinds of crystals. Of these, the first kind possessed poor end faces on account of the predominance of (001) and (010). Their form was that of a rectangular prism elongated along the [a] axis with domatic ends, whereas the second kind, on which all the observed faces were present were tabular on (001). He assigned them to the monoclinic prismatic class.

The crystals which were employed in this investigation were those of the first kind. The results of goniometric measurements made during the present work were in close agreement with those of O.Pavel, and furthermore, the end faces proved to be (110). As regards the axial ratios calculated from x-ray data these also proved closely to agree with those mentioned in the paper by O.Pavel.

The analysis of the oscillation photographs showed no general (hkl) halvings, (h0l) halved for h odd and (0k0) absent for k odd. These results indicate that the lattice is simple, the presence of a glide plane parallel to [a] and that the symmetry [b] axis is a screw axis. The space group is $P2_{1/a}$ (C_{2h}^5).

There were two molecules to the unit cell.

Discussion of the Space group.

The space group C_{2h}^5 can be obtained with four asymmetric units of structure per unit cell. Since

there are only two molecules per unit cell in the ester, each of these must possess some symmetry. Seeing that the only molecular symmetry permissible is a centre, the molecule must have a centre of symmetry. This fact immediately fixes the position of the molecule in a special position in the assemblage of points in the space group, viz., at a centre of symmetry.

Now in the space group C_{2h}^5 the centres of symmetry lie at (a) 000, $\frac{1}{2}\frac{1}{2}0$ (b) $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (c) $\frac{1}{2}00$, $0\frac{1}{2}0$ (d) $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, and furthermore if the centre of symmetry of the molecule lies at 000, the centre of another must lie at $\frac{1}{2}\frac{1}{2}0$, and so on.

The discovery that the molecule possesses a center of symmetry excludes the hyponitrite structure for the ester of Roussin's salt and does not disfavour the nitrosyl configuration . Moreover it confirms the bimolecular nature of the molecule.

With this in view a model could be constructed assuming such a configuration with a centre of symmetry. Since a centre of symmetry has no degree of freedom a definite position could be assigned to the two molecules in the model of the unit cell which had been previously constructed. The two points 000, $\frac{1}{2}\frac{1}{2}0$ were chosen and by the method of trial and error a suitable orientation was found for the molecules. Subsequently a set of structure factors were obtained for the orders of (001). These are shown in the table in the appendix, page v.

Some agreement is shown but it was realised that there were many other possibilities when dealing with such a molecule. Owing to the existence of these it has not been possible to draw any definite conclusions. But further investigation is continuing.

EXPERIMENTAL

Goniometry.

These measurements were made on the Pye Universal Photo-goniometer and the crystals examined were found to agree very closely with the description of the first kind given by O.Pavel. They belong to the monoclinic prismatic class and the forms observed were,

c $\{001\}$; b $\{010\}$; m $\{110\}$

Cell dimensions.

From rotation photographs about the three axes, the dimensions of the unit cell proved to be,

$[a] = 7.77$ A.U. ; $[b] = 12.60$ A.U. ; $[c] = 6.98$ A.U.

whence the axial ratios are,

a ; b : c = 0.6166 : 1 : 0.5540.

O.Pavel found by goniometry that the ratios were,

a : b : c = 0.6132 : 1 : 0.5554

and angle β 111° 47'.

Density

Found, 1.83 g./cc Calculated, 1.85 g/cc.

The number of molecules per unit cell is two.

Space Group.

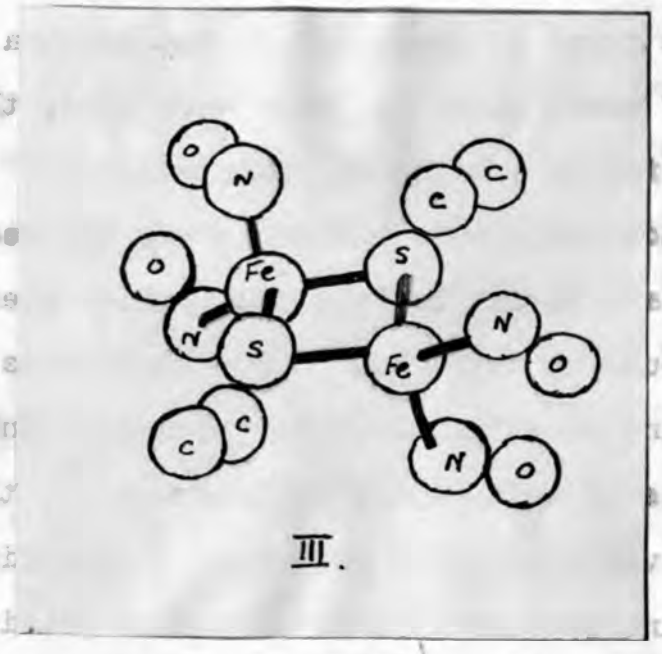
The results of the analysis of [a] and [b] oscillation photographs showed that there were no general (hkl) halvings, indicating a primitive lattice. (h0l) was halved for h odd as was (0k0) for k odd. Consequently a glide plane exists parallel to [a] and the [b] axis is a screw axis. The space group is $P2_1/a$ (C_{2h}^5)

Measurement of Absolute Intensities from an extended face.

For this purpose large crystals were used on which the (001) face was well defined. The crystal was set to oscillate about this face and photographs of the orders of this plane were taken in duplicate, the oscillation range being 5 degrees. On the same film was registered the (400) Rock salt line, under the same conditions of oscillation range. To ensure a workable depth of blackness in the spectra aluminium screens of known reducing power were used, these being corrected for in subsequent calculations. Both lines on each photograph were photometered, the readings tabulated and screen corrections applied when the ratio 001/400 could be obtained. The duplicates were averaged and these mean results converted into absolute intensities by multiplying by 0.38×10^{-4}, the absolute intensity value of (400) Rock salt. The five orders of (001) intensities (ρ) were used to obtain the structure amplitudes F. The results are shown in the tables in the appendix, page i.

Calculation of Structure Factors by the method of Trial and Error.

The importance of these details which follow lies in the possibility of their general application to complicated structures rather than in the particular results obtained for the ester of Roussin's salt.



III.

To carry out this method a model of the molecule, a model of the unit cell, the wall goniometer and the frame calculator are used.

The scale used for constructing the model (III) was 3 cms ≡1.15 A.U. The ring Fe-S-Fe-S was made flat, the iron taken as tetrahedral and the planes containing the nitrosyl groups were arranged perpendicular to the ring mentioned above.

The same scale was used for constructing the unit cell which was erected with the [a] axis vertical, i.e., the whole cell was tilted so that the (010) plane made 22 degrees with the horizontal. This was done merely for convenience.

It has already been pointed out that the molecule must possess a centre of symmetry and that the halvings deduced from oscillation photographs indicate the presence of a glide plane and screw axis . Furthermore the special positions in the space group are centres of symmetry. One model of the molecule was placed with its symmetry centre at 000 and the second at $\frac{1}{2}\frac{1}{2}0$, these being arranged so as to satisfy the conditions required by the space group. A third model was arranged one primitive translation from 000 and by the method of trial and error adjusted to satisfy the packing conditions. There were no restrictions as regards orientation except that the centre of symmetry of the molecule must lie on one of the centres of symmetry in the unit cell.

Thus the molecule could be rotated about the b-axis, the c-axis or the a-face normal, a fact which conferred many possible orientations on the molecule. The position which seemed most satisfactorily to conform with the packing conditions was such that one Fe-S bond made an angle of 33 degrees with the b-axis, while the other Fe-S bond and the c-axis were parallel.

Measurement of the z-co-ordinates of the atoms.

Since the spectra of the orders of (001) had been used for measuring absolute intensities and thence their structure amplitudes, it was necessary then to obtain the distances of the atoms in the experimental model from the (001) face, such distances being the z-co-ordinates.

The model was transferred to the wall-goniometer, the horizontal arm of which, was considered, for convenience, as the direction of the c-axis. It was fixed so that it had the same orientation with regard to the horizontal arm of the goniometer as it had with respect to the c-axis in the unit cell model. The orientation with regarded to the b-axis was also adjusted, i.e. perpendicular to the c-axis. Clearly, after these adjustments had been made the model had the same orientation with respect to the drawing board as it had with respect to the (010) plane in the model cell. To find the z-co-ordinates of the atoms the model was projected on to the (010) and their perpendicular distances measured from the direction of the a-axis, i.e., from the (001) face.

On the goniometer, the three directions about which the molecule was free to rotate were represented by,

(a) Rotation about the axis of projection, the b-axis, effected by rotating the frame co-ordinate calculator.

(b) Rotation about the c-axis by rotating the arm of the goniometer on which the model is secured. Angles hereon are described as σ in the tables in the appendix, pages ii and iii.

(c) Rotation about the (100) face-normal by sliding the mounting arm of the goniometer over the two arcs fixed in a plane perpendicular to the arm itself. Such angles are described as φ in the tables in the appendix, pages ii and iii.

The z/d co-ordinates were measured by means of the special frame, the distances between the strings having been previously adjusted so that 10 spaces were equal to d_{001} on the scale 6.41 A.U. $\equiv$ 13.56 cms.

The centre of symmetry was marked on the model itself by fixing a wire on to one of the atoms so that the end coincided with the centre of symmetry. The shadow of this then marked the correct position of the centre of symmetry in the projection, this being taken as the origin in subsequent readings.

The only orientation of the frame used was such that the 'axis' string passed through the centre of symmetry and was parallel to the projection of the Fe-S link which was inclined to the axis of projection.

The angle φ on the goniometer was set at 0° and the z/d co-ordinates read off for all values of σ (actually set at 0°). The angle was then adjusted to 10° and readings taken for $\pm 10^\circ, \pm 20^\circ, \pm 30^\circ, \pm 40^\circ$, and $\pm 50^\circ$. This procedure was repeated for $\varphi = 20^\circ$, -10°, and -20°. The results of the z/d co-ordinates were tabulated and the data obtained as shown in table IV shown in the appendix, page ii, which is a specimen table for $\varphi = 0^\circ \sigma = 0^\circ$ for (001)

The structure amplitudes were then calculated from the formula $F_{001} = 4\sum f_\theta \cos 2\pi z/d_{001}$, where f_θ is the atomic scattering factor, a function of $\sin\theta/\lambda$ and equal to the atomic number when $\sin\theta$ equals 0. Curves of this function were drawn for the atoms concerned. From these the values of f_θ could be obtained. The list of values is given in table III, appendix page ii. Table V in the appendix indicates the comparison between the observed and calculated F values.

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TABLE I.

PHOTOMETRIC RESULTS.

hkl.	Ph.reading.	(400) reading.	hkl reading / (400) reading	Aver.	Av. X .38 X 10^{-4}
001	141300	112700	1.253	1.626	6.179 X 10^{-5}
001	177500	88800	1.999		
002.	24700	124300	0.1987	0.1941	7.38 X 10^{-6}
002	22470	118400	0.1895		
003	2271	11900	0.0191	0.0165	6.27 X 10^{-7}
003	1030	74330	0.0138		
004	2203	68570	0.0321	0.0317	1.205 X 10^{-6}
004	1662	52860	0.0314		
005	2015	76380	0.0264	0.0264	1.00 X 10^{-6}
005	1744	83220	0.0264		

TABLE II

OBSERVED STRUCTURE AMPLITUDES .

Plane	Observed value
001	99
002	49
003	18
004	32
005	33

TABLE III.

ATOMIC SCATTERING FACTORS.

Plane	d (001)	$\sin\theta/\lambda$	Fe	S	N	O	C
001	6.413	0.0779	24	14.3	6.1	7.3	5.1
002	3.206	0.1559	20.5	11.8	4.8	6.05	3.55
003	2.138	0.2337	17.8	10.0	3.7	4.7	2.60
004	1.603	0.3116	15.3	8.8	2.9	3.8	2.16
005	1.283	0.3895	13.5	8.0	2.32	2.98	1.90

TABLE IV

Calculated structure factors from z/d co-ordinates.
Specimen table for $\varphi = 20^\circ$ $\sigma = 40^\circ$

Plane 004

Atom	f_θ	z/d	$f_\theta \cos 2\pi$ z/d +	z/d −
Fe	15.3	.52		1.49
S	8.8	.04	8.52	
N_1	2.9	.48		2.88
N_2	2.9	.20	0.90	
O_1	3.8	.64		2.42
O_2	3.8	.84	2.04	
C_1	2.2	.92	1.93	
C_2	2.2	.36		1.40
	Totals		13.39	8.19

Structure factor equals 4 X Total

i.e. 4 X 5.2 = 20.80

TABLE V.

Comparison of Calculated and Observed Structure factors.

Position showing some agreement :-

$\varphi = -10^{\circ}$ $\sigma = 40^{\circ}$

Plane	Calculated	Observed
001	-71	± 99
002	-95	± 49
003	-32	± 18
004	32	± 32
005	25	± 33

TABLE VI.

showing the results obtained during the determination of the a axis length from a rotation photograph of

Tripyridyl zinc chloride I.

Radius of Camera 2.992 cms.

L.H.S. Pt.	L.H.S. Microm. reading.	R.H.S. Pt.	R.H.S. Microm. reading	L.H.S. L.	L.H.S. 2x.	R.H.S. L.	R.H.S. 2x	L.H.S. x	R.H.S x	Aver'ge
6	9.0648	6	13.7215	6	5.4126		5.286	2.706	2.643	2.675
5	9.7447	5	13.0761	5	3.9905		3.995	1.995	1.997	1.996
4	10.2759	4	12.5018	4	3.0034		2.951	1.502	1.476	1.489
3	10.6515	3	12.0916	3	2.1823		2.099	1.091	1.050	1.070
2	11.0852	2	11.7353	2	1.3392		1.387	0.669	0.694	0.682
1	11.4371	1	11.3576	1	0.6641		0.701	0.332	0.351	0.341
$\bar{1}$	12.101	$\bar{1}$	10.6565							
$\bar{2}$	12.4251	$\bar{2}$	10.3479							
$\bar{3}$	12.8336	$\bar{3}$	9.9919							
$\bar{4}$	13.2789	$\bar{4}$	9.5506							
$\bar{5}$	13.7348	$\bar{5}$	9.0813							
$\bar{6}$	14.4773	$\bar{6}$	8.4351							

log x/R	log cosec tan x/R	log n cosec tan x/R	Axis	Aver.	Error
9.9513	10.1762	11.1416	13.86		
9.8243	10.2558	11.1419	13.87		
9.6768	10.3673	11.1566	14.34		
9.55359	10.4726	11.1469	14.03		
9.3577	10.6533	11.1415	13.86		
9.0572	10.9456	11.1329	13.58		
				13.89	±0.09

2x equals $N - \bar{N}$ where $\bar{N}$ and N are the micrometer readings of the Nth layer line.

Method of calculating the number of molecules per unit cell

e.g. Tripyridyl zinc chloride II

Observed density by flotation method using methylene iodide and carbon tetrachloride 1.72gm/cc.

Axis lengths $a = 16.08$ A.U.

$b = 8.20$ A.U.

$c = 10.90$ A.U.

$\beta = 93^{\circ}44'$

Let number of molecules per unit cell be Z

Volume of unit cell $= \frac{abc\sin\beta \times 10^{-24}}{Z}$ cc.

Molecular volume $= \frac{abc\sin\beta \times 10^{-24}}{Z}$ cc.

Molecular weight $= 369.4$

Molecular Mass $= \frac{\text{Molecular weight}}{\text{Avogadro number}} = \frac{369.4}{6.023 \times 10^{23}}$

$\therefore$ Density $= \frac{369.4 \times Z}{6.023 \times 10^{23} \times abc\sin\beta \times 10^{-24}}$

$\therefore$ $1.72 = \frac{369.4 \times 10 \times Z}{6.023 \times 16.08 \times 8.20 \times 10.90 \times 0.9979}$

Whence $Z = 4.03$

Hence there are 4 molecules per unit cell

Calculation of the linear absorbtion coefficient μ for Copper K_α radiation.

e.g. Iron. The ester of Roussin's salt, $[Fe(NO)_2SEt]_2$

$$\mu = d\Sigma\rho\frac{\mu}{\sigma}$$

where d = density = 1.85 g/cc

ρ = fraction contributed to unit mass by the constituent whose mass absorbtion coefficient is $\frac{\mu}{\sigma}$

For Copper K_α radiation

Absorber	μ/σ
Fe	324
N	8.51
O	12.70
S	91.30
C	5.50

Percentage composition : Fe, 31.56 ; N, 15.83 ; O, 18.09 ; S, 18.09 ; C, 13.57 %

$$\therefore \mu = 1.85[324X.3156 + 8.51X.1583 + 12.7 X .1809 + 91.3X.1809 + 5.5 X 13.57]$$

$$= 1.85 [102.2 + 1.347 + 2.298 + 16.52 + 0.7463]$$

$$= \underline{227.8}$$

Lorentz Factors .

The following table gives the values which correspond to the values of θ in the case of the planes , (001) , (002) , (003), (004) , (005) whose absolute intensities have been calculated for the Ester of Roussin's Red salt.

Plane.	θ	Lorentz Factor.
001	7°	8.00
002	$13^{\circ}44'$	3.88
003	21°	2.35
004	$28^{\circ}22'$	1.55
005	$36^{\circ}9'$	1.15

Table showing results of analysis of oscillation photograph .

Tripyridyl zinc chloride . Oscillation photograph about [c] (O1O) parallel to the beam at 317 .

Range of oscillation 312 to 322 .
Left hand side.

hkO	$\sin\theta$ calc.	Zero layer line	
		$\sin\theta$ obser'd	Intensity.
$0\bar{1}0$	0.175		
$1\bar{3}0$	0.520	0.520	315
$2\bar{3}0$	0.555		
$2\bar{4}0$	0.715	o.720	63
$3\bar{4}0$	0.760		
$3\bar{5}0$	0.915		
$4\bar{5}0$	0.960		
$5\bar{5}0$	1.020	1.020	23
$6\bar{5}0$	1.090		
$5\bar{6}0$	1.160		
$6\bar{6}0$	1.220	1.220	15
$7\bar{5}0$	1.160		
$7\bar{6}0$	1.285		
$8\bar{6}0$	1.360	1.360	4
$9\bar{6}0$	1.430		
$10,\bar{6}0$	1.520	1.520	7
$12,\bar{5},0$	1.590		
$11,\bar{6},0$	1.600		
$12,\bar{6},0$	1.690		
$13,\bar{5},0$	1.690		
$14,\bar{5},0$	1.785		

Same photograph,

Right hand side .

hk0	ξ calc.	Zero layer line.	
		ξ observed	Intensity.
010	0.175		
130	0.520	0.520	315
230	0.550		
240	0.715	0.720	63
340	0.760		
350	0.915		
450	0.960		
550	1.020	1.020	23
650	1.090		
560	1.160		
660	1.220	1.220	10
750	1.160		
760	1.285		
860	1.360	1.360	3
960	1.430		
10,6,0	1.520	1.520	7
12,5,0	1.590		
11,6,0	1.60		
12,6,0	1.690		
13,5,0	1.690		
14,5,0	1.785		

Table showing the characteristics of the observed planes.

Tripyridyl zinc chloride I.

Plane	ξ	θ°.	L	Intensity	F^2	F^2 X 1.23
020	0.340	10	5.45	300	55.20	68.00
040	0.680	20	2.51	135	53.90	66.30
060	1.025	31	1.38	26	18.85	23.20
080	1.360	43	1.00	15	14.86	18.30
0,10,0	1.700	58½	1.32	2	1.53	1.89
110	o.205	6	9.45	270	28.55	35.15
130	0.520	15	3.48	150	43.10	53.00
150	0.850	25	1.82	68	37.15	45.60
170	1.190	36½	1.12	6	5.36	6.59
190	1.530	49½	1.02	3	2.94	3.615
200	0.225	6½	9.75	540	55.40	68.60
220	0.400	11½	6.75	180	26.70	32.85
240	0.720	21	2.34	63	26.90	33.10
260	1.045	31½	1.32	14	10.69	13.14
280	1.370	44	1.01	3	2.97	3.66
2,10,0	1.720	59½	1.39	2	1.47	1.81
330	0.600	17½	2.95	25	8.95	11.00
310	0.375	11	4.94	7	1.44	1.77
350	0.910	27½	1.60	6	3.74	4.60
370	1.230	38½	1.08	15	13.87	17.07
390	1.565	51½	1.02	2	1.96	2.41
400	0.450	14	4.08	27	6.61	8.14
420	0.660	16½	3.15	62	19.69	2.42
440	0.820	24½	1.88	153	81.30	100.00
460	1.115	34	1.21	26	21.44	26.40
480	1.430	46	1.01	2	1.98	2.44
4,10,0	1.760	62	1.58	5	3.16	3.89
510	0.580	17	3.04	72	23.64	29.10
530	0.755	22	2.19	9	4.08	5.02
550	1.010	30½	1.38	21	15.21	1.872
570	1.315	41	1.02	2	1.96	2.41
590	1.625	54½	1.15	9	7.83	9.64
600	0.675	19½	2.54	25	9.84	12.10
620	0.755	22	2.18	25	11.45	14.10
640	0.960	29	1.50	100	66.75	82.10
660	1.220	37½	1.08	18	16.65	20.48
680	1.515	49	1.01	12	11.90	14.63
6,10,0	1.800	64	1.74	2	1.15	1.42
710	0.800	23½	1.98	8	4.07	5.02
730	0.940	28	1.58	54	34.10	42.00
750	1.150	35	1.18	2	1.68	2.07
770	1.425	45½	1.00	4	4.00	4.92
790	1.720	59½	1.39	15	10.77	13.22
800	0.900	27	1.65	81	49.10	60.44
820	0.960	29	1.49	14	9.38	11.52
840	1.120	34	1.21	4	3.36	4.13
860	1.350	42½	1.01	4	3.96	4.87

Continuation of Table from page xi

Plane	$\mathfrak{E}$	θ°	L	intensity	F^2	$F^2 \times 1.23$
880	1.63	$54\frac{1}{2}$	1.15	18	15.64	1.92
910	1.025	31	1.38	11	7.98	9.82
930	1.135	34	1.21	11	9.10	11.20
950	1.310	$40\frac{1}{2}$	1.02	3	2.94	3.62
970	1.560	$51\frac{1}{2}$	1.02	2	1.96	2.41
10,0,0	1.12	34	1.21	72	59.50	73.20
10,2,0	1.170	36	1.14	10	8.77	10.79
10,4,0	1.310	41	1.02	2	1.96	2.41
10,6,0	1.510	49	1.01	7	6.93	8.53
10,8,0	1.760	62	1.58	9	5.68	6.99
11,1,0	1.240	$38\frac{1}{2}$	1.08	2	1.85	2.28
11,3,0	1.335	42	1.01	2	1.98	2.44
11,5,0	1.490	48	1.01	12	11.87	14.60
11,7,0	1.715	59	1.38	2	1.45	1.78
12,0,0	1.350	$42\frac{1}{2}$	1.01	2	1.98	2.44
12,2,0	1.380	44	1.00	4	4.00	4.92
12,4,0	1.500	$48\frac{1}{2}$	1.01	16	15.83	19.49
12,6,0	1.69	58	1.31	2	1.53	1.88
13,1,0	1.470	$47\frac{1}{2}$	1.01	2	1.98	2.44
13,3,0	1.545	$50\frac{1}{2}$	1.04	2	1.92	2.36
13,5,0	1.680	57	1.28	15	11.71	14.40
14,0,0	1,570	$51\frac{1}{2}$	1.o2	2	1.96	2.41
14,2,0	1.600	53	1.11	4	3.62	4.45
14,4,0	1.710	59	1.38	6	4.32	5.32
15,1,0	1.690	58	1.30	2	1.54	1.89
15,3,0	1.760	63	1.58	2	1.39	1.71
16,0,0	1.790	64	1.74	2	1.15	1.42

Summary of Structure Factors from pages xii & xi

$F^2 \times 1.23$

h \ k	0	1	2	3	4	5	6	7	8	9	10
0			34		33		12		9		1
1	[illegible]	35		53		46		7		4	
2	34		33		33		13		4		2
3		2		11		5		17		2	
4	4		2		100		26		2		4
5		29		5		2		2		10	
6	6		14		82		20		15		1
7		5		42		2		5		13	
8	30		12		4		5		2		
9		10		11		4		2			
10	37		11		2		9		7		
11		2		2		15		2			
12	1		5		20		2				
13		2		2		14					
14	1		4		5						
15		2		2							
16	1										

The Patterson Synthesis.

$$\sum_{0}^{H} F_{hk0}^{2} \cos 2\pi hx$$

k \ x	0	1	2	3	4	5	6
0	113	80	13	-35	-28	13	48
1	80	72	44	19	8	4	3
2	114	94	55	32	34	41	45
3	127	103	60	18	1	10	31
4	278	233	134	44	-15	-62	-99
5	88	65	26	20	45	61	43
6	86	72	41	11	-7	-12	34
7	33	30	22	12	4	1	-1
8	38	30	16	-2	-5	-2	5
9	28	24	11	-3	-14	-17	-11
10	7	7	5	3	1	-2	-3

continued from page xiv

7	8	9	10	11	12	13	14	15
41	3	-36	-44	-33	-13	-15	-32	-43
8	15	19	21	30	36	36	22	0
40	38	31	23	14	10	5	-2	-9
54	64	56	28	2	-19	-23	-15	0
-100	-52	17	64	65	48	36	33	34
17	13	26	30	19	5	6	6	0
-10	-8	-4	8	18	19	13	6	2
-4	-6	-9	-12	-12	-14	-12	-6	0
8	12	13	18	19	16	4	-8	-14
-2	9	13	12	7	-1	-4	-4	0
-3	-3	-1	-1	1	1	3	3	3

The Patterson Synthesis .

$$\sum_{0}^{H} F^{2}_{hk0} \cos 2\pi hx \sum_{0}^{K} \cos 2\pi ky$$

x \ y	0	1	2	3	4	5	6	7	8	9	10
0	992	895	642	330	65	$\overline{107}$	$\overline{177}$	$\overline{117}$	$\overline{166}$	$\overline{132}$	$\overline{72}$
1	811	730	521	264	48	$\overline{93}$	$\overline{151}$	$\overline{3}$	$\overline{147}$	$\overline{120}$	$\overline{75}$
2	427	381	265	122	0	$\overline{77}$	$\overline{108}$	$\overline{114}$	$\overline{108}$	$\overline{95}$	$\overline{74}$
3	129	105	81	26	23	$\overline{61}$	$\overline{85}$	$\overline{98}$	$\overline{107}$	$\overline{109}$	$\overline{86}$
4	24	25	27	21	0	$\overline{31}$	$\overline{51}$	$\overline{57}$	$\overline{42}$	$\overline{20}$	$\overline{2}$
5	35	42	53	60	32	25	8	7	26	44	53
6	61	94	86	73	58	39	53	80	109	125	110
7	49	55	69	86	101	110	112	107	88	58	16
8	79	83	70	60	55	56	52	39	10	29	66
9	125	112	73	29	$\overline{8}$	$\overline{31}$	$\overline{48}$	$\overline{71}$	$\overline{94}$	$\overline{107}$	$\overline{120}$
10	147	126	74	11	$\overline{45}$	$\overline{80}$	$\overline{98}$	$\overline{111}$	$\overline{132}$	$\overline{129}$	$\overline{109}$
11	132	114	67	9	$\overline{37}$	$\overline{62}$	$\overline{76}$	$\overline{75}$	$\overline{72}$	$\overline{66}$	$\overline{51}$
12	87	78	55	22	$\overline{2}$	$\overline{21}$	$\overline{25}$	$\overline{23}$	$\overline{16}$	$\overline{9}$	$\overline{1}$
13	49	46	31	21	6	$\overline{9}$	$\overline{18}$	$\overline{21}$	$\overline{16}$	$\overline{3}$	17
14	3	4	2	$\overline{3}$	$\overline{15}$	$\overline{31}$	$\overline{47}$	$\overline{58}$	$\overline{32}$	$\overline{35}$	$\overline{8}$
15	$\overline{27}$	$\overline{27}$	$\overline{27}$	$\overline{32}$	$\overline{42}$	$\overline{58}$	$\overline{77}$	$\overline{80}$	$\overline{88}$	$\overline{73}$	$\overline{48}$

continued from page xvi

11	12	13	14	15	16	17	18	19	20	21	22
10	102	180	220	222	184	154	118	80	38	- 14	-58
-10	378	130	166	170	154	126	96	80	17	- 34	-77
-46	-8	24	50	62	64	54	40	8	-25	-63	-88
-41	-53	-52	-41	-39	-33	-32	-49	-57	-72	-83	-77
-2	-19	-43	-63	-76	-81	-89	-97	-98	-86	-52	-6
38	5	-35	-62	-76	-86	-93	-91	-73	-25	38	104
65	2	-61	-107	-122	-113	-83	-32	35	106	189	205
-34	-57	-75	-82	-78	-68	-49	-11	38	99	156	192
79	83	70	60	55	56	52	39	10	-29	-66	-84
-103	-71	-38	-23	-32	-53	-68	-67	-47	-18	1	4
-84	-30	11	24	7	-28	-63	-84	-81	-67	-57	-60
-26	8	31	38	21	-12	-48	-67	-74	-69	-66	-72
15	30	37	37	21	-3	-33	-54	-67	-64	-63	-64
32	41	35	23	4	-15	-33	-49	-60	-67	-71	-72
-34	-10	-11	-15	-19	-15	-11	-10	-34	-48	-73	-88
11	20	13	0	-15	-22	-29	-38	-51	-68	-81	-88

continued from page xvii

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23	24	25	26	27	28	29	30
-85	-77	-35	34	122	204	259	280
-101	-91	-53	10	86	155	202	220
-102	-94	-69	-99	14	57	89	101
-67	-51	~~140~~	-70Z	-24	-21	-15	-13
33	51	40	25	-20	-43	-61	-95
151	158	127	70	10	-41	-74	-83
206	175	115	54	9	-18	-39	-35
196	140	120	58	-2	-53	-85	-97
105 ~~101~~	75	42	1	-34	-68	-95	-105
-3	-20	-32	-44	-59	-71	-80	-85
-71	-82	-84	-75	-53	-34	-18	-11
~~-28-~~	~~-62~~	~~-84~~	~~-81~~	~~-67~~	~~-57-~~	~~-60-~~	
-89	-111	-112	-87	-50	-9	28	41
-77	-91	-98	-82	-42	11	56	73
-75	-80	-81	-70	-41	-2	30	43
-86	-80	-69	-55	-43	-23	-10	-3
-80	-77	-58	-42	-32	-27	-27	-27

Beryllium acetylacetone.

This was placed in the monoclinic system.

Faces occurring,

(010) ; (001) ; (101) ; (100) ; (110).

Cell dimensions.

[a] = 13.30 A.U.

[b] = 11.40 A.U.

[c] = 7.80 A.U.

Angle β, 100°

There are no general halvings but (010) is absent.

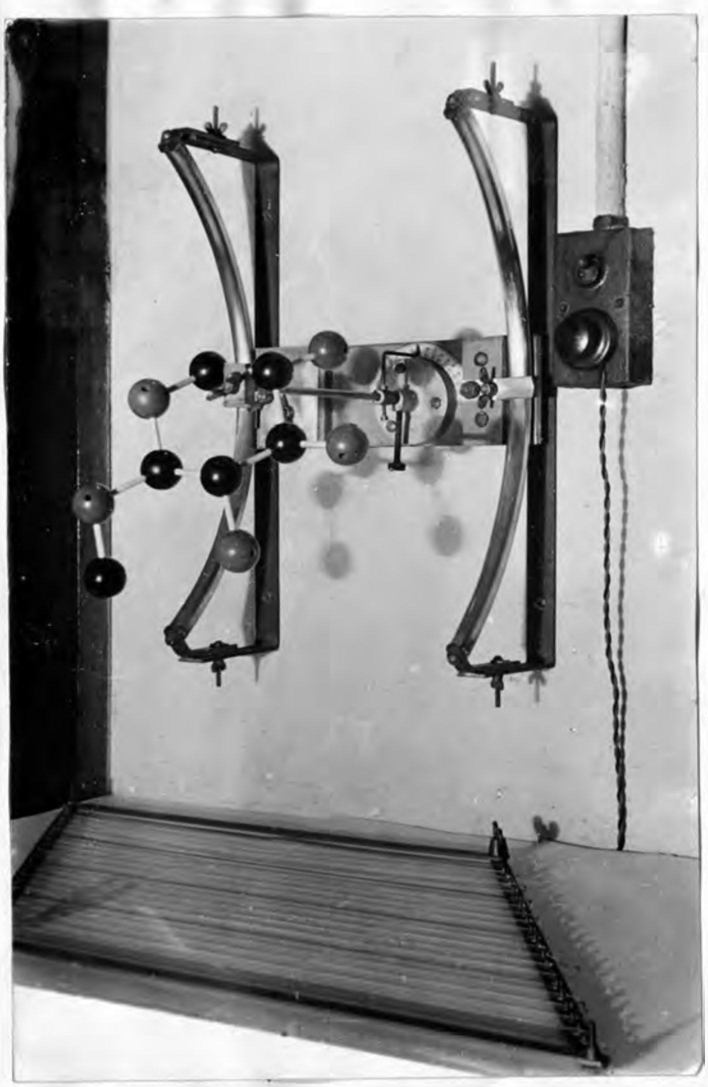
{100} and {001} are apparently not halved.

The space group is probably P_{2_1}/m or possibly P_{21}

Density

Calculated for 4 molecules/cell , 1.14 g/cc.

Observed, 1.17 g/cc.



The Wall goniometer.

A parallel beam of light after reflection from a mirror, inclined at 45° to the wall, projects a shadow of the model of the molecule on to a drawing board. An arm connected to the goniometer secures the model. The arcs shown in the photograph are those over which the model can be rotated in a vertical plane; the arm holding the model may also be rotated. An adjustable clamp situated between the end of the arm and the model enables an additional rotation of the model about a vertical axis to take place. Hence rotation is possible about all three directions.

The fractional co-ordinates are measured by means of the frame calculator which consists of four brass strips constructed in the form of a rhombus and pivoted at each corner. At equal distances across the frame threads are passed, the distance between adjacent threads being .05 of the total distance. A dark coloured thread occurred at every fifth position, so that the position of a point within the frame could be read off to .01 very easily.

For each plane whose F was being calculated a preliminary adjustment of the frame was made, in oder to make the spacing of the plane (d) equal to the distance between the extreme threads.

A circle of radius equal to that of the shadow of the model atom was drawn on a thin piece of wood.

This was placed under the threads so that the shadow of the atom fell within the circumference of the circle. The fractional co-ordinate of its centre was then read off from the frame calculator. In this manner the co-ordinates of all projected atoms could be read off very speedily.