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# Rotational Disorder in the Crystal Lattice of Cobalt(III) bis Dimethyl Glyoximino Diammine Nitrate. An X-ray Investigation

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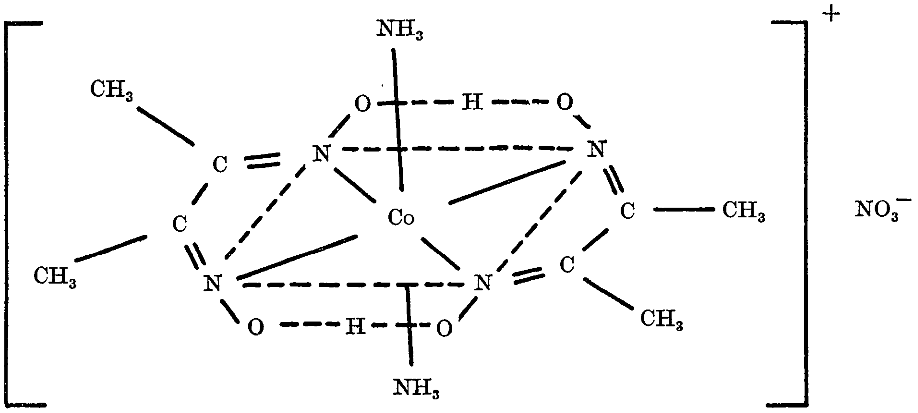
The crystal structure of cobalt(III) bis dimethyl glyoximino diammine nitrate has been determined and refined using two-dimensional X-ray data. The unit cell is monoclinic with

$$a = 9{\cdot}80 \pm 0{\cdot}03,\ b = 6{\cdot}32 \pm 0{\cdot}02,\ c = 12{\cdot}47 \pm 0{\cdot}04\ \text{Å};\ \beta = 97^\circ .$$

The space group is $P2_1/c$ with two molecules in the unit cell. The oxygen atoms belonging to the nitrate ion rotate freely around nitrogen, about an axis nearly parallel to the crystallographic $b$ axis. The cobalt atom, lying on a centre of symmetry, is surrounded octahedrally by nitrogen atoms. The atoms of the dimethyl glyoxime groups and the cobalt atom are very nearly coplanar.

## Introduction

Cobalt(III) bis (dimethyl glyoximino) diammine nitrate has the structural formula:



Preliminary X-ray work on this compound revealed that the nitrate ions form a defect lattice. From the space group and symmetry considerations, it became apparent that the nitrogen atom of the nitrate ion has to be at a centre of symmetry. The trigonal planar nitrate ion will have the apparent symmetry centre only if a rotational or a statistical disorder exists. In the former type the oxygen atoms rotate about an axis passing through nitrogen whereas in the latter the oxygen atoms distribute statistically around nitrogen in such a manner that the average distribution has a centre of symmetry. Recently Kinoshita *et al.* (1959) have reported on the possiblity of a statistical distribution of oxygen atoms in bis(glutaronitrilo) and bis(adipo nitrilo) copper(I) nitrates. The present investigation is concerned with a detailed study of the nature of the disorder in the cobalt complex.

## Experimental

The unit cell (Kunchur & Viswanathan, 1960) is monoclinic having

$$a = 9{\cdot}80 \pm 0{\cdot}03,\ b = 6{\cdot}32 \pm 0{\cdot}02,\ c = 12{\cdot}47 \pm 0{\cdot}04\ \text{Å}\ ,\quad \beta = 97^\circ .$$

The density determined by flotation is 1·69 g.cm.$^{-3}$. The density calculated assuming two molecules per unit cell is 1·58 g.cm.$^{-3}$. The systematic absences of X-ray reflexions are

$$0k0 \text{ for } k \text{ odd}\ ,$$
$$h0l \text{ for } l \text{ odd}\ .$$

This establishes the space group unequivocally as $C^5_{2h}$-$P2_1/c$. The absorption coefficient for Fe $K\alpha$ radiation is 50 cm.$^{-1}$.

Oscillation and Weissenberg photographs were taken around all the three axes using Mn-filtered Fe $K\alpha$ radiation. The intensity data were collected using the multiple-film technique. The intensity of $h0l$, $0kl$ and *hk*0 reflexions were estimated visually and corrected for Lorentz and polarization factors. No absorption correction was made as small crystals were used. The relative $F_o$ values were scaled into absolute values by Wilson's method and in the final stages the scale was improved by comparison with calculated values.

## Structure determination

### (i) *The* (010) *projection*

The space group $P2_1/c$ has four sets of special equivalent positions which are at symmetry centres.

(*a*) $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2}$.
(*b*) $\frac{1}{2}, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
(*c*) $0, 0, \frac{1}{2};\ 0, \frac{1}{2}, 0$.
(*d*) $\frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0$.

Since there are two formula units in the unit cell, the metal atoms and the nitrate ions must occupy two of these special positions, and the cobalt atoms may be placed arbitrarily at (*a*). The nitrate ions can then occupy any one of the remaining positions.

The (010) projection was considered first. Positive signs were assigned to all the structure factors in this

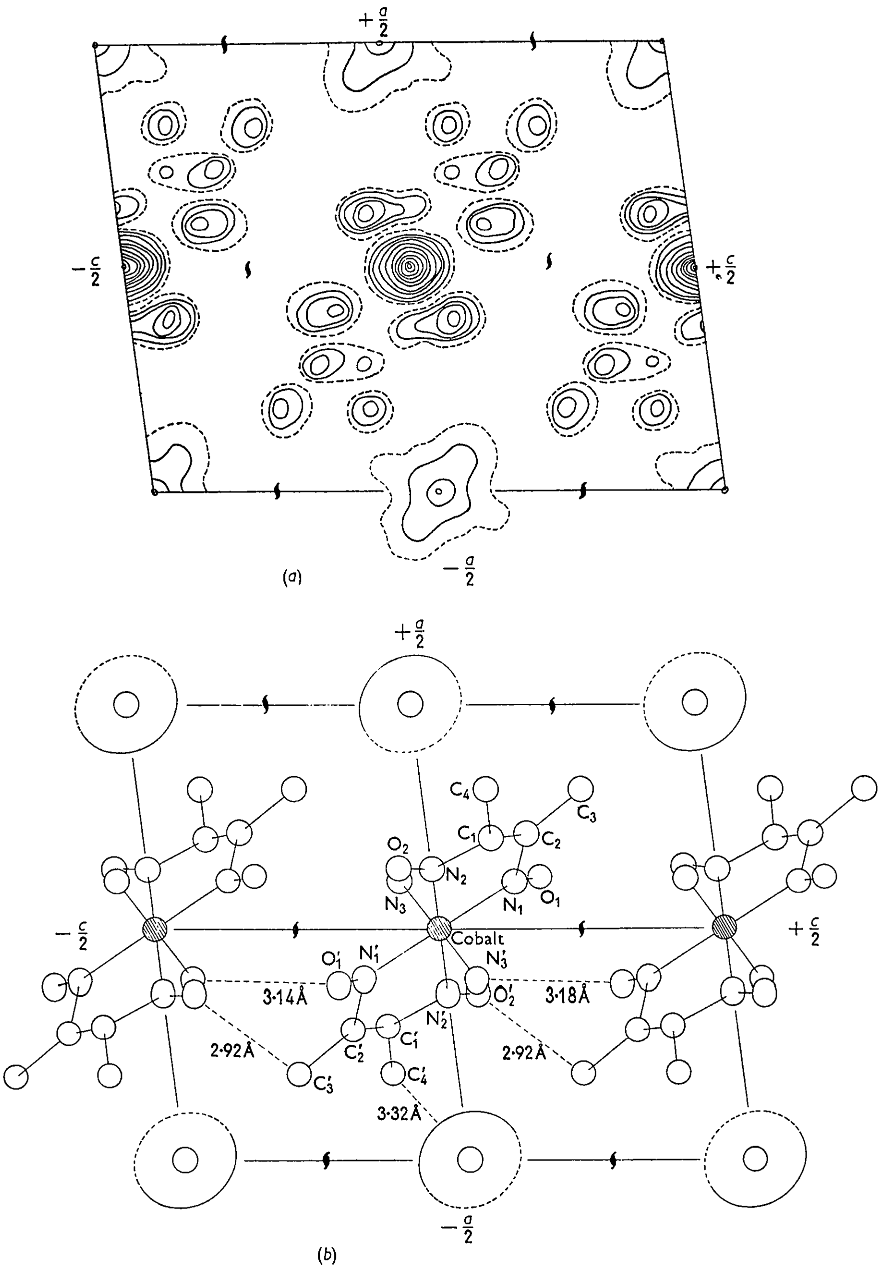


Fig. 1. (*a*) Electron-density projection along the *b* axis. Contours are drawn at equal arbitrary intervals. (*b*) Interpretation diagram for (*a*). Circles round N show the free circular rotation of the oxygen atoms belonging to the nitrate ion.

zone and a Fourier projection $\varrho(x, z)$ calculated. The electron-density map clearly showed the structural details of the molecule. The nitrogen atom of the nitrate ion was found to be at either (*b*) or (*d*) (both these positions are identical in this projection). Around this nitrogen atom the electron density is distributed uniformly in an ellipse. This may be due to a free rotation of oxygen atoms around nitrogen with the axis of rotation tilted slightly to the *b* axis. Structure factors $F_{h0l}$ were calculated with the atomic coordinates obtained from this Fourier diagram. Atomic scattering factors were taken from James & Brindley (1931). An isotropic temperature-correction factor was applied with $B = 2{\cdot}5$ Å$^2$. The contribution of the oxygen atoms of the nitrate ion to the structure factors as discussed by Zachariasen (1945) and Bijvoet & Ketelaar (1932) is

$$F = \sum_{j=1}^{N} f_j J_0(x_j)\ ,$$

where $J_0(x_j)$ is the zero-order Bessel function of argument $x_j$ (Watson, 1952) and

$$x_j = (4\pi a_j/\lambda)\ (\sin\theta \sin\alpha)$$

$a_j$ being the distance of the oxygen atoms from the axis of rotation. This is taken as 1·2 Å, being the N–O bond length in nitrates ($\alpha$ is the angle between the plane containing the rotating atoms and the plane of reflexion). The summation is taken over all the three oxygen atoms of the nitrate ion. For calculation, the axis of rotation is taken as parallel to the crystallographic *b* axis, so that $\alpha = \pi/2$ for the (*h*0*l*) planes. The equation for the *F* values as used in this projection is obtained from the general formula:

$$F_{hkl} = \exp -B\ (\sin^2\theta/\lambda^2)\big[\sum_j f_j \exp 2\pi i(hx_j + ky_j + lz_j) + \sum_{j'} f_{j'} J_0\ (4\pi a_j/\lambda)\ (\sin\theta \sin\alpha)\big]\ ,$$

where $j$ refers to atoms in fixed positions and $j'$ to the atoms involved in free rotation.

The atomic coordinates were refined by successive $(F_o - F_c)$ syntheses. The final reliability index

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$$

is 0·112. Structure factors were also calculated on the assumption of a statistical distribution of nitrate ions, but the results gave a higher *R* value of 0·13 which indicates that free rotation is more probable. Atomic parameters for the oxygen atoms in the statistical distribution model were found by trial-and-error methods.

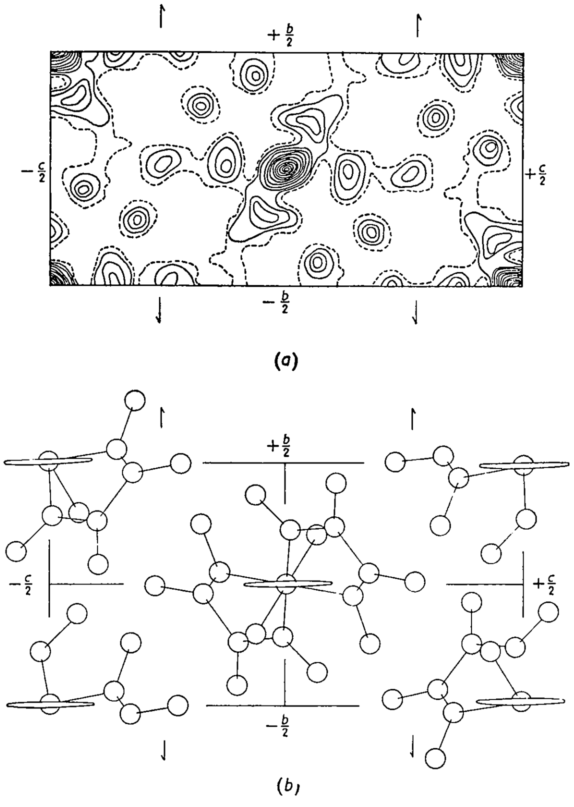


Fig. 2. (*a*) Electron density projection along the *a* axis. Contours are drawn at equal arbitrary intervals. (*b*) Interpretation diagram for (*a*).

### (ii) *The* (100) *projection*

The cobalt atoms and the nitrate ions occupying the special positions do not contribute to reflexions with $k + l$ odd and thus do not help to fix the phases of the structure factors of these reflexions. A Patterson synthesis $P(y, z)$ was therefore carried out. Atomic parameters were determined and structure factors calculated; $\varrho(y, z)$ was then calculated using the signs of the calculated $F_c$'s. The nitrate ion was found to be at the position (*b*). The atomic coordinates were refined by $(F_o - F_c)$ syntheses. The final *R* value is 0·103.

Structure factors $F_{hk0}$ were also calculated and the *R* value for this projection is 0·112. The contribution of the nitrate ions to the structure factors of *hk*0 and 0*kl* reflexions is calculated on the basis of a free rotation of oxygen atoms around nitrogen about an axis parallel to *b* axis.

To obtain a convincing description of the nitrate group, difference syntheses of all the three projections were computed with the contributions of all except the oxygen atoms of the nitrate group subtracted out. In the (010) projection of this synthesis (Fig. 3(*a*)) the maximum of electron density is distributed over a ring 1·2 Å away from the nitrogen atom. This supports the phenomenon of free rotation rather than the statistical distribution because in the latter case one expects six peaks for oxygen atoms around nitrogen. Figs. 3(*b*) and (*c*), which show the difference maps for the (001) and (100) projections, support these conclusions.

The final coordinates are listed in Table 1 and the structure factors are tabulated in Table 3. The final

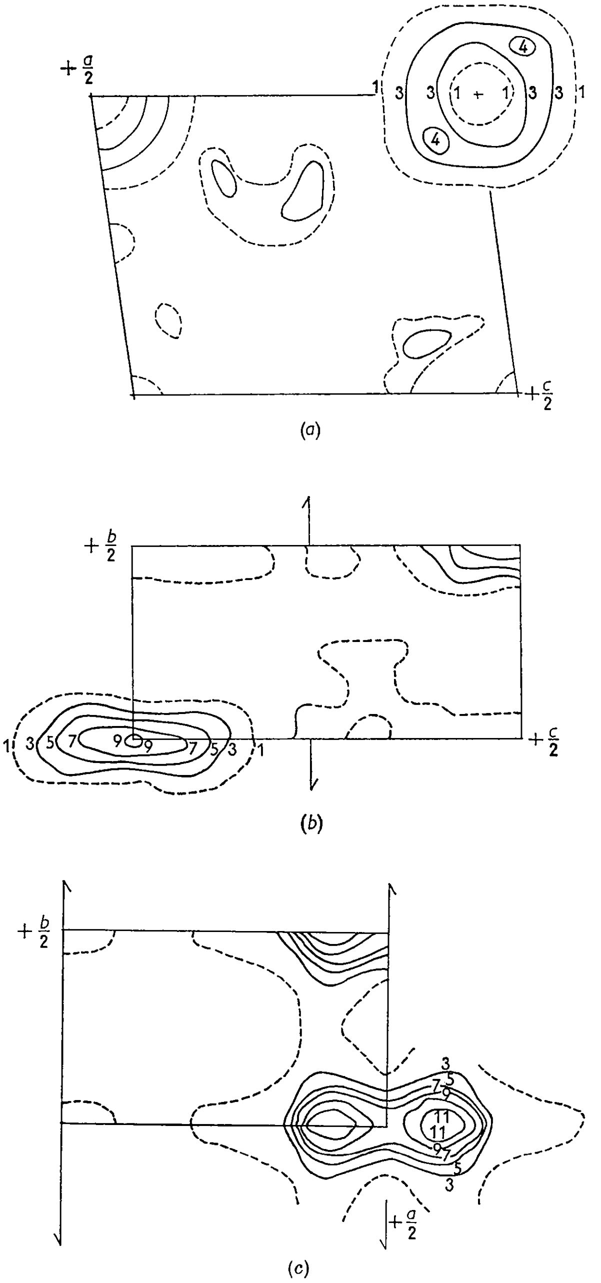


Fig. 3. (*a*), (*b*), (*c*). Difference syntheses for (*h*0*l*), (0*kl*), (*hk*0) projection respectively, with the contributions of all the atoms except the oxygen atoms of the nitrate ion subtracted out from the $F_o$'s.

projections upon (010) and (100) are shown in Figs. 1(*a*) and 2(*a*).

## Description of the structure

The bond lengths and bond angles obtained from the final coordinates are shown in Table 2 and Fig. 4. The arrangement of molecules and the various approaches between them projected upon (010) and (100) are shown in Figs. 1(*b*) and 2(*b*). The intermolecular distances correspond to a normal van der Waals contact. The distance between $O_2$–$O_1'$ and $O_1$–$O_2'$ is 2·65 Å indicating the presence of hydrogen bonds between them.

Table 1. *The final atomic co-ordinates*

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Co | 0·000 | 0·000 | 0·000 |
| $N_1$ | 0·109 | 0·943 | 0·140 |
| $N_2$ | 0·142 | 0·214 | 0·012 |
| $N_3$ | 0·883 | 0·198 | 0·067 |
| $N_4$ | 0·500 | 0·000 | 0·000 |
| $C_1$ | 0·212 | 0·233 | 0·098 |
| $C_2$ | 0·216 | 0·040 | 0·172 |
| $C_3$ | 0·314 | 0·003 | 0·274 |
| $C_4$ | 0·316 | 0·405 | 0·103 |
| $O_1$ | 0·101 | 0·748 | 0·180 |
| $O_2$ | 0·135 | 0·366 | 0·933 |

$N_4$ is the nitrogen atom belonging to the nitrate ion.

Table 2. *The bond lengths and bond angles in the Cobalt DMG nitrate*

| Bond-lengths | | Bond-angles | |
|---|---|---|---|
| Co–$N_1$ | 1·97 Å | Co–$N_2$–$C_1$ | 119° |
| Co–$N_2$ | 1·94 | Co–$N_1$–$C_2$ | 123 |
| $N_1$–$O_1$ | 1·33 | $N_2$–$C_1$–$C_2$ | 115 |
| $N_2$–$O_2$ | 1·37 | $C_1$–$C_2$–$N_1$ | 105 |
| $N_2$–$C_1$ | 1·21 | Co–$N_2$–$O_2$ | 116 |
| $N_1$–$C_2$ | 1·23 | $O_2$–$N_2$–$C_1$ | 123 |
| $C_1$–$C_2$ | 1·52 | $N_2$–$C_1$–$C_4$ | 116 |
| $C_1$–$C_4$ | 1·47 | $C_4$–$C_1$–$C_2$ | 127 |
| $C_2$–$C_3$ | 1·52 | $C_1$–$C_2$–$C_3$ | 126 |
| Co–$N_3$ | 1·96 | $C_3$–$C_2$–$N_1$ | 128 |
| $O_2 \cdots O_1$ | 2·65 | $C_2$–$N_1$–$O_1$ | 116 |
| | | Co–$N_1$–$O_1$ | 118 |
| | | $N_3$–Co–$N_2$ | 90 |
| | | $N_3$–Co–$N_1$ | 90 |
| | | $N_2$–Co–$N_1$ | 78 |

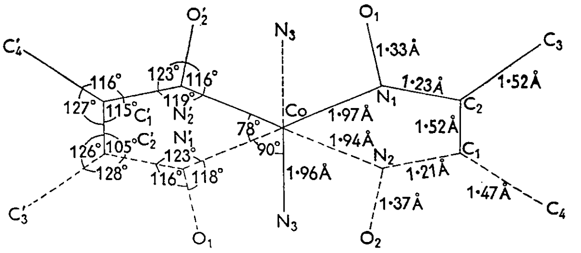


Fig. 4. Bond lengths, bond angles and labelling of atoms in the $[CoDMG_2(NH_3)_2]^+$ complex ion.

## Discussion

The nitrogen atoms are octahedrally coordinated around cobalt atom at distances varying between 1·94–1·97 Å. In the valence-bond description the orbitals involved in the hybridization are $3d\gamma^2 4s4p^3$ of the cobalt atom. An octahedral diamagnetic complex would result. In the ligand-field description the strong crystal field provided by the ligands splits up the *d* orbitals of the cobalt atom and thus causes pairing of electrons in the $3d_\varepsilon$ subshell.

Table 3. *Observed and calculated structure factors*

| *hkl* | $F_o$ | $F_c$ |
|---|---|---|
| 100 | 38 | 45 |
| 200 | 22 | 18 |
| 300 | 4 | −9 |
| 400 | 25 | −24 |
| 500 | 16 | −15 |
| 600 | 3 | 10 |
| 700 | 17 | 18 |
| 800 | 23 | 24 |
| 900 | 28 | 29 |
| 10,0,0 | 23 | 24 |
| 002 | 46 | 51 |
| 004 | 14 | 12 |
| 006 | 17 | 15 |
| 008 | 10 | 8 |
| 0,0,10 | 13 | 13 |
| $\bar{9}02$ | 6 | 4 |
| $\bar{8}02$ | 17 | 15 |
| $\bar{7}02$ | 30 | 23 |
| $\bar{6}02$ | 28 | 30 |
| $\bar{5}02$ | 26 | 27 |
| $\bar{4}02$ | 8 | 8 |
| $\bar{3}02$ | 20 | −12 |
| $\bar{2}02$ | 48 | 45 |
| $\bar{1}02$ | 43 | 43 |
| 102 | 3 | −4 |
| 202 | 30 | 29 |
| 302 | 3 | 3 |
| 402 | 2 | −1 |
| 502 | 10 | 11 |
| 602 | 5 | 8 |
| 702 | 20 | 20 |
| 802 | 36 | 36 |
| 902 | 15 | 15 |
| $\bar{8}04$ | 21 | 21 |
| $\bar{7}04$ | 41 | 37 |
| $\bar{6}04$ | 31 | 32 |
| $\bar{5}04$ | 20 | 20 |
| $\bar{4}04$ | 17 | 17 |
| $\bar{3}04$ | 10 | −8 |
| $\bar{2}04$ | 10 | −12 |
| $\bar{1}04$ | 14 | −12 |
| 104 | 30 | 29 |
| 204 | 50 | 58 |
| 304 | 42 | 45 |
| 404 | 25 | 19 |
| 504 | 10 | 10 |
| 604 | 18 | 14 |
| 704 | 3 | −1 |
| 804 | 7 | 7 |
| $\bar{8}06$ | 14 | 16 |
| $\bar{7}06$ | 8 | 8 |
| $\bar{6}06$ | 20 | 19 |
| $\bar{5}06$ | 31 | 25 |
| $\bar{4}06$ | 19 | 12 |
| $\bar{3}06$ | 16 | 14 |
| $\bar{2}06$ | 25 | 22 |
| $\bar{1}06$ | 14 | 12 |
| 106 | 44 | 44 |
| 206 | 24 | 25 |
| 306 | 10 | 11 |
| 406 | 26 | 21 |
| 506 | 9 | 9 |
| 606 | 3 | 2 |
| 706 | 9 | 7 |
| 806 | 17 | 13 |
| $\bar{8}08$ | 5 | 5 |
| $\bar{7}08$ | 6 | 5 |
| $\bar{6}08$ | 14 | 12 |
| $\bar{5}08$ | 10 | 10 |
| $\bar{4}08$ | 20 | 20 |
| $\bar{3}08$ | 40 | 34 |
| $\bar{2}08$ | 19 | 22 |
| $\bar{1}08$ | 17 | 13 |
| 108 | 3 | 0 |
| 208 | 7 | 5 |
| 308 | 8 | 9 |
| 408 | 16 | 17 |
| 508 | 15 | 14 |
| 608 | 15 | 18 |
| 708 | 11 | 11 |
| 1,0,10 | 14 | 13 |
| 2,0,10 | 18 | 16 |
| 3,0,10 | 16 | 16 |
| 4,0,10 | 16 | 17 |
| 020 | 40 | 36 |
| 040 | 43 | 46 |
| 060 | 3 | 3 |
| 011 | 39 | 48 |
| 012 | 7 | −5 |
| 013 | 29 | 27 |
| 014 | 23 | −23 |
| 015 | 27 | 27 |
| 016 | 10 | −6 |
| 017 | 34 | 35 |
| 018 | 5 | 5 |
| 019 | 14 | 14 |
| 0,1,10 | 4 | −5 |
| 021 | 2 | 2 |
| 022 | 17 | 17 |
| 023 | 10 | −10 |
| 024 | 22 | 21 |
| 025 | 20 | −18 |
| 026 | 15 | 16 |
| 027 | 9 | −10 |
| 028 | 27 | 24 |
| 029 | 7 | 7 |
| 0,2,10 | 3 | 2 |
| 0,2,11 | 3 | 7 |
| 031 | 28 | 30 |
| 032 | 8 | 7 |
| 033 | 10 | 12 |
| 034 | 15 | 18 |
| 035 | 18 | 11 |
| 036 | 3 | 0 |
| 037 | 22 | 20 |
| 038 | 3 | −2 |
| 039 | 8 | 6 |
| 0,3,10 | 6 | 6 |
| 041 | 7 | 7 |
| 042 | 10 | 10 |
| 043 | 19 | −17 |
| 044 | 27 | 22 |
| 045 | 3 | 3 |
| 046 | 26 | 23 |
| 047 | 7 | −5 |
| 048 | 16 | 14 |
| 049 | 3 | 0 |
| 051 | 28 | 30 |
| 052 | 2 | −2 |
| 053 | 20 | 20 |
| 054 | 7 | −8 |
| 055 | 10 | 7 |
| 056 | 3 | −1 |
| 057 | 11 | 9 |
| 061 | 3 | 0 |
| 062 | 14 | 14 |
| 063 | 3 | 2 |
| 064 | 13 | 15 |
| 110 | 15 | −17 |
| 210 | 7 | 7 |
| 310 | 18 | 20 |
| 410 | 9 | 13 |
| 510 | 6 | 7 |
| 610 | 4 | −5 |
| 710 | 3 | −8 |
| 810 | 3 | 3 |
| 120 | 23 | −22 |
| 220 | 25 | 25 |
| 320 | 40 | 39 |
| 420 | 35 | 34 |
| 520 | 27 | 24 |
| 620 | 25 | 20 |
| 720 | 20 | 14 |
| 820 | 9 | 7 |
| 920 | 6 | 6 |
| 130 | 6 | −7 |
| 230 | 6 | −4 |
| 330 | 3 | −3 |
| 430 | 14 | −13 |
| 530 | 3 | 2 |
| 630 | 3 | 3 |
| 730 | 6 | 3 |
| 830 | 5 | 5 |
| 140 | 14 | 10 |
| 240 | 18 | 20 |
| 340 | 14 | 11 |
| 440 | 25 | 23 |
| 540 | 16 | 15 |
| 640 | 14 | 15 |
| 740 | 6 | 6 |
| 150 | 5 | 5 |
| 250 | 3 | −7 |
| 350 | 13 | 13 |
| 450 | 11 | 9 |

Other bond lengths and bond angles in the molecule agree well with the generally accepted values (Frasson *et al.*, 1959). The lengths of chemically identical bonds agree within experimental error. All the atoms belonging to the two dimethyl–glyoximine groups together with the cobalt atom lie in one plane within the standard deviation.

Many crystalline materials are known to exhibit rotational disorder. Pauling (1930) has shown that above 125 °C., the $NO_3$ group in $NH_4NO_3$ is freely rotating in all orientations. Bijvoet & Ketelaar (1932) have shown that a similar molecular rotation exists in the high-temperature form of $NaNO_3$. A realistic demonstration of the rotation of $SO_3$ molecules in the structure of triphenylamine sulfur trioxide has been given by Shimizu & McLachlan (1953).

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# Isomorphous Replacement Method in Non-centrosymmetric Structures

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Even though the advantages of the isomorphous replacement method over the heavy atom method have been recognized for a long time, this method has not had as wide an application in solving non-centrosymmetric structures as the heavy atom method. Viewing the problem of structure analysis as that of 'unfolding' the vector map of the structure, it is seen that in principle the isomorphous series method should have exactly the same applicability as the heavy atom method in the case of non-centrosymmetric structures also. A Fourier synthesis based on data from two non-centrosymmetric isomorphous crystals is suggested and this synthesis is shown to be of considerable value in solving such structures.

## Introduction

Some of the most successful analyses of complicated organic crystal structures have been achieved with the help of either the isomorphous replacement method or the heavy atom method. Even though at first sight these two methods seem very different with regard to their applicability in any particular case, more detailed study shows that the principles used in deducing the structure from the measured intensities of reflections are almost identical in the two cases. In theory, the heavy atom technique applied to a crystal with an infinitely heavy atom and with intensities measured with no errors will give the same results as the isomorphous series. Hence, the isomorphous series will have the same applicability, limitations and ambiguities as the corresponding idealized heavy atom method. The advantage of the isomorphous series method over the heavy atom method is in the accuracy with which the light atom positions can be determined for a given accuracy in the intensity measurements. Indeed, this fact has been recognized by crystallographers for a long time and applied in many successful structure analyses. However, in all these analyses, the isomorphous technique has been applied to the centrosymmetric cases; the heavy atom method being more widely used in non-centrosymmetric cases *even when isomorphous crystals were easily available*. Regarding the problem of structure analysis of isomorphous crystals as a problem in 'unfolding' the difference Patterson (D.P.) of the structure, it has been shown (Kartha & Ramachandran, 1955) that this can be done as easily in the acentric as in the centric case, and that it is possible to recover the original structure from the (D.P.) in 219 of the 230 space groups, if the replaceable atoms are in general positions. For the remaining 11 polar space groups, the structure duplicated by its inverse is obtained if there is only one replaceable atom per asymmetric unit. This ambiguity can also be removed if the structure contains more than one replaceable atom per asymmetric unit. The same treatment applies to the Patterson of the heavy atom structure and the same limitations also apply. It is thus clear that, viewing the problem of structure analysis as an 'unfolding' problem, there is no difference in principle between the two methods as applied to either the centric or non-centric cases.

It was pointed out in the paper cited above (Kartha & Ramachandran, 1955) that the problem of non-centric structures viewed as an 'unfolding' problem using superposition and minimum function methods can be solved without ambiguity, whereas trying to solve the problem by determining the phases of the reflections gave ambiguous results. However, it was felt that two isomorphous non-centrosymmetric crystals contained enough information to 'arrive' at the structure by the phase method, provided the problem is suitably formulated. With this aim the author made a detailed study of the way in which the simplified Patterson, containing only vectors involving heavy or replaceable atoms can be 'unfolded' by a superposition method to enable a complementary Fourier series formulation using measured amplitudes and inferred phases, which also gives the same solution. As a result, a modified Fourier series is obtained which extends the isomorphous series method to non-centric cases, so that we can make use of the obvious advantages of this method over the more commonly used heavy atom method. As the success of the suggested Fourier is capable of a surprisingly simple intuitive explanation, such an argument leading to the suggested series is developed in the next sections.

## Phase ambiquity in non-centric structures

If we consider the vector diagram (Fig. 1) describing the scattering from two isomorphous crystals $\mathbf{C}_1$ and

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