There is some shortening in both of the C–C single bonds in the rings, but this is in accord with values found for other five-membered cyclic systems. The shortening by resonance of the central bond in the conjugated dioxime ether is worthy of note. The resonance interaction would help to keep the system in the more stable transoid form in which it is found to exist in the solid state. The ultraviolet absorption spectrum is very similar to that of dimethylglyoxime dimethyl ether, and both compounds have similar absorption in the significant infrared regions.

The full circle goniometer used in this work was a prototype made available to us by Electronics and Alloys, Inc. Ridgefield, N.J.

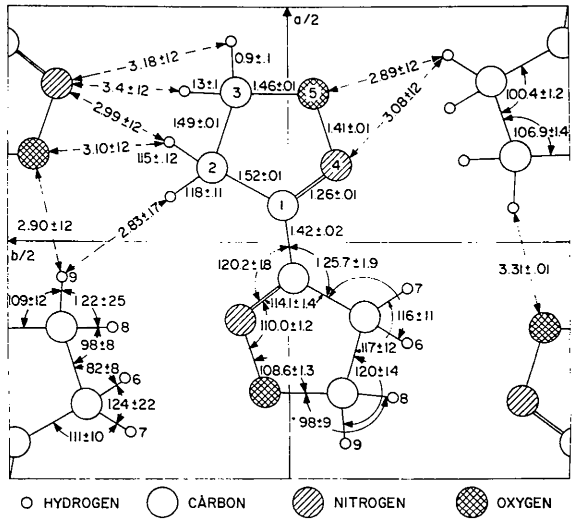

Fig. 4. Bond distances and angles in 3,3′-bi-2-isoxazoline.

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Solution of the Phase Problem in Centrosymmetric Structures with Heavy Atoms in Special Positions

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(*Received* 11 *January* 1965 *and in revised form* 1 *April* 1965)

The number of the signs of unitary structure factors of a centrosymmetric structure determined by the presence of heavy atoms in special positions is expressed in terms of probability relationships. Some methods for complete solution of the phase problem in this case are considered.

Introduction

The 'heavy-atom' method of solving centrosymmetric crystal structures has been proved to be most promising in the determination of molecular structures. A criterion for deciding the degree of resolution of the crystal structure by the heavy-atom method was given by Luzzati (1953), Woolfson (1956) and Sim (1957).

The present paper deals with a case when the heavy atoms of a centrosymmetric structure are in special positions.

Basic relations

Let heavy atoms occupy special positions whose multiplicity α is lower than the multiplicity of the general positions. Further let us suppose that the following equation is valid for indices h_1, h_2, h_3:

$$\frac{h_1}{u_1}+\frac{h_2}{u_2}+\frac{h_3}{u_3}=\sum_{s=1}^{3}\frac{h_s}{u_s}=\mathbf{h}\,.\,\mathbf{r}=\text{integer}\,. \qquad (1)$$

$1/u_s$ are the fractional coordinates of the heavy atoms, $\mathbf{h}$ is the reciprocal lattice vector, $\mathbf{r}$ is the direct lattice vector.

For a structure containing heavy atoms in special positions the unitary structure factor $U_{\mathbf{h}}$ may be written:

$$U_{\mathbf{h}}=C_H+\sum_{j=\alpha+1}^{N} n_j \cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j=C_H+C_L\,. \quad (2)$$

The unitary structure factors will be of two types – those for which

$$C_H=\alpha n_H \quad (2\text{i})$$

and those for which

$$C_H=0\,. \quad (2\text{ii})$$

The probability P_+ that the sign of $U_{\mathbf{h}}$ is the same as that of C_H was given by Woolfson (1956):

$$P_+(C_H,\ U_{\mathbf{h}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left(|U_{\mathbf{h}}|C_H/\varepsilon\right)\,, \quad (3)$$

where

$$\varepsilon=\sum_{j=\alpha+1}^{N} n_j^2. \quad (4)$$

Using equation (2i) this relation can be rewritten as follows:

$$P_+(C_H,\ U_{\mathbf{h}})=\frac{\exp\left(2\alpha n_H|U_{\mathbf{h}}|/\varepsilon\right)}{1+\exp\left(2\alpha n_H|U_{\mathbf{h}}|/\varepsilon\right)}\,. \quad (5)$$

Using only reflexions which fulfil condition (1) we must take into account that in the corresponding fictitious structure new symmetry elements arise, and in addition to the basic arrangement of atoms new symmetrically related atoms appear. When the number of atoms in general positions is increased by a factor k, the unitary atomic scattering factors n_j of these atoms change to n_j/k and then

$$\varepsilon=\frac{1}{k^2}\sum_{j=\alpha+1}^{kN} n_j^2\sim\frac{1}{k^2}\sum_{j=\alpha+1}^{kN} Z_j^2/F(000)^2. \quad (5\text{i})$$

Z_j is the atomic number of the jth atom; $F(000)$ is the number of electrons in the unit cell.

With this value of ε the mean value of $\langle U^2\rangle$ does not change because

$$\langle U^2\rangle=k\varepsilon\,, \quad (6)$$

where the factor k takes account of the symmetry elements (Wilson, 1949).

The probability that $|U_{\mathbf{h}}|$ lies between $|U|$ and $|U|+dU$ follows from the expression for the probability distribution of the structure factors given by Wilson (1949) and modified by Woolfson (1956):

$$P(U_{\mathbf{h}})dU=(2\pi\varepsilon)^{-\frac{1}{2}}\left[\exp\left\{-\frac{(|U_{\mathbf{h}}|+|C_H|)^2}{2\varepsilon}\right\}+\exp\left\{-\frac{(|U_{\mathbf{h}}|-|C_H|)^2}{2\varepsilon}\right\}\right]. \quad (7)$$

The probability function (7) has its maximum at $(U_{\mathbf{h}})_{\max}$ given by the condition:

$$\frac{\operatorname{arc\,tanh}\{(U_{\mathbf{h}})_{\max}/|C_H|\}}{(U_{\mathbf{h}})_{\max}/|C_H|}=|C_H|^2/\varepsilon\,. \quad (8)$$

In most cases $(U_{\mathbf{h}})_{\max}\sim C_H$: this means that most of the unitary structure factors with a contribution from the heavy atoms are to be found in the range of high probability P_+.

If $k=1$, a direct solution of the problem is possible. In this case the heavy atom lies on the origin of the unit cell. Relations (4) and (7) enable the fraction of structure factors determined in sign by the presence of a heavy atom to be evaluated readily. If this fraction is high enough, the Fourier synthesis with positive coefficients F_h may be computed which shows the structure model directly.

If $k=2$, the heavy atoms in special positions contribute to just half the structure factors. The Fourier synthesis calculated with only these structure factors shows $2(N–2)$ peaks for $(N–2)$ atoms and we have to find $(N–2)$ positions of the basic structure. For the solution of this problem we have, however, the following possibilities:

(*a*) A modified Patterson synthesis $P(uvw)$, computed from $|F'_h|^2$ with no heavy atom contribution, gives us information on interatomic distances between the atoms in general positions.

(*b*) Other structural information may be useful.

(*c*) For 'zero' reflexions the following equation is valid:

$$\sum_{j=\alpha+1}^{N} n_j\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j=-2n_\alpha\,. \quad (9)$$

This information could be useful if some atomic positions were already known. But we must take into account that 'zero' reflexions actually can have intensities different from zero and in such a case equation (9) is not strictly fullfilled.

(*d*) For the unitary structure factors $U_{\mathbf{h}}'$ with no heavy atom contribution we can use the probability relationship (Woolfson, 1961):

$$S(U_{\mathbf{h}}')\approx S\Big(\sum_{\mathbf{h}'} U_{\mathbf{h}}'U'_{\mathbf{h}+\mathbf{h}'}\Big) \quad (10)$$

where the summation is taken over all available products. $U_{\mathbf{h}}'$ and $U_{\mathbf{h}'}'$ are unitary structure factors with no heavy atom contribution, $U_{\mathbf{h}+\mathbf{h}'}'$ are unitary structure factors from which the heavy atom contribution has been removed. These are given by:

$$U'_{\mathbf{h}+\mathbf{h}'}=(U_{\mathbf{h}+\mathbf{h}'}-C_H)\frac{\varepsilon+\alpha n_H^2}{\varepsilon}\,. \quad (11)$$

The relation (11) is only probably true as it assumes that C_H and $U_{\mathbf{h}+\mathbf{h}'}$ have the same sign. The expression $(U_{\mathbf{h}+\mathbf{h}'}-C_H)$ may be of the same sign as C_H, if $U_{\mathbf{h}+\mathbf{h}'}>C_H$ or of opposite sign, if $U_{\mathbf{h}+\mathbf{h}'}<C_H$, therefore $U'_{\mathbf{h}+\mathbf{h}'}$ may be positive or negative. All these principles were applied in the structure analysis of $Cu[NH_2\,.\,C(CH_3)_2\,.\,CH_2\,.\,CH(CH_3){=}NH]_2(NO_3)_2$.

Application

The complex compound $Cu[NH_2\,.\,C(CH_3)_2\,.\,CH_2.\,CH(CH_3){=}NH]_2(NO_3)_2$ crystallizes with monoclinic symmetry and has the following unit-cell parameters (Hanic & Serator, 1964):

$$a=7{\cdot}10,\ b=14{\cdot}63,\ c=9{\cdot}24\ \text{Å};\ \beta=99^\circ\ 21'\ .$$

The unit-cell content is $Cu_2C_{24}N_{12}O_{12}H_{56}$. Space group $P2_1/c$. $F(000)=438$.

The Cu atoms are in the special position (*a*) with coordinates: (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$). They contribute only to the reflexions h_1, h_2, h_3 for which $h_2+h_3=2n$.

In the volume of the limiting sphere 761 independent reflexions were observed, 530 with a contribution from heavy atoms and 231 with no heavy atom contribution. The number of zero reflexions in the first group ($h_2+h_3=2n$) was 42, in the second group ($h_2+h_3=2n+1$) 264.

In Fig. 1, (*a*) (*b*) show the probability distribution of $U_{\mathbf{h}}$ for reflexions with $h_2+h_3=2n$ and $h_2+h_3=2n+1$ respectively; the full lines indicate the distribution curves of the experimental unitary structure factors and the dashed lines represent the theoretical curves. The agreement with the theoretical curves is remarkable. The value of C_H in general varies with $\sin\theta/\lambda$ and equation (7) was evaluated with an average value of C_H ($\bar{C}_H=0{\cdot}172$). The value of ε may be treated as a constant and this is given by (5i) ($\varepsilon=0{\cdot}0059$). The maximum of the experimental curve in Fig. 1(*a*) is at 0·170, in agreement with condition (8).

The probability P_+ increases very rapidly with increasing $U_{\mathbf{h}}$ (Fig. 2). At $|U_{\mathbf{h}}|\geq 0{\cdot}15$ all signs of $U_{\mathbf{h}}$ with a contribution from the copper atom are the same as those of C_H, *i.e.* positive. The total number of signs determined by the heavy atoms is 95·8%; the theoretical value evaluated by (4) and (7) is 96·3%. It is worth noting that Sim (1957) considered the proportion of signs given correctly by the heavy atom contributions when they are in general positions. This proportion is calculated in terms of the ratio r of the root-mean-square contribution to the structure factors of the heavy atoms p to that of the remainder of the molecule q, and is expressed as a fraction N of the total number of structure factors:

$$r=p/q\ . \tag{12}$$

But Sim's method is not directly applicable to the case when heavy atoms are in special positions. In this case the probability that unitary structure factors $U_{\mathbf{h}}$ with a contribution from heavy atoms are of the same sign as C_H is higher than would follow from (12), and the correct result is given only by relations (4) and (7). Of course, we may suppose that 50% of $U_{\mathbf{h}}'$ with no contribution from the heavy atoms are of the same sign as C_H. If we add this number to the fraction of unitary structure factors determined in sign by the presence of heavy atoms in special positions we can get a result in satisfactory agreement with the value deduced by Sim's method. But application of the probability relationship (10) enables us to find a higher proportion of correct signs of $U_{\mathbf{h}}'$.

For this purpose we combined $U_{\mathbf{h}}'$ with selected $U_{\mathbf{h}'}'$, with a high value of $|U_{\mathbf{h}'}'|$ and with low indices h_1', h_2', h_3'. In this case the selected $U_{\mathbf{h}'}'$ was $U'_{11\bar{2}}$ with an absolute value of 0·2703. We combined every $U_{\mathbf{h}}'$ with $U_{11\bar{2}}$, $U_{\bar{1}12}$, $U_{\bar{1}\bar{1}2}$ and $U_{1\bar{1}\bar{2}}$. Each sum $\sum_{\mathbf{h}}$ was taken in this way over four products:

$$U'_{112}\,.\,U'_{h1+1,\ h2+1,\ h3-2}+U'_{\bar{1}12}\,.\,U'_{h1-1,\ h2+1,\ h3+2}$$
$$+U'_{\bar{1}\bar{1}2}\,.\,U'_{h1-1,\ h2-1,\ h3+2}+U'_{1\bar{1}\bar{2}}\,.\,U'_{h1+1,\ h2-1,\ h3-2}\,.$$

The frequency with which (10) holds is shown in Table 1. A considerable number of correct signs has been determined by this simple method. The probability of correct sign determination is generally reduced as the absolute value of $|U_{\mathbf{h}}'|$ decreases, but we can

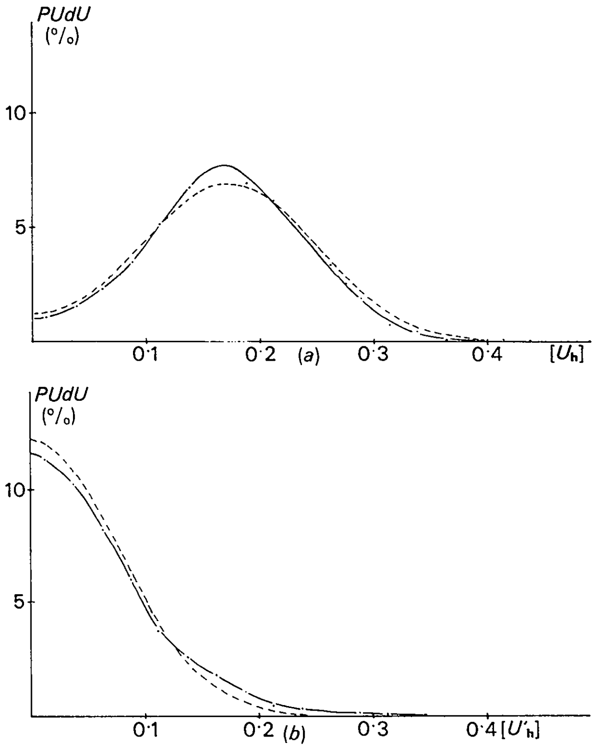

Fig. 1. Probability distribution of $U_{\mathbf{h}}$ (*a*) with heavy atom contribution, (*b*) without heavy atom contribution. Full lines indicate the distribution curves of the experimental unitary structure factors, the dashed lines represent the theoretical distribution.

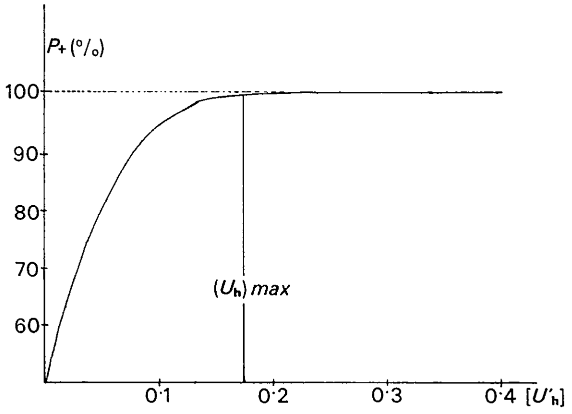

Fig. 2. Probability P_+ as a function of | $U_{\mathbf{h}}$ |.

omit all U_h' with an absolute value less than 0·1 without any serious influence on the resolution of the atomic positions by computation of the electron density function.

Table 1. *Number of unitary structure factors U_h' determined in sign by application of probability relation* (10)

Only reflexions without contribution of heavy atoms are involved.

U_h'	Number of reflexions	Number of correct signs (%)
0·00–0·05	33	69·7
0·05–0·10	82	71·5
0·10–0·15	67	81·3
0·15–0·20	32	90·6
0·20–0·25	9	100·0
0·25–0·30	8	100·0

The presence of further heavy atoms in the structure influences the probability P_+ unfavourably. We can compare the structure of $Cu_2C_{24}N_{12}O_{12}H_{56}$ considered above with the structure of $Cu_2C_8N_{12}O_{16}H_{28}K_2$ (Freeman, Smith & Taylor, 1961). Both $F(000)=422$ and $2n_{Cu}=0{\cdot}178$ of the latter structure are comparable to corresponding values of the first structure, but the value of ε differs considerably ($\varepsilon=0{\cdot}0097$). The fraction of structure factors determined in sign by the presence of heavy atoms in special positions is 89·7% .The theoretical value is 90·4%.

The method described in this paper is sufficiently effective for a complete solution of the phase problem in the case of a structure with heavy atoms in special positions. The only condition is a high probability P_+ for reflexions with a contribution from the heavy atoms. This may be tested by relations (4) and (7) before starting the structure determination.

I am very indebted to Professor M. A. Porai-Koshits for suggesting the possibility of using equation (22).

I wish to thank Miss O. Šalyová for her assistance with the computations.

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The Crystal Structure of Triphenylmethylphosphonium Bis(1,2-dicyanoethylene-1,2-dithiolato)nickelate(III)*

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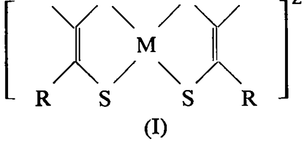
(*Received* 29 *December* 1964 *and in revised form* 7 *April* 1965)

$PCH_3(C_6H_5)_3^+Ni[S_2C_2(CN)_2]_2^-$ crystallizes as a checkerboard arrangement of cationic and anionic columns, the latter containing ions of nearly D_{2h} symmetry essentially identical in dimensions with the isostructural dinegative ions. The anion radicals are so packed that spin–spin coupling through intermediacy of sulfur (Ni · · · S = 3·59 Å) rather than direct Ni–Ni bonding (Ni · · · Ni ≥ 4·40 Å) is presumably responsible for the low magnetic moment. Average lengths of 2·146 ± 0·001 Å for Ni–S bonds and 1·714 ± 0·004 Å for S–C bonds suggest that sulfur is sp^2 hybridized and involved in multiple bonding to the metal. The cationic column has a spine of face-to-face phenyl rings with projecting $PCH_3(C_6H_5)_2$ side groups. $P{-}C_{phenyl}$ bonds average 1·799 Å, somewhat shorter than the few previous reference values.

Introduction

The thiocoordinate chelates of generic formula (I)



(I)

have a number of unusual characteristics. The metal atom (M) can appear in unfamiliar valence states, and a given chelate can have various total charges. Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel, for example, has been prepared having a total charge of $z=0, 1-$, or $2-$, and having nickel in formal oxidation states IV, III, or II. In addition, residual electron spins of paramagnetic chelates are often strongly coupled in the solid state. The nickel complex $Ni[S_2C_2(CN)_2]_2^-$ especially shows a high degree of spin–spin coupling, its tetraethylammonium salt having a magnetic moment

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* Contribution No. 1050.

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