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The Crystal Structure of Nickel Salicylaldoxime*

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The structure of nickel salicylaldoxime, $Ni[OCC_6H_4CH{=}NOH]_2$, has been studied by X-ray single-crystal methods. The unit cell is monoclinic, space group $P2_1/n$, two molecules per unit cell, and $a = 13{\cdot}83$, $b = 4{\cdot}89$, $c = 10{\cdot}20$ Å, $\beta = 110°\ 26'$. The nickel atoms are required to be at symmetry centers and the bonds around the nickel atom must be in a *trans* planar arrangement. The whole molecule is planar. There appears to be a very strong, short, hydrogen bond (2·52 Å) between the phenolic oxygen atom of one organic residue and the oxime oxygen atom of the second organic residue in each molecule.

1. Introduction

This laboratory has been investigating the structures of chelate complexes of analytical importance for the past few years. One of the substances used for the precipitation of nickel is salicylaldoxime (Ephraim, 1931). A preliminary investigation of the structure of nickel salicylaldoxime was made by Cox, Pinkard, Wardlaw & Webster (1935), who showed the crystals to be monoclinic, space group $P2_1/n\text{–}C^5_{2h}$; $a = 13{\cdot}63$, $b = 4{\cdot}89$, $c = 10{\cdot}20$ Å, $\beta = 110°\ 30'$ and $Z = 2$. Since the nickel atoms must be at symmetry centers and the molecules must be centrosymmetrical, this substance was selected for further study because of the ease of determination and, furthermore, the comparison of this structure and that of nickel dimethylglyoxime (Godycki, Rundle, Voter & Banks, 1951; Godycki & Rundle, 1953) might be interesting.

2. Experimental

The salicylaldoxime used was an Eastman Kodak Co. product, m.p. 56·5–57·5° C. with a slight tan color. Its nickel salt was formed according to the method employed by Cox *et al.* (1935). The green precipitate was filtered, washed with cold water, sucked dry on a Buchner funnel and allowed to dry overnight in the air. Single crystals were grown by dissolving some precipitate in boiling chloroform, allowing the chloroform to cool and then to evaporate slowly at room temperature. Small plates with an average size of about 1·5 × 1·0 × 0·5 mm. result. Small, needlelike crystals with a nearly uniform diameter of about 0·5 mm. were selected for X-ray work. The unit-cell dimensions were obtained from measurements of rotation and precession photographs around the principal axes. Since the repeat distance was appreciably longer than that reported by Cox *et al.* (1935), this distance was carefully determined by superimposing the (600) and (10,0,0) reflections and a sodium chloride powder pattern on the same film. The parameters are

$$a = 13{\cdot}83,\ b = 4{\cdot}88,\ c = 10{\cdot}20\ \text{Å}$$
$$\beta = 110°\ 26'\ \text{(by method of } \omega \text{ separations)}\,.$$

The space group is uniquely determined by the systematic extinctions to be $P2_1/n$ (Cox *et al.* (1935) reported $P2_1/m$ apparently owing to a typographical error). The observed density of 1·73 g.cm.$^{-3}$ indicates two molecules per unit cell; calculated density = 1·70 g.cm.$^{-3}$. The molecules must be centrosymmetrical with nickel atoms at symmetry centers.

Multiple-film equi-inclination Weissenberg photographs were taken about [010] for layers $n = 0$ to $n = 3$ and about [001] for layers $n = 0$ to $n = 5$ with Cu $K\alpha$ radiation. Altogether 1097 reflections of measurable intensity were observed and, in addition, 200 reflections were observed to be absent either owing to systematic space-group extinctions or to the fact that they were too weak to be recorded. Intensities were estimated visually by comparison with an intensity strip prepared by a series of timed exposures of typical reflection. A film factor of 3·7 was used. Intensities were corrected in the usual manner for Lorentz and polarization factors and for oblique penetration of the film by the X-rays and the time factor of reflections on non-equatorial layers. All intensities were reduced to a common level by cross-comparison of reflections common to pairs of films.

After the first refinements had been completed, there were still several large discrepancies between observed and calculated structure factors which might have been due to secondary extinction or absorption effects. Consequently, all ($h0l$) reflection intensities were measured again on the Weissenberg camera, using a smaller crystal of about 0·05 × 0·04 mm. cross section and Mo $K\alpha$ radiation. Also the intensities of

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the $(11\bar{2})$, $(21\bar{1})$, $(21\bar{2})$, $(31\bar{1})$, $(31\bar{2})$, $(42\bar{4})$ and $(52\bar{3})$ reflections were similarly remeasured. Eastman Kodak No-Screen X-ray films interleaved with 1·1 mil copper foil were employed and the film factor was experimentally determined to be 3·9. The intensities of the $(hk0)$ reflections were likewise remeasured on the precession camera, using the same small crystal and Mo $K\alpha$ radiation.

3. The structure determination

Since the nickel atoms are located at symmetry centers (000) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, most reflections of the type $(h0l)$ should have positive structure factors, especially if F_o is large. One can start immediately with an electron-density projection upon (010), using about 142 $(h0l)$ reflections which have F_o values larger than 5 and assigning these structure factors positive signs. Actually a Patterson function projected upon (010) was prepared and structure factors were calculated for the reflections from the positions of the atoms read from this projection. The projection shows quite clearly a picture of the molecule. After each electron-density projection, the centers of the atoms were determined by the method of Carpenter & Donohue (1950). New structure factors were calculated and the least-squares best values of k, the scale factor, and B, the coefficient in the exponent of the isotropic temperature factor in equation (1), were determined.

$$kF_o = |F_c| \exp\left[-B \sin^2 \theta/\lambda^2\right] . \qquad (1)$$

The atomic scattering factors used in the preliminary structure-factor calculations were taken from the *Internationale Tabellen* (1935) with corrections for nickel for the dispersion due to the K electrons with Cu $K\alpha$ radiation being applied according to the formulas of Hönl (1933) (see also James, 1950).

After the fourth electron-density projection upon (010) there were no further sign changes in the structure factors and this method of refinement was discontinued. The value of R, defined by

$$R = \Sigma[kF_o - |F_c| \exp(-B \sin^2 \theta/\lambda^2)] \div \Sigma kF_o ,$$

was, however, still 0·24, using all 164 observable reflections of the type $(h0l)$. Fig. 1 shows the fourth electron-density projection upon the (010) plane.

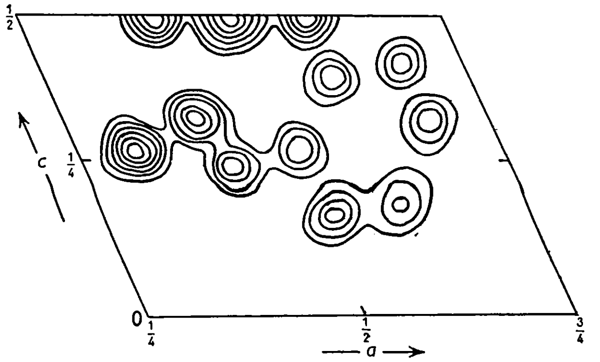

Fig. 1. Electron-density projection of one asymmetric unit of nickel salicylaldoxime upon (010); Cu $K\alpha$ data. Contours are at intervals of 1 e.Å^{-2}, starting with 3 e.Å^{-2}, except around the nickel atom where the intervals are 3, 5, 10, 15, 20 and 25 e.Å^{-2}.

With the x and z parameters of the atoms now fairly well established, it was necessary to find the y parameters. A first approximation was obtained by noting that the projected bond lengths parallel to [100] were much shorter than the accepted values for the bond lengths, while the projected lengths of bonds perpendicular to [100] were about normal. Using Pauling's (1948) values of bond lengths, the average angle of tilt was about $49\frac{1}{4}$° about an axis lying in the [010] plane and making an angle of $39\frac{1}{2}$° with [001] in obtuse β. Assuming that the molecule was planar and was tilted in this manner, it was possible to calculate approximate values of the y parameters of the atoms.

Structure factors were then calculated for the 1097 observed reflections. The value of R, defined above, was 0·47. Three bounded electron-density projections for the matter in the region $x = 0$ to a, $y = 0$ to b and $z = 0$ to $\frac{1}{2}c$ reduced R to 0·33 for the 450 reflections employed. A three-dimensional electron-density synthesis was calculated for thirteen sections parallel to (010). The intervals chosen were $x = 0$ to $\frac{1}{2}a$ by sixtieths, $z = 0$ to c by sixtieths and $y = 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12$ and 14 thirtieths of b.

Centers of atoms were again calculated by the method of Carpenter & Donohue (1950); structure factors were calculated and least-squares best values of k and B were obtained. The value of R for all 1097 observed reflections was 0·32 while R for only the $(h0l)$ reflections was 0·22, showing that the greatest errors were in the y parameters.

The y parameters were refined by one application of the method of least-squares as developed by Hughes (1941), using the relationship

$$\Delta y_i \doteq \frac{\Sigma(F_o - F_c)\partial F_c/\partial y_i}{\Sigma(\partial F_c/\partial y_i)^2} .$$

Reflections whose signs of F_c were uncertain were given weights of zero and all others were weighted 1 in this approximation. R was reduced to 0·27 by this refinement, including all 1297 reflections whether observed or not. In the case of an unobserved reflection, $F_o - F_c$ was taken as zero if F_c was less than half the minimum observable value for that region of the film and otherwise it was taken as $\frac{1}{2}F_{\text{min.}} - F_c$, where $F_{\text{min.}}$ is the minimum observable value for that region of the film.

The least-squares refinement was applied to all parameters and after calculating new structure factors and k and B values, R fell to 0·24 for all 1297 reflections and was 0·19 for the $(h0l)$ reflections. A further refinement of the y parameters only, by the method of least-squares, brought no improvement and only slight shifts of the atomic positions. An attempt to apply an anisotropic temperature factor was unsuccessful.

In order to reduce the value of R still further, molybdenum data for ($h0l$) and ($hk0$) reflections and a few other reflections with large discrepancies were obtained, as described above. The x and z parameters were refined by two difference syntheses, using the ($h0l$) data. The difference syntheses indicated that the thermal vibration was much less for the nickel atom than for the other atoms. Consequently, two values of B were used in subsequent calculations, i.e. $B = 1{\cdot}50$ Å^2 for the nickel atom and $B = 2{\cdot}85$ Å^2 for the lighter atoms. Structure factors were calculated for the ($h0l$) reflections, using McWeeny's (1951) values for atomic scattering factors for carbon, nitrogen and oxygen atoms. The value of R was 0·13.

The ($hk0$) molybdenum data were employed for a calculation of the projected electron density on (001) and also for one difference synthesis. The value of R fell to 0·20 for this zone.

Structure factors for all reflections were then calculated, using the parameters refined, as described above, and McWeeny's (1951) scattering factors. The value of R for the reflections measured with Cu$K\alpha$ radiation was 0·19 while the value for all reflections measured with Mo $K\alpha$ radiation was 0·15. The hydrogen atoms were included in this calculation. The hydrogen positions were calculated from the equation of the plane of the molecule, using a C–H bond distance of 1·05 Å and angles of 120° with C–C bonds. The hydrogen attached to the oxime oxygen was placed 1·0 Å from that atom and on a line between that atom and the neighboring phenolic oxygen.

Table 1. *Atomic parameters in nickel salicylaldoxime*

	x/a	y/b	z/c		x/a	y/b	z/c
Ni	0·000	0·000	0·000	N_{10}	0·093	0·086	0·177
O_2	−0·096	0·260	−0·002	O_{11}	0·184	−0·043	0·233
C_3	−0·091	0·435	0·109	H_{12}	−0·238	0·575	−0·020
C_4	−0·176	0·605	0·081	H_{13}	−0·238	0·920	0·169
C_5	−0·180	0·793	0·184	H_{14}	−0·103	0·986	0·395
C_6	−0·101	0·811	0·311	H_{15}	0·047	0·663	0·429
C_7	−0·013	0·649	0·336	H_{16}	0·137	0·311	0·363
C_8	−0·010	0·466	0·230	H_{17}	0·178	−0·173	0·156
C_9	0·076	0·286	0·265				

Values of the atomic parameters are shown in Table 1; interatomic distances and bond angles are shown in Fig. 2.

All atoms of the molecule lie nearly on a plane. The equation of the least-squares best plane in terms of the unit-cell vectors is

$$x + 0{\cdot}3893y - 0{\cdot}7112z = 0\,.$$

Distances of the atoms from this plane vary from zero to 0·05 Å, with an average value of 0·02 Å.

Tables of F_c and F_o are available upon request to the authors.*

4. Discussion of structure

The average length of the benzene ring bonds is 1·39 Å, which is in good agreement with the generally accepted value of 1·39–1·40 Å. The benzene ring bonds vary in this determination from 1·36 to 1·41 Å. The molecule turns out to be nearly planar with no atom more than 0·05 Å from the least-squares best plane.

Infra-red measurements, carried out by Mr Jack Young, indicate an O_2'–O_{11} hydrogen bonded distance of 2·47 Å, which is in close agreement with the distance of 2·52 Å calculated from this structure determination. There is some evidence of resonance in the six-

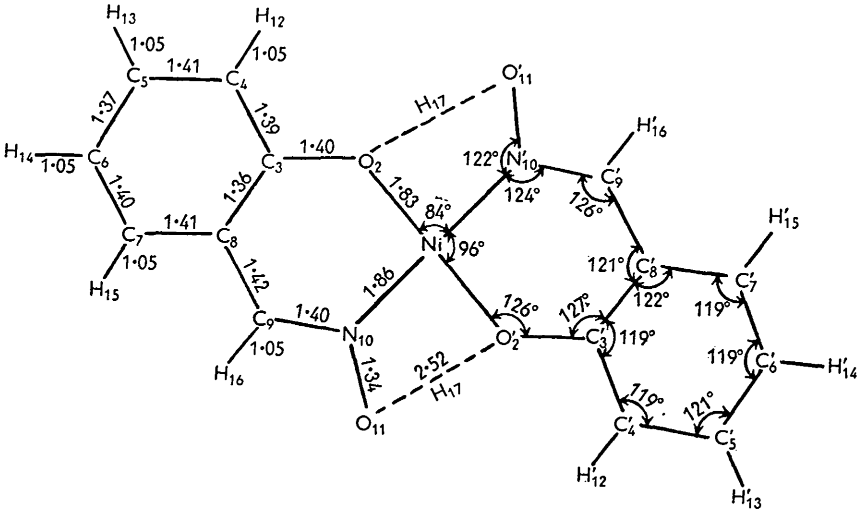

Fig. 2. Interatomic distances and bond angles in nickel salicylaldoxime.

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membered ring containing the nickel atom. Each single bond appears to be 0·04–0·12 Å shorter than a normal single bond, and the double bond appears to be 0·15 Å longer than the normal isolated double bond. The double bond between C_3 and C_8, which is involved in the six-membered chelate ring and the benzene ring, is the shortest (1·36 Å) of the bonds in the benzene ring. Since the true values for the Ni–O and Ni–N bonds are not precisely known, it cannot be stated definitely that these bonds are shortened. If there really is some resonance in this chelate ring, then some 4*d* orbitals must be involved.

The short O–O hydrogen bond distance was unexpected. The two oxygen atoms in this complex are bonded differently and are not exactly similar, as they are in nickel dimethylglyoxime in which Rundle & Parasol (1952) believe there is a symmetrical hydrogen bond. It is probable that the bond is not symmetrical in this complex although it is very short.

There are no unusually close approaches between atoms of different molecules and thus the crystal must be held together primarily by van der Waals forces. There is no indication in this complex of nickel-nickel bonding as there is in the nickel dimethylglyoxime crystals (Godycki & Rundle, 1953).

Before any conclusions can be drawn about the distortion of the salicylaldoxime molecule upon formation of the nickel complex the structure of salicylaldoxime must be determined. We hope to work upon this structure in the near future.

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High-Temperature Structure Transitions in Sodium Niobate*

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A detailed X-ray 'powder' study of sodium niobate at high temperatures has confirmed the conclusion, reached from optical investigations on single crystals, that the crystal structure does not become strictly cubic until the temperature reaches 650° C.

At temperatures between 420° C. and 480° C. the X-ray evidence is consistent with a slightly distorted multiple unit cell with a tetragonal axial ratio very near to 2. At temperatures above 480° C. tetragonal-type diffraction line splitting reappears and the axial ratio increases to 2·0038 at 560° C. This effect is accompanied by a reduction in the intensity of superlattice reflexions. At 640° C. both these reflexions and the line splitting disappear, indicating a completely isotropic perovskite-type structure.

An explanation of the X-ray effects is suggested in terms of atomic displacements.

1. Introduction

Single-crystal X-ray studies of sodium niobate ($NaNbO_3$) by Wood (1951) and Vousden (1951) have shown that the room-temperature structure is orthorhombic. The structure may also be referred to a pseudo-cubic perovskite-type unit cell with monoclinic axes. The presence of extra X-ray reflexions indicates that this cell is multiple, containing 16 molecules and possessing doubled a_0 and c_0 dimen-

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* Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.