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The Molecular Structures of Lifschitz Nickel(II) Complexes. II. The Crystal Structures of One of the Blue and of One of the Yellow Forms of Bis(*meso*-stilbenediamine)nickel(II) Dichloroacetate

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The crystal structures of the blue(I) and of the yellow(II) forms of the dichloroacetate complex have been determined from three-dimensional X-ray data using Patterson and Fourier methods. As indicated by magnetic and spectroscopic data, the blue crystals contain octahedrally coordinated nickel, while the yellow crystals are found to contain both octahedral six-coordinate nickel and planar four-coordinate nickel, the crystal cell containing two molecules of the former type and one molecule of the latter. The Ni-N bond distances in the two types of molecule differ, being 2.05 ± 0.03 Å. in the paramagnetic octahedral molecules and 1.89 ± 0.03 Å. in the diamagnetic planar molecule. In all complex molecules the chelate rings have the *kk'* configuration described by Corey and Bailar.²

Introduction

In part I³ of this series we described the isolation of several crystalline modifications of the complex of *meso*-stilbenediamine with nickel dichloroacetate and showed that the spectroscopic and magnetic properties of the blue forms of the complex are consistent with those expected for octahedrally coordinated nickel, while the magnetic properties of the yellow complex lead one to expect the presence of a mixture of paramagnetic "octahedral" molecules and planar diamagnetic molecules in 2:1 ratio in the solid crystal. In order to determine definitely the stereochemistry of the nickel ions in these compounds and to ascertain the mechanism by which the changes in color and magnetic properties are brought about in many of these complexes, both in the solid state and in solution, a three-dimensional X-ray study was undertaken and the results of the analyses are presented here.

Experimental

Blue(I) crystals and yellow(II) crystals suitable for X-ray analysis were grown from acetone and from 95% ethanol solutions as previously described. The former are obtained as small plates exhibiting faces of the form {100} and {011} while the latter have acicular habit (the crystallographic *x* axis being the needle axis) with faces of the form {010} and {001} predominating.

Crystal Data.—Crystals of blue(I) belong to the monoclinic system, with $a = 14.98 \pm 0.06$, $b = 11.34 \pm 0.04$, $c = 11.64 \pm 0.04$ Å., $\beta = 109.5^\circ$, $V = 1862 \pm 18^\circ$ Å.³. The observed density (determined by flotation in mixtures of chloroform and toluene and carbon tetrachloride and *m*-xylene) was 1.44 g. cc.⁻¹. Assuming a molecular weight of 811 (equivalent to the formula $\text{Ni}(\text{C}_{14}\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{CHCOO})_2 \cdot 4\text{H}_2\text{O}$, suggested by chemical analysis and later verified by the X-ray analysis), $Z = 2$ and the calculated density is 1.445 g. cc.⁻¹.

Yellow(II) crystals are triclinic and have the following unit cell dimensions: $a = 12.81 \pm 0.05$, $b = 15.12 \pm 0.06$, $c = 18.17 \pm 0.07$ Å., $\alpha = 96.0^\circ$, $\beta = 106.25^\circ$, $\gamma = 120.75^\circ$, $V = 2770 \pm 33$ Å.³. The observed density was 1.42 g. cc.⁻¹ (measured by flotation). Chemical analysis again indicated the presence of solvent

(both ethanol and water) in the crystals, the stoichiometric ratio $\text{Ni}(\text{C}_{14}\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{CHCOO})_2 \cdot 2/3\text{C}_2\text{H}_5\text{OH} \cdot 4/3\text{H}_2\text{O}$ being verified by the structure analysis. Therefore, using a molecular weight of 794, $Z = 3$ and the calculated density is 1.425 g. cc.⁻¹.

Data Collection.—Since the computer facilities available to us at the time this work was carried out were limited, it was necessary to keep the experimental and hence the computational effort to a minimum by restricting the number of measured reflections to those for which $0 < \sin \theta \leq \sqrt{2}/2$ for the blue(I) crystals and $0 < \sin \theta \leq 0.6$ for the yellow(II) crystals. Using Cu K α radiation, these limits give *ca.* 1500 independent reflections for blue(I) and 2800 for yellow(II). [The upper limit for the yellow(II) crystals was also fixed by the requirements of the Fourier program used in these analyses.] The crystals used in the collection of intensity data had the approximate dimensions $0.25 \times 0.4 \times 0.4$ mm. Whereas the relative absorption errors for a spherical crystal of diameter 0.4 mm. and linear absorption coefficient 37 cm.⁻¹ will be small and negligible, there will be more serious errors arising from the nonsphericity in the specimen used in this work. However, these will be diminished on correlation of the data as described below.

The intensity data were collected on a Leeds Weissenberg goniometer, using the multiple film technique. Unfiltered Cu K α radiation generated by a demountable X-ray tube of the type described by Rymer and Hambling⁴ was used. Equi-inclination levels $h0l$ to $h7l$ and $hk0$ to $hk7$, and $0kl$ to $8kl$ and $h0l$ to $h9l$, were recorded for the blue(I) and for the yellow(II) crystals, respectively.

The intensities of all reflections were estimated by visual comparison with a standard set of "spots" made using a rotating sector. The usual *Lp* corrections were carried out graphically⁵ and, in addition, reflections on upper layer photographs were also corrected for spot extension when necessary, using the graphical method devised by Phillips.⁶

All reflections were put on the same relative scale by correlation of intensities of common reflections observed on different films and then converted to an approximately absolute scale by Wilson's method.⁷ The average isotropic temperature factors found by this method were 3.28 Å.² for the blue(I) crystals and 5.04 Å.² for the yellow(II) crystals.

Results

Structure Analyses. (a) Blue(I) Crystals.—From the systematic absences ($h0l$ reflections absent for $l =$

(1) Communications regarding this paper should be directed to S. C. N.

(2) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).(3) W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, **3**, 463 (1964).(4) T. B. Rymer and P. G. Hambling, *J. Sci. Instr.*, **29**, 192 (1952).(5) W. Cochran, *ibid.*, **25**, 253 (1948).(6) D. C. Phillips, *Acta Cryst.*, **9**, 819 (1956).(7) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

$2n + 1$ and $0k0$ reflections absent for $k = 2n + 1$), the space group was assigned as $P2_1/c$ (No. 14). A very weak reflection, 050 , was ignored and subsequently shown to be spurious by the successful completion of the analysis.

Since there are four general equivalent positions in the space group $P2_1/c$, the nickel atoms are required to occupy special positions at centers of symmetry. Hence half one complete molecule forms the asymmetric unit. An attempt was made initially to locate the two chlorine atoms in the asymmetric unit, from (010) and (001) Patterson and Fourier projections. However, while several feasible positions could be chosen for these atoms, there was ambiguity and it seemed unwise to proceed to a three-dimensional analysis with uncertain coordinates. After an unsuccessful attempt to solve the Harker section, $P(x, 1/2, z)$, for the chlorine positions, the complete three-dimensional Patterson function was computed, using all 1500 independent $F^2(hkl)$ values. With the nickel atoms in special positions, the nickel-chlorine vector peaks will be situated at $\pm [x, y, z; x, 1/2 + y, 1/2 + z; x, \bar{y}, z; \text{ and } x, 1/2 - y, 1/2 + z]$. Inspection of the Patterson function [computed for the unique quarter of the cell, $x(0 \rightarrow 1); y(0 \rightarrow 1/2); z(0 \rightarrow 1/2)$] showed clearly the vector peaks x, y, z and $\bar{x}, 1/2 - y, 1/2 - z$, expected for each independent chlorine atom. There were four vectors in all, each of roughly the same peak height, and, as expected, these occurred as two pairs, the members of each pair being separated by *ca.* 2.9 Å.—the Cl-Cl distance in the dichloroacetate ion.

From the nickel and chlorine positions obtained above, structure factors were calculated, using as the scattering curve for the nickel ion that tabulated by Thomas and Umeda,⁸ and for chlorine, that tabulated by Tomiie and Stam.⁹ The phases obtained were used to calculate a three-dimensional Fourier synthesis. Reflections having high observed and low calculated values for their structure factors (notably 041 , $10\bar{4}$, and 102) were omitted, as they were of uncertain sign.

From this first Fourier synthesis, all the light atoms of the diamine molecule and of the dichloroacetate ion were unambiguously located, and it was evident that the anion was not coordinated directly to the nickel ion as was originally supposed. The two water molecules thought to be present on the basis of chemical analysis also showed up clearly, and there were only a few minor spurious peaks. Three successive Fourier refinements including these 22 light atoms, in addition to the nickel and chlorine atoms, confirmed the formula $\text{Ni}(\text{C}_{14}\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{CHCOO})_2 \cdot 4\text{H}_2\text{O}$ and reduced the residual, R , to 0.206 (calculated giving reflections of zero intensity a value $F_{\text{min. obsd}}/2$). There were only 11 changes in sign in the final structure factor calculation and these were for reflections of low F_{obsd} , so that refinement for our purpose was considered to

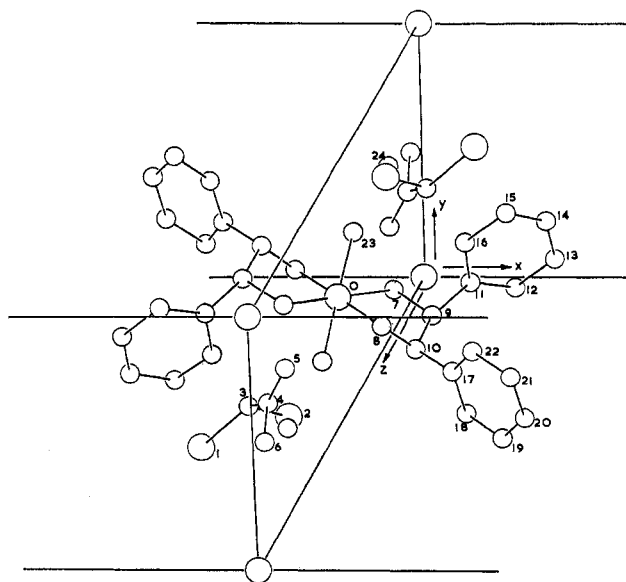


Fig. 1.—Clinographic view of one complex molecule in the blue(I) crystals. The nickel atom is situated at $0, 1/2, 1/2$.

be complete.¹⁰ The light atom scattering factors used in this analysis were those tabulated by Berghuis, *et al.*¹¹ The average temperature factor of 3.28 Å.² was used throughout.

The peak densities in the final Fourier synthesis were as follows: nickel, 31.0 e/Å.⁻³; chlorine, 14.2–15.3 e/Å.⁻³; oxygen, 6.6–7.2 e/Å.⁻³; nitrogen, 6.2 e/Å.⁻³; carbon, 4.2–5.3 e/Å.⁻³. The final set of fractional and orthogonal atomic coordinates, the latter calculated taking the X and Y axes coincident with the monoclinic x and y axes, are given in Table I and refer to the molecule with the nickel atom situated at $0, 1/2, 1/2$. This molecule, depicted in Fig. 1, shows clearly the hexacoordination of the nickel atom with two of the four water molecules occupying the axial positions of a slightly distorted octahedron. The details of the bond lengths and bond angles, important from the viewpoint of this analysis, namely those involving the nickel atom, are given in Table II; for the benzene ring bond lengths and angles and the angles at the aliphatic carbon atoms of the diamine, only the observed average values are quoted.

As anticipated, there is an extensive network of hydrogen bonding present in the crystal, which links together neighboring molecules. This system, which involves the two water molecules, the carboxylate oxygen atoms of the anion, and one of the diamine nitrogen atoms, is shown in Fig. 2 by means of a projection of the structure viewed down the crystallographic x axis, omitting the benzene ring carbon atoms, for the sake of clarity.

(10) Tables of calculated and observed structure factors are deposited as Document Number 7854 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and remitting \$2.75 for photoprints or \$2.00 for 35-mm. microfilm in advance, payable to: Chief, Photoduplication Service, Library of Congress.

(11) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(8) L. F. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(9) Y. Tomiie and C. H. Stam, *Acta Cryst.*, **11**, 126 (1958).

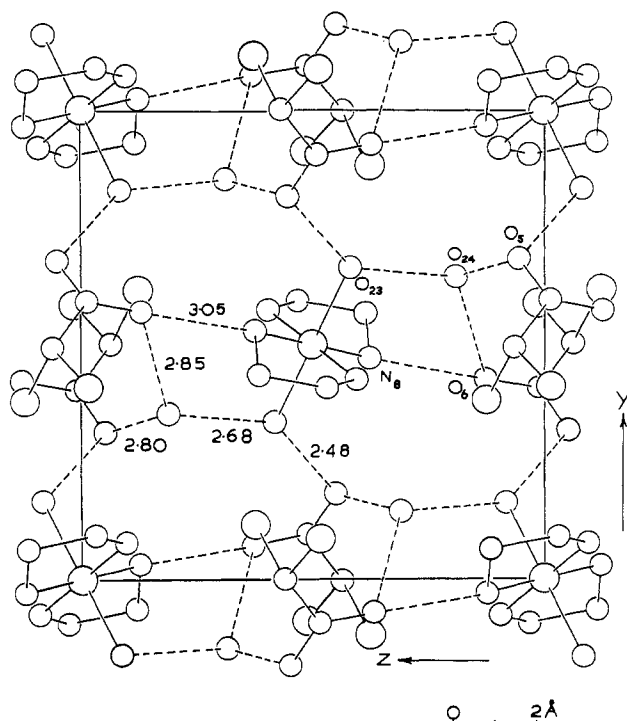


Fig. 2.—The structure of the blue(I) crystals (omitting the benzene ring carbon atoms) viewed down the crystallographic x axis and showing the intermolecular hydrogen bonding. The distances indicated are in Å.

TABLE I
FRACTIONAL AND ORTHOGONAL ATOMIC COORDINATES IN BLUE(I)

	x/a	y/b	z/c	$X, \text{Å}$	$Y, \text{Å}$	$Z, \text{Å}$
Ni(0)	0	0.5000	0.5000	-1.942	5.671	5.484
Cl(1)	0.1375	0.3980	0.1210	1.591	4.514	1.327
Cl(2)	0.2700	0.4280	-0.0120	4.095	4.854	-0.131
C(3)	0.2020	0.5000	0.0650	2.776	5.671	0.713
C(4)	0.1375	0.6000	-0.0100	2.100	6.805	-0.109
O(5)	0.0995	0.5760	-0.1300	1.996	6.533	-1.426
O(6)	0.1120	0.6860	0.0530	1.473	7.780	0.581
N(7)	0.0805	0.4270	0.4060	-0.370	4.843	4.453
N(8)	0.1285	0.5330	0.6260	-0.504	6.045	6.866
C(9)	0.1820	0.4070	0.4820	0.856	4.616	5.286
C(10)	0.1925	0.4330	0.6160	0.493	4.911	6.756
C(11)	0.2480	0.4970	0.4450	1.990	5.637	4.881
C(12)	0.3290	0.4510	0.4220	3.293	5.115	4.628
C(13)	0.3950	0.5265	0.3920	4.400	5.971	4.299
C(14)	0.3670	0.6400	0.3550	4.123	7.258	3.893
C(15)	0.2860	0.6850	0.3740	2.835	7.769	4.102
C(16)	0.2220	0.6170	0.4120	1.728	6.998	4.519
C(17)	0.2970	0.4335	0.7000	1.734	4.916	7.678
C(18)	0.3430	0.3270	0.7460	2.245	3.708	8.182
C(19)	0.4830	0.3200	0.8250	3.362	3.629	9.049
C(20)	0.4920	0.4250	0.8520	4.067	4.820	9.345
C(21)	0.4520	0.5340	0.8030	3.658	6.056	8.807
C(22)	0.3540	0.5380	0.7310	2.468	6.102	8.018
O(23)	0.0030	0.6670	0.4200	-1.588	7.565	4.606
O(24)	-0.0120	0.6500	0.1840	-0.894	7.362	2.018

The packing of the molecules in the unit cell is shown by means of a projection of the structure onto (010) depicted in Fig. 3. Apart from the hydrogen bonding, a nearest neighbors calculation showed that all intermolecular contacts comply well with those expected from van der Waals radii.

(b) **Yellow(II).**—These crystals belong either to space group $P1$ or $P\bar{1}$ and in order to decide between these alternatives, the statistical test of Howells, Phillips, and Rogers¹² was used. The intensity dis-

(12) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

TABLE II

BOND LENGTHS AND ANGLES IN THE BLUE(I) CRYSTALS^a

Bond lengths, Å.		Bond angles	
Ni(0)-N(7)	2.05	N(7)-Ni(0)-N(8)	82.8°
Ni(0)-N(8)	2.03	N(7)-Ni(0)-O(23)	89.9°
Ni(0)-O(23)	2.12	N(8)-Ni(0)-O(23)	88.6°
C(9)-N(7)	1.50	Ni(0)-N(7)-C(9)	114.8°
C(10)-N(8)	1.51	Ni(0)-N(8)-C(10)	106.3°
C(9)-C(10)	1.54	Cl(1)-C(3)-Cl(2)	111.7°
C(9)-C(11)	1.57	Cl(1)-C(3)-C(4)	111.8°
C(10)-C(17)	1.55	Cl(2)-C(3)-C(4)	114.0°
Cl(1)-C(3)	1.77	C(3)-C(4)-O(5)	114.7°
Cl(2)-C(3)	1.77	C(3)-C(4)-O(6)	117.3°
C(3)-C(4)	1.56	O(5)-C(4)-O(6)	127.6°
C(4)-O(5)	1.34		
C(4)-O(6)	1.34		

^a Average C-C distance in the benzene rings (12 values) = 1.41 Å; min. = 1.38 Å; max. = 1.43 Å. Average C-C-C bond angle in the benzene rings (16 values) = 120.3°; min. = 117.0°; max. = 123.5°. Average bond angle at the chelate ring carbon atoms 9 and 10 (6 values) = 111.2°; min. = 106.9°; max. = 118.6°.

tribution curve calculated using all the three-dimensional data lay very close to, and slightly below, the theoretical curve for $\bar{1}$. Allowing for the different weights of the atoms, using the results of Collin,¹³ the experimental points lay almost exactly on the theoretical curve. The space group was therefore taken to be $P\bar{1}$.

Since the unit cell of the crystal contains three molecules, there are two possible arrangements for the three nickel atoms. One nickel atom could be placed on one of the eight centers of symmetry, with the other two in general positions related by a center, or, alternatively, all three nickels could be placed on symmetry centers. Inspection of the three-dimensional Patterson function (computed as sections parallel to the x - y plane) indicated the latter alternative, the three heaviest peaks (apart from the origin peak) being located at $1/2, 0, 0$; $0, 0, 1/2$; and $1/2, 0, 1/2$. The three nickel atoms were accordingly placed at the origin; $0, 0, 1/2$; and $1/2, 0, 1/2$, respectively.

With twelve chlorine atoms in general positions, there are 36 double weight nickel-chlorine vector peaks in the vector cell, with coordinates $\pm [x_n, y_n, z_n; x_n, y_n, z_n - 1/2]$ and $x_n - 1/2, y_n, z_n - 1/2]$ ($n = 1 \dots 6$). In the computed half of the cell there will be 18 such peaks, appearing as nine pairs, the members of each pair being separated by $ca.$ 2.9 Å. While calibration of the Patterson peaks indicated that there were many possible candidates for nickel-chlorine vectors, the criterion regarding the separation of vectors arising from chlorine atoms in the same anion, coupled with the fact that for every vector x, y, z , there are two related vectors with coordinates $x, y, z - 1/2$ and $x - 1/2, y, z - 1/2$, led to an unambiguous assignment of these vectors and hence to the six chlorine positions.

The Fourier refinement of the crystal structure of yellow(II) followed a somewhat similar course to that for blue(I), except that in the initial synthesis a con-

(13) R. L. Collin, *ibid.*, **8**, 499 (1955).

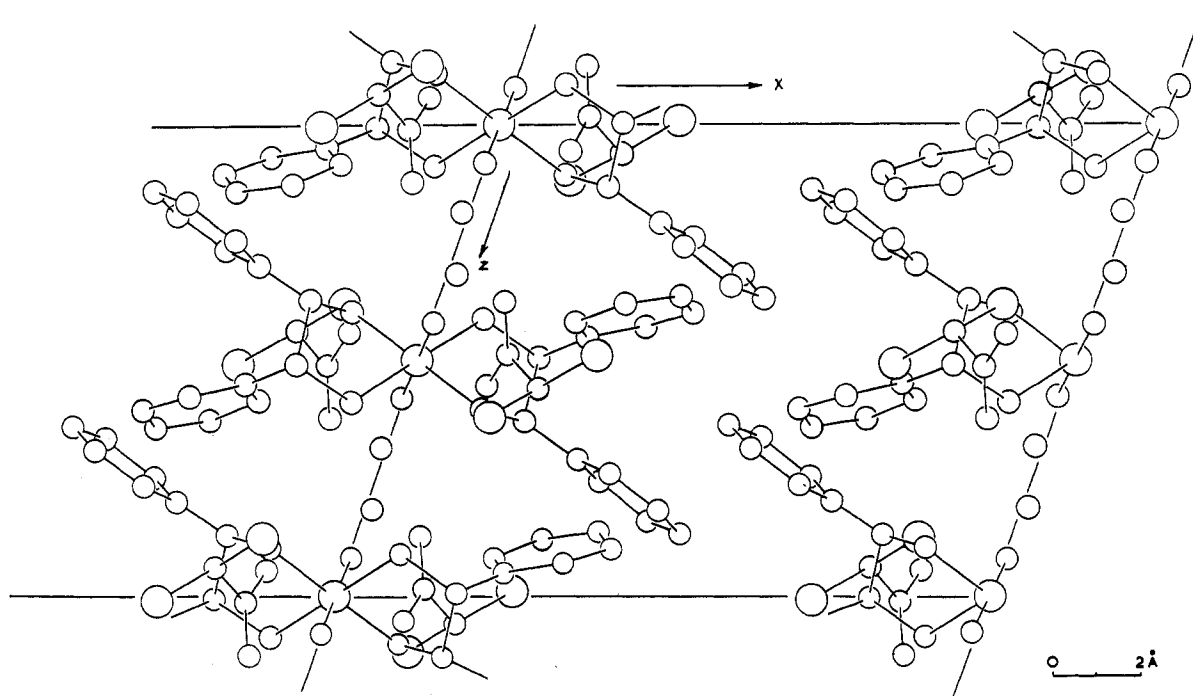


Fig. 3.—Projection of the structure of the blue(I) crystals on (010) illustrating the molecular packing.

siderable number of peaks appeared to be spurious and in stereochemically unacceptable positions. Also, the resolution of the light atoms in the diamine molecules and the anions was much poorer than in the initial Fourier synthesis for blue(I).

The refinement was thus slower, since only the atoms of the three anions, the six nitrogen atoms, and two of the benzene rings were included in the second cycle. Two further cycles established the remainder of the diamine atoms fairly certainly and reduced the residual to 0.38. However, there were still several peaks, which appeared with increased density after the third cycle, which were taken to be the atoms of solvent molecules (water and ethanol). These are expected to be present from chemical analysis and from the observed crystal density. Two of the five prominent peaks were isolated from each other and from surrounding atoms by *ca.* 3 Å., while the three others were obviously bonded together. The former were taken to be the oxygen atoms of water molecules, while the latter were taken to be the three atoms of an ethanol molecule. The stoichiometric formula of the complex is thus shown to be $3\text{Ni}(\text{stien})_2(\text{Cl}_2\text{CHCOO})_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 4\text{H}_2\text{O}$.

Two further cycles of refinement were carried out with nickel, chlorine, and all 65 light atoms. The residual at this stage was still high, having fallen only to 0.285, but there were insufficient sign changes to warrant further refinement in this manner.¹⁰ Since the desired information regarding the stereochemistry of the nickel atoms was known at this point, it was decided to curtail the analysis.

The peak densities in the final Fourier synthesis were as follows: nickel, 24–25 $\text{e}/\text{Å}^{-3}$; chlorine, 9.3–11.2 $\text{e}/\text{Å}^{-3}$; oxygen, 4.2–6.1 $\text{e}/\text{Å}^{-3}$; nitrogen, 4.5–5.2 $\text{e}/\text{Å}^{-3}$; carbon, 2.0–3.5 $\text{e}/\text{Å}^{-3}$.

The final set of fractional and orthogonal atomic coordinates—the latter calculated taking the *Y* axis coincident with the triclinic *y* axis and the *Z* axis normal to the *x,y* plane—are listed in Table III. The structures of the three molecules and their relation to each other in the unit cell are shown by means of projections down the *x* and *z* crystal axes, and are depicted in Fig. 4 and 5. These diagrams show clearly the “octahedral” coordination of the nickel atoms situated at the origin of the unit cell (molecule A) and at $1/2, 0, 1/2$ (molecule C) and the planar coordination of the nickel atom at $0, 0, 1/2$ (molecule B). The presence in the crystal of alternate layers of molecules of type A in the plane $z = 0$ and of types B and C in the $z = 1/2$ plane can also be seen.

Details of the bond lengths and bond angles for bonds involving the nickel atoms are given in Table IV. As before, the bond lengths and angles in the benzene rings and the anions are given as the observed average value, together with the highest and lowest observed values.

As in the case of the blue(I) crystals, there is also an extensive network of hydrogen bonding present, which links together the three crystallographically independent complex molecules, the “free” dichloroacetate anion, the ethanol, and the water molecules. This bonding system is shown by means of an oblique view of the *b* face of the unit cell in Fig. 6, the diamine carbon atoms being omitted for clarity. Apart from the hydrogen bond distances, a nearest neighbors calculation showed that all the intermolecular contacts comply reasonably well with those expected from van der Waals radii.

Errors in the Structure Analyses.—The value of the residual, *R*, for the two final sets of structure factors gives some indication of the accuracy of the two analy-

TABLE III
FRACTIONAL AND ORTHOGONAL ATOMIC
COORDINATES IN YELLOW(II)

	x/a	y/b	z/c	$X, \text{\AA}$	$Y, \text{\AA}$	$Z, \text{\AA}$
Ni(0)	0.0	0.0	0.0	0.0	0.0	0.0
N(1)	0.0240	0.1270	-0.0420	0.561	1.830	-0.699
N(2)	0.0910	0.1175	0.1075	0.306	0.980	1.789
C(3)	0.1415	0.2430	0.0185	1.427	2.712	0.307
C(4)	0.1125	0.2270	0.0970	0.555	2.511	1.614
C(5)	0.1680	0.3470	0.0020	1.835	4.142	0.033
C(6)	0.2880	0.4330	0.0240	3.001	4.615	0.399
C(7)	0.3040	0.5210	0.0000	3.346	5.886	0.000
C(8)	0.1940	0.5290	-0.0340	2.375	6.792	-0.565
C(9)	0.6900	0.4380	-0.0535	1.136	6.272	-0.890
C(10)	0.5400	0.3460	-0.0320	0.820	4.496	-0.532
C(11)	0.0170	0.2470	0.1205	-0.662	3.394	2.005
C(12)	-0.1070	0.1715	0.1065	-1.928	3.091	1.772
C(13)	-0.1860	0.2060	0.1325	-2.981	4.081	2.204
C(14)	-0.1400	0.3135	0.1610	-2.675	5.351	2.679
C(15)	-0.0110	0.3920	0.1790	-1.382	5.659	2.978
C(16)	0.0625	0.3630	0.1515	0.379	4.791	2.251
Ni(17)	0.0000	0.0000	0.5000	-3.523	-0.949	8.320
N(18)	-0.1840	-0.1040	0.4520	-5.210	1.225	7.521
N(19)	0.0165	-0.1110	0.4570	-3.038	-2.654	7.604
C(20)	-0.2180	-0.2040	0.3930	-5.169	-2.403	6.539
C(21)	-0.1040	-0.2200	0.4270	-4.153	-3.456	7.105
C(22)	-0.3570	-0.3120	0.3650	-6.502	-3.072	6.073
C(23)	-0.4070	-0.3360	0.4210	-7.447	-3.214	7.005
C(24)	-0.5270	-0.4300	0.3960	-8.592	-3.802	6.589
C(25)	-0.5990	-0.5010	0.3150	-8.814	-4.250	5.241
C(26)	-0.5490	-0.4770	0.2610	-7.883	-4.112	4.343
C(27)	-0.4280	-0.3830	0.2860	-6.727	-3.530	4.759
C(28)	-0.1060	-0.2700	0.4980	-4.676	-4.334	8.286
C(29)	-0.1580	-0.3780	0.4850	-5.157	-5.601	8.070
C(30)	-0.1600	-0.4230	0.5490	-5.630	-6.390	9.135
C(31)	-0.1090	-0.3600	0.6250	-5.604	-5.916	10.400
C(32)	-0.0570	-0.2520	0.6380	-5.123	-4.648	10.616
C(33)	-0.0550	-0.2090	0.5730	-4.643	-3.888	9.534
Ni(34)	0.5000	0.0000	0.5000	1.981	-4.224	8.320
N(35)	0.3075	-0.0870	0.4170	0.446	-4.121	6.938
N(36)	0.4870	-0.1370	0.4570	2.141	-6.921	7.604
C(37)	0.2620	-0.1980	0.4240	-0.103	-5.515	7.055
C(38)	0.3440	-0.2290	0.3810	1.102	-6.439	6.339
C(39)	0.1180	-0.2780	0.3580	-1.223	-5.656	5.957
C(40)	0.0770	-0.2610	0.2860	-1.167	-4.993	4.759
C(41)	-0.0510	-0.3320	0.2270	-2.161	-5.117	3.777
C(42)	-0.1420	-0.4230	0.2400	-3.254	-5.921	3.993
C(43)	-0.1010	-0.4400	-0.3120	-3.310	-6.583	5.191
C(44)	0.0340	-0.3690	0.3710	-2.240	-6.506	6.173
C(45)	0.3640	-0.2270	0.3010	1.688	-6.270	5.008
C(46)	0.3850	-0.1280	0.2790	2.272	-4.987	4.642
C(47)	0.3830	-0.1260	0.2030	2.768	-4.799	3.378
C(48)	0.3480	-0.2230	0.1490	2.781	-5.934	2.479
C(49)	0.3090	-0.3220	-0.1710	2.196	-7.217	2.845
C(50)	0.3070	-0.3240	0.2470	1.639	-7.378	4.110
Cl(51)	0.4452	0.1135	-0.0265	5.088	-1.149	-0.441
Cl(52)	0.5036	0.2790	0.1063	4.795	0.718	1.768
C(53)	0.4450	0.1450	0.0640	4.448	-0.843	1.065
C(54)	0.3080	0.0785	0.0660	2.925	-0.955	1.098
O(55)	0.1930	0.0630	0.0060	2.090	-0.338	0.100
O(56)	0.2850	0.0410	0.1215	2.290	-1.505	2.019
Cl(57)	-0.2905	-0.2416	0.1395	-4.181	-2.015	2.321
Cl(58)	-0.2820	-0.0683	0.2387	-4.786	0.361	3.972
C(59)	-0.1980	-0.1050	0.1895	-3.515	-0.650	3.153
C(60)	-0.0595	-0.0540	0.2395	-2.342	-0.881	3.985
O(61)	-0.0270	-0.0533	0.3155	-2.520	-1.228	5.250
O(62)	0.0080	-0.0260	0.1980	-1.307	-0.821	3.294
Cl(63)	0.5942	0.1340	0.2645	4.677	-2.368	4.401
Cl(64)	0.8095	0.2967	0.4088	6.031	-1.592	6.802
C(65)	0.7190	0.1590	0.3460	5.477	-2.962	5.757
C(66)	0.6590	0.0890	0.3970	4.457	-3.724	6.606
O(67)	0.7240	0.0440	0.4180	5.025	-4.870	6.955
O(68)	0.5710	0.0860	0.4250	3.291	-3.246	7.072
O(69)	0.2490	-0.0030	0.2650	0.874	-2.179	4.409
O(70)	0.2390	0.0875	0.4120	-0.272	-1.025	6.855
C(71)	0.3910	0.2570	0.2880	2.275	0.777	4.792
C(72)	0.5030	0.3120	0.3670	2.951	0.725	6.106
O(73)	0.4800	0.2340	0.4180	2.438	-0.458	6.955

TABLE IV
BOND LENGTHS AND ANGLES IN THE YELLOW(II) CRYSTALS

Bond lengths, \AA		Bond angles	
Molecule at (0,0,0)			
Ni(0)-N(1)	2.05	N(1)-Ni(0)-N(2)	81.2°
Ni(0)-N(2)	2.05	O(55)-Ni(0)-N(1)	86.4°
Ni(0)-O(55)	2.16	O(55)-Ni(0)-N(2)	84.6°
N(1)-C(3)	1.58	Ni(0)-N(1)-C(3)	106.4°
N(2)-C(4)	1.58	Ni(0)-N(2)-C(4)	112.9°
C(3)-C(4)	1.58		
Molecule at ($1/2, 0, 1/2$)			
Ni(34)-N(35)	2.07	N(35)-Ni(34)-N(36)	82.6°
Ni(34)-N(36)	2.04	O(68)-Ni(34)-N(35)	92.5°
Ni(34)-O(68)	2.08	O(68)-Ni(34)-N(36)	100°
N(35)-C(37)	1.50	Ni(34)-N(35)-C(37)	102°
N(36)-C(38)	1.65	Ni(34)-N(36)-C(38)	112.9°
C(37)-C(38)	1.67		
Molecule at (0,0, $1/2$)			
Ni(17)-N(18)	1.89	N(18)-Ni(17)-N(19)	86.5°
Ni(17)-N(19)	1.90	Ni(17)-N(18)-C(20)	111.2°
N(18)-C(20)	1.53	Ni(17)-N(19)-C(21)	115.1°
N(19)-C(21)	1.46		
C(20)-C(21)	1.57		
Ethanol molecule			
C(71)-C(72)	1.55	C(71)-C(72)-O(73)	111.3°
C(72)-O(73)	1.48		

BOND LENGTHS AND ANGLES IN THE DIAMINE MOLECULES AND THE ANIONS

	Average	Maximum	Minimum
Benzene C-C (36 values)	1.40 \AA	1.52 \AA	1.32 \AA
Exocyclic C-C (6 values)	1.54 \AA	1.57 \AA	1.48 \AA
C-Cl (6 values)	1.75 \AA	1.82 \AA	1.69 \AA
Anion C-C (3 values)	1.51 \AA	1.53 \AA	1.46 \AA
C-O (6 values)	1.30 \AA	1.34 \AA	1.24 \AA
Benzene C-C-C (48 values)	120.2°	124.0°	117.0°
Angle at chelate ring carbon atoms (18 values)	110.8°	127.0°	100.0°
Cl-C-Cl (3 values)	113.2°	116.9°	110.1°
Cl-C-C (6 values)	110.2°	117.2°	105.1°
O-C-C (6 values)	116.6°	126.0°	107.0°
O-C-O (3 values)	124.0°	130.1°	116.6°

102, and 113), the agreement is satisfactory for a structure refined by this method. For the yellow(II) crystals, the agreement for many reflections is much poorer, and this is reflected in the higher value of the final residual, 0.285. Here again, several reflections suffer from extinction (notably 013, 024, 053, $0\bar{2}4$, and 112). However, both structures satisfy the usual qualitative criteria which are characteristic of a correct structure determination; *i.e.*, both are stereochemically reasonable, there are no unusually short intermolecular distances (other than hydrogen bonds), and there are no spurious peaks or large negative voids (apart from the diffraction ripples around the nickel ions) on the final electron density sections.

While the limitations on θ will introduce errors due to termination of Fourier series and affect the resolution of the atoms to a certain extent, it is probable that the main errors in the calculated structure factors arise from the use of an average temperature factor, rather than individual values for each atom, since, in structures containing a variety of atoms of different weight, there is usually a fairly wide spread of values. The use of an average value will increase the residual.

ses, although not a satisfactory one. Examination of the agreement achieved between individual structure factors is a better guide, and for the blue(I) crystals, except for several reflections of low $\sin \theta$, which obviously suffer from extinction (reflections 020, 100,

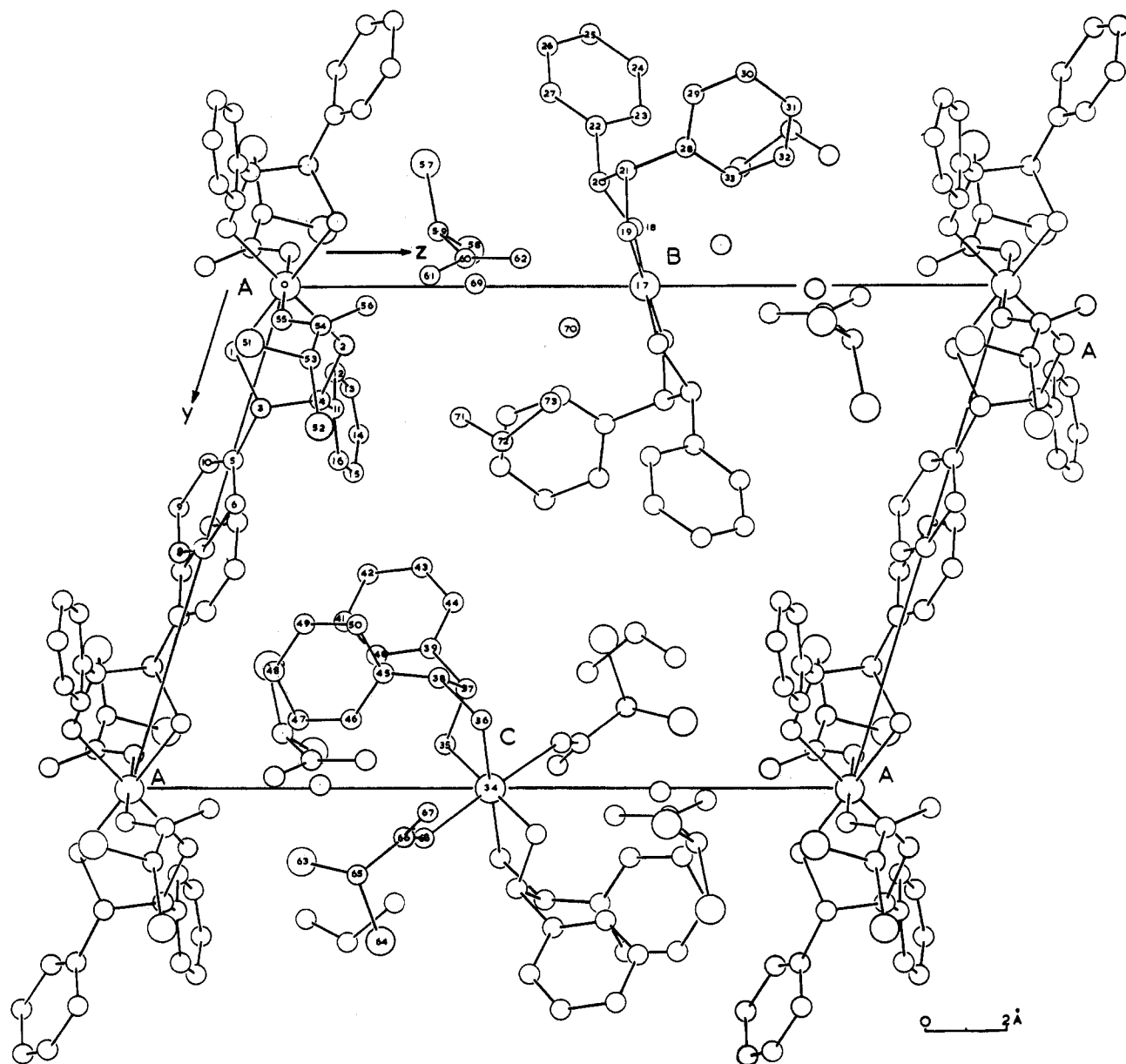


Fig. 4.—The crystal structure of yellow(II) viewed down the crystallographic x axis, showing the three crystallographically independent complex molecules and their relative orientation. Molecule A has the nickel atom at the origin, B has the nickel atom at $0, 0, \frac{1}{2}$, and C has the nickel atom at $\frac{1}{2}, 0, \frac{1}{2}$. In this projection, molecules B and C are actually superimposed when viewed down the x axis—in this diagram they are separated for clarity.

Comparison of the computed electron density sections for the two structures suggested that this variation is likely to be much larger in the yellow(II) crystals than in the blue(I) crystals, as the light atoms nearest to the nickel atoms in the former have a much higher peak density than those atoms which are more distant from the nickel atoms, namely the benzene ring carbon atoms. It seems that the average value of 5.04 \AA^2 used for these latter atoms in the structure factor calculations is too low.

In the blue(I) crystals, on the other hand, all the light atoms are well resolved and, in contrast to many atoms in the yellow(II) structure, reasonably reliable coordinates could be derived for them. This difference in the reliability of the light atom coordinates, which is borne out by the greater spread of values obtained for the bond lengths and bond angles in the

yellow(II) structure, is thus probably the main cause of the discrepancy between the two final residuals. It is fortunate from the viewpoint of the analyses that the coordinates of the nitrogen atoms are probably the most accurate of those in the yellow(II) structure and that the observed difference in nickel-nitrogen bond distances found for the two types of molecule is quite reliable and chemically significant.

While further refinement of both structures would have been desirable and would probably have brought many of the observed discrepancies in bond distances and bond angles (*e.g.*, the O(5)–O(23) hydrogen bond distance and the C–O distances in the anion in the blue complex, and many of the light atom bond distances in the yellow complex) more into keeping with their accepted values, unfortunately this could not be carried out with the facilities available to us at the time.

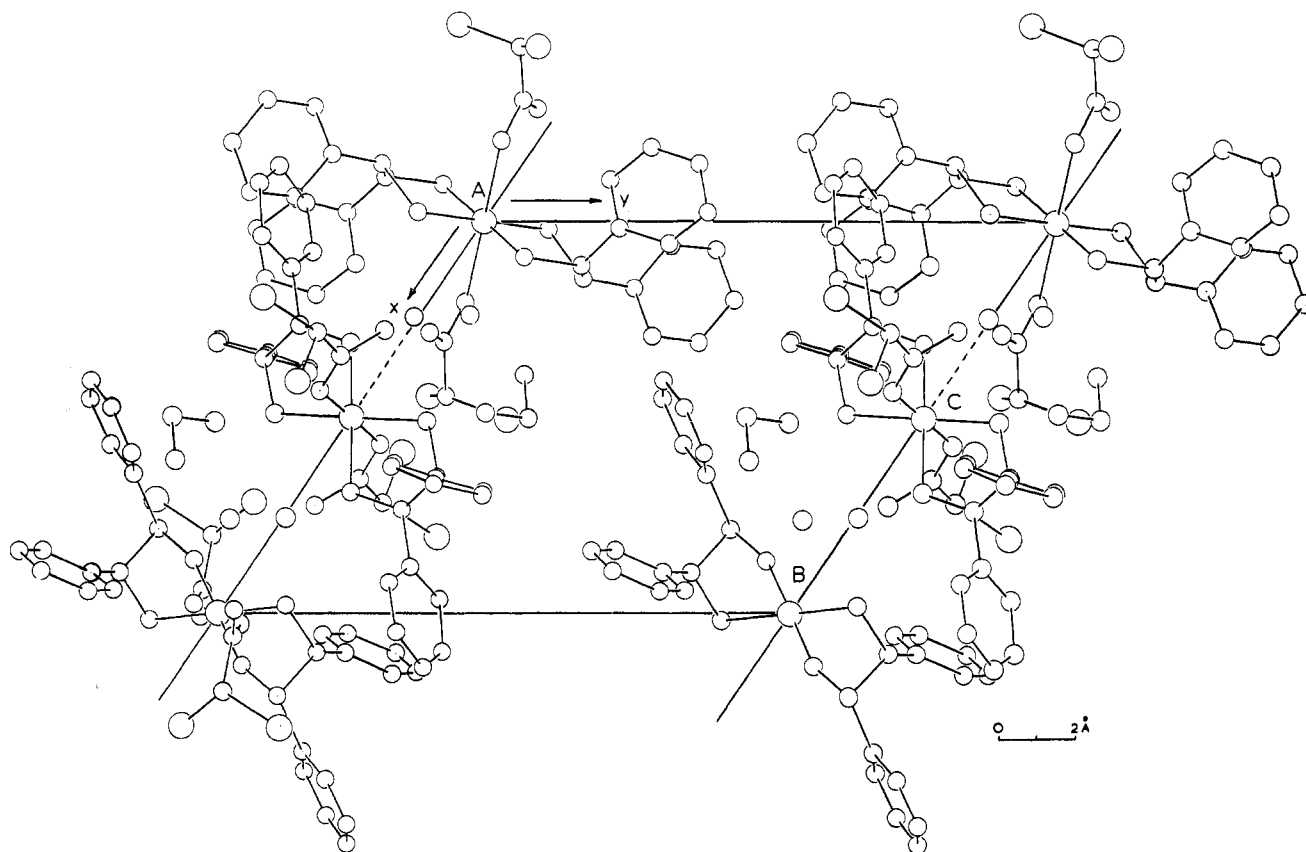


Fig. 5.—The crystal structure of yellow(II) crystals viewed down the crystallographic z axis, showing the relative orientation and indicating the alternation of molecules A at the level $z = 0$, and molecules B and C at the level $z = 1/2$.

However, the main object of the analyses, namely the determination of the conformation of the chelating diamine molecules and the establishment of the stereochemistry of the nickel ions in the two crystals, had been accomplished.

The crystal structure programs used in this work for the three-dimensional Fourier series and structure factor calculations were those written by Rollett¹⁴ for the English Electric DEUCE computer.

Discussion

The main result of the two structure analyses described above is the demonstration of the existence in these compounds of the two types of stereochemistry predicted from spectroscopic¹⁵ and magnetic data.

In the blue(I) crystals, the ligands form a slightly distorted octahedral array about the nickel atom, the symmetry of the resulting ligand field being D_{2h} within experimental error. The deviation from O_h symmetry is not too great and, as noted in part I, not sufficient to have a large effect on the absorption spectrum.

In the yellow(II) crystals, the two crystallographically independent octahedral molecules have essentially the same structure, except for a slight difference in the two Ni–O bond distances and, as regards their spectroscopic and magnetic properties, can be considered to

be essentially similar to the molecules in blue(I). (Although the ligand field in these two molecules will not have true D_{2h} symmetry, owing to the deviations of the N–Ni–O bond angles from 90° , for the purpose of this discussion these deviations can be neglected.)

Comparison of the nickel–nitrogen bond distances and the N–Ni–N bond angles for the three molecules shows that, within experimental error, these are all identical, the mean bond length being 2.05 ± 0.03 Å. and the mean bond angle, N–Ni–N, 82.3° . The observed bond distance lies in the range 2.0–2.15 Å., recorded for Ni–N bonds in similar types of paramagnetic complex, *e.g.*, $\text{Ni}(\text{en})_3(\text{NO}_3)_2$.¹⁶ Likewise, the nickel–oxygen distances in the three molecules are also comparable with those found in other complexes, *e.g.*, in nickel acetate tetrahydrate.¹⁷ The third molecule in the yellow(II) crystals is planar and tetracoordinate, there being no ligand in the axial position. The nearest atom to the nickel ion is an oxygen atom of the “free” dichloroacetate ion O(62) at a distance of 3.25 Å., and this lies an appreciable distance from the axis normal to the nickel–nitrogen plane. The nickel–nitrogen bond distance in this molecule, 1.89 Å., is significantly less than that found in the octahedral molecules and is comparable to that of 1.85 Å. observed in nickel dimethylglyoxime¹⁸ and to those in several

(14) J. S. Rollett in “Computing Methods and the Phase Problem in X-Ray Crystal Analysis,” R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, London, 1961, p. 87.

(15) C. Furlani, *Gazz. chim. Ital.*, **88**, 279 (1958).

(16) L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 637 (1960).

(17) J. N. van Niekerk and F. K. L. Schoening, *ibid.*, **6**, 609 (1953).

(18) L. E. Godycki and R. E. Rundle, *ibid.*, **6**, 487 (1953).

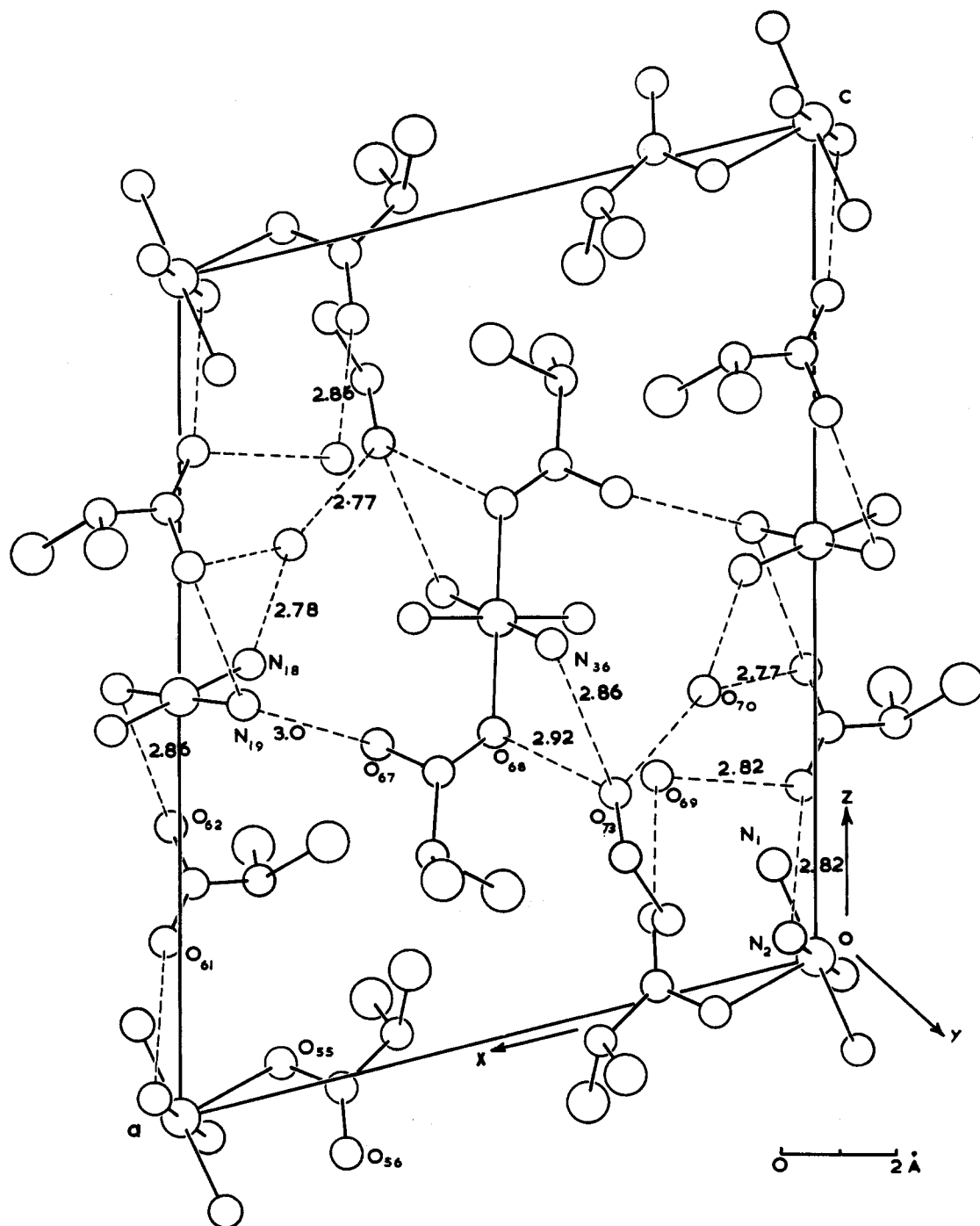


Fig. 6.—An oblique view of the *b* face of the unit cell of the yellow(II) crystals, showing the intermolecular hydrogen bonding system. The diamine carbon atoms are omitted. The distances indicated are in Å.

other diamagnetic complexes of nickel. From these results, taken in conjunction with the measured magnetic moment of 2.58 B.M., it is concluded that this planar molecule is diamagnetic. These crystals therefore consist of a mixture of paramagnetic octahedral molecules and planar diamagnetic molecules in a ratio of 2:1.¹⁹

(19) The preliminary results of an X-ray analysis of another similar molecular compound of nickel(II) in which the metal ions exhibit two types of stereochemistry and hence have differing magnetic properties have just come to our notice [B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963)]. In this compound there is also a ratio of paramagnetic to diamagnetic molecules of 2:1 in the crystal, although here the paramagnetic molecules contain tetrahedrally coordinated nickel(II).

In agreement with the results of structure analyses of other complex molecules containing ethylenediamine or related ligands,²⁰ the diamine molecules in these complexes also adopt a *gauche* configuration. As a result, the five-membered chelate rings are markedly nonplanar, and, since the two rings in each molecule are related by a center of symmetry, the molecules have the *kk'* configuration described by Corey and Bailar.² A consequence of this nonplanarity is that substitution on the ring carbon atoms can occur in two distinct positions, and, by analogy with

(20) H. Scouloudi, *Acta Cryst.*, **6**, 651 (1953).

cyclohexane, these are termed axial and equatorial. With *meso*-stilbenediamine as ligand, one of the phenyl groups is axial to the ring and the other equatorial, while, in the case of the active isomers, both groups are equatorial. The relative disposition of the two phenyl groups is clearly seen in the diagrams of the two crystal structures. To this difference in stereochemistry, between the complexes containing the *meso* isomer on the one hand and the active isomer on the other, can thus be attributed the much greater tendency of the former to give planar, tetracoordinate complexes,²¹ as in these the axial positions are sterically hindered to a large degree, preventing the close approach of bulky anions or large solvent molecules, and the absence of tris-complexes with the *meso* isomer. In contrast, the active bases readily form hexacoordinated complexes containing either two or three molecules of diamine, which are very similar to the nickel ethylenediamine complexes.

In conclusion, then, it can be seen that the mechanism put forward by Ballhausen and Liehr²² to explain the changes in magnetic and spectroscopic properties which occur on dissolution, solvation, etc., is confirmed,

(21) I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

(22) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

although some of their detailed predictions regarding the structures of these complexes and their probable similarity to the Cu(II) acetate bridged systems are incorrect. It is clear that in all the compounds described by Lifschitz,²¹ the planar coordination of diamine molecules is retained throughout and the changes are brought about by variation in the axial ligand field. In the yellow diamagnetic complexes, the effective axial ligand field is zero and the strong in-plane ligand field, due to the diamine molecules, causes the singlet $^1A_{1g}$ state to be the ground state, whereas in the blue octahedral complexes, the axial ligand field stabilizes the triplet $^3A_{2g}$ state (assuming a ligand field of O_h symmetry) and the complexes are paramagnetic. It is interesting to note that the in-plane field in these is weaker than that in the yellow complex according to the observed bond length differences in the two molecules.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Complexes of Nickel with N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine and Sodium Hydroxide¹

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Complex ions formed by the nickel(II) ion with N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine, TKED, have been investigated in dilute aqueous solution. Spectrophotometric data and potentiometric titrations give evidence of the formation of the complex ion containing one molecule of TKED per nickel(II) ion ($NiTKED^{+2}$). This complex ion behaves as a dibasic acid by reacting with hydroxyl ions to form complexes of the type $Ni(TKED-H^+)^+$ and $Ni(TKED-2H^+)^0$. However, only the first dissociation constant could be calculated: $pK_{A1} = 9.07$. The acid dissociation constants for the protonated TKED molecule, $TKEDH_2^{+2}$, were determined and the average values are $K_{AH_2} = 3.54 \times 10^{-6}$ and $K_{AH} = 3.54 \times 10^{-9}$. The formation constant for the formation of $NiTKED^{+2}$ was found to be 3.17×10^6 .

Introduction

This paper reports a study of the complexes of nickel(II) ion with N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) in the presence and absence of a strong base. On chelation, the four nitrogen-to-oxygen chains are in favorable position for the formation of stable five-membered chelate rings as well as the nitrogen chain. The hydroxyl radicals of TKED are found to have nearly negligible acidic properties in water solution. Their acidity increases appreciably, however, when the hydroxyl radical becomes a part of

the chelate ring.² The ions formed by the successive additions of protons to the first and second nitrogen atoms of TKED will be designated $TKEDH^+$ and $TKEDH_2^{+2}$, respectively. The complex ion formed from the nickel(II) ion and TKED will be designated $NiTKED^{+2}$, the ion formed by the removal of a single proton from a coordinated hydroxyl group of the $NiTKED^{+2}$ complex ion will be written as $Ni(TKED-H^+)$, while the corresponding neutral molecule formed by the removal of two such protons will be written as $Ni(TKED-2H^+)^0$.

(1) Presented before the Division of Inorganic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9-14, 1962.

(2) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback, and H. Hyytiainen, *J. Am. Chem. Soc.*, **79**, 3036 (1957). See this article for several references to previous work.