688. *Crystal Structure of a Hydrated Nickel Cyanide Ammoniate.*

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A structure analysis of single crystals of $Ni(CN)_2,NH_3,nH_2O$ shows a modified form of the tetragonal planar nickel complex found in the inclusion compound of benzene, $Ni(CN)_2,NH_3,C_6H_6$. The layers are puckered slightly, the angle Ni–C–N in the Ni–C–N–Ni sequence of atoms being 173°. The layers are staggered so that the projecting ammonia groups of one point towards the holes in the square networks of its neighbours. They are, therefore, packed much more closely than is possible in the benzene compound. The probable water content is represented by the formula $Ni(CN)_2,NH_3,\frac{1}{4}H_2O$. It is shown that single crystals of the tetragonal benzene compound in the presence of moisture change to this hydrate structure, the main plane of the puckered layer remaining parallel to the original layers whose axial directions also remain unchanged.

HOFMANN and HÖCHTLEN [1] state that an ammoniacal nickel cyanide solution several days after preparation deposited hopper-shaped crystals of composition $Ni(CN)_2,4H_2O$. Attempted repetitions of their experiments with solutions of the same composition gave no crystals in the first few weeks, but one solution in the course of a year deposited a hydrated nickel cyanide–ammonia complex. This consisted of small crystals in spherical aggregates about 2 mm. in diameter and some single crystals about 0·25 mm. long.

RESULTS

The crystals are orthorhombic, pseudo-tetragonal bipyramids. Inter-edge angles, measured under the microscope, showed {121} as the principal faces with {001}, {010}, and {100} small. Of these {010} were rounded. There is a marked cleavage parallel to (001).

X-Ray examination was carried out by oscillating-crystal methods with copper radiation filtered through nickel. Intensities of reflexions were determined from Weissenberg photographs obtained with oscillation about principal axes.

The unit cell dimensions are $a = 7·24$, $b = 14·32$, $c = 8·74$ Å. Hence from the density 1·98 g./c.c. (flotation) there are eight molecules of composition $Ni(CN)_2,NH_3,nH_2O$ ($n = 0·4$). The value of n so determined is insensitive to changes in the density. Since the value from the

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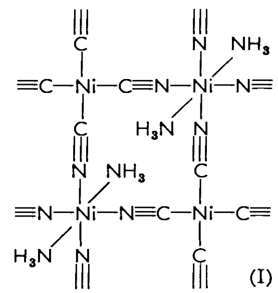
[1] Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149.

analytical figures is also insensitive, a probable value of n is deduced later from the structure analysis. Absent spectra are hkl when $h + k + l$ is odd. Reflexions of type $hk0$ are absent when either h or k is odd, with the exceptions of a very weak reflexion 110 and a still weaker 130. If these reflexions, which are mentioned later, are disregarded, the space group is I*mma* or I*ma* and the first examination of the structural possibilities was limited to these groups. The unit cell dimensions are related to those of the tetragonal unit cell of the compound $Ni(CN)_2,NH_3,C_6H_6$,[2] which has $a = b = 7{\cdot}24$, $c = 8{\cdot}3$ Å. The new structure has a the same and b approximately double. From this it may be concluded that the structure contains a network similar to that in the benzene compound (I), and that its plane is perpendicular to the pseudo-tetragonal axis. This agrees with the cleavage and optical properties. The c dimension of the hydrated complex is not so simply related to that of the benzene compound. It is 8·74 Å but in this height there are twice as many $Ni(CN)_2,NH_3$ layers as in the 8·28 Å c dimension of the benzene compound.


(I)

If it is assumed that ammonia groups are attached to alternate nickel atoms as in the benzene compound the arrangement of the layers must be different. In the benzene complex ammonia groups of adjacent layers are almost in contact and only a slight contraction of the interlayer spacing would be possible if the benzene molecules were removed. But if the benzene molecules are imagined as removed and alternate layers of the remaining structure are displaced through $\frac{1}{2}a$, a large decrease in interlayer spacing is possible. Ammonia groups now (cf. Fig. 5, p. 3417) project towards the holes of the squared pattern instead of towards the other ammonia groups. This arrangement requires consistent weakness but not complete absence of some classes of X-ray reflections. For the orthorhombic cell of the hydrated complex the arrangement places the nickel atoms on a face-centred sub-cell with sides a, $\frac{1}{2}b$, c. Consequently, reflexions for which h, $k/2$, and l are neither all odd nor all even should be weak. They are observed to be so.

From this starting point the full structure was developed, through several stages of Fourier approximations and then by least-squares refinements. The nickel position being known, co-ordinates may be estimated for the other atoms of the complex consistent with the space group I*mma* and the probable bond lengths. Structure factors F_{hk0}, calculated from these co-ordinates, gave an agreement factor of 0·23. For these first calculations atomic scattering factors for carbon and nitrogen were those of the International Tables for the Determination of Crystal Structures; f_{NH_3} was taken equal to f_N and for f_{Ni} Brindley's measurements [3] for metallic nickel were used. The general correctness of the structures was shown by a Fourier synthesis of the $hk0$ structure factors. From a total of 38 observed values only six small terms of doubtful sign were omitted. All the observed peaks correspond to parts of the complex. The low agreement factor ($R = 0{\cdot}23$) and the resulting projection show that the analysis is essentially correct. The water molecule is not shown by any peak and must be hidden under the nickel atom at $0\frac{1}{2}0$. Its position at $0\frac{1}{2}z$ is a four-fold one in the space-group I*mma* and would require an ideal formula $Ni(CN)_2,NH_3,\frac{1}{2}H_2O$. When an allowance was made in structure factors for a water molecule at this place the agreement factor improved to 0·17. A second Fourier synthesis including all 38 terms gave the electron density map of Fig. 1.

Small movements of the lighter atoms did not change the signs of the structure factors, so that further refinement was undertaken by the method of difference syntheses. Fig. 2 shows a synthesis in which the coefficients are the algebraic differences between the observed and the calculated structure factors (both taken with the calculated signs). At a short distance along the b axis from the origin, there is a prominent peak. For calculation of the structure factors, ammonia groups had been assumed to lie along the c direction above and below the origin. The difference synthesis suggests that they should be moved, consistently with the symmetry, some distance along b. Depressions may be seen in the positions of the carbon and the cyanide nitrogen atoms. To correct these a temperature factor was applied to the contributions of these atoms. The scattering factor for the ammonia groups was then taken as ten times the value of J. M. Robertson's general factor for light atoms.[4] This factor is applicable to organic

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[2] Rayner and Powell, *J.*, 1952, 319.

[3] Brindley, *Phil. Mag.*, 1936, **21**, 786.

[4] Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106.

structures. It has been used here since a similar treatment improved agreement in the benzene compound. This implies that the ammonia group has more freedom of movement than the CN group. The change in the co-ordinates of the ammonia nitrogen atom reduced the disagreement factor from 0·17 to 0·16. A further reduction to 0·14 resulted on application of a temperature factor $\exp\{-B(\sin\theta/\lambda)^2\}$ to the contributions of carbon and nitrogen of the CN groups. For these tightly bound atoms the low value of $B = 1{\cdot}0$ was selected. However, an increase of B to 2·0 has a negligible effect on the agreement factor. The difference synthesis with these re-calculated structure factors is shown in Fig. 3. Elimination of the large peak near the origin is evident and the depressions are in part removed.

The tilt of the NH_3–Ni–NH_3 line away from the c axis and the fact that the b axis is about 1% smaller than the corresponding distance in the benzene compound suggest that there is some slight tilt of the layers out of the (001) plane. Patterson syntheses and calculation of structure factors F_{0kl} confirm this and show that the nickel atom Ni(2) attached to four carbon atoms has a z co-ordinate approximately 0·05 and Ni(1) which is linked to four cyano- and two ammonia-nitrogen atoms has $z = 0$. For the calculation of the first set of $0kl$ structure factors ($R = 0{\cdot}27$) these Ni co-ordinates were used, and carbon and nitrogen atoms were assumed to lie on straight lines joining two nickel atoms. Quantities used in these calculations of F_{0kl} were: f_{Ni}, from Brindley; [3] f_C and f_N of CN from International Tables modified by a temperature factor with $B = 2{\cdot}0$; f_{NH_3} = ten times Robertson's general factor,[4] the z parameter for Ni(2) = 0·047. The resulting Fourier synthesis showed, however, that the carbon atoms did not lie on the line joining Ni(1) to Ni(2) but had the same z co-ordinate as Ni(2). A difference synthesis led to some changes of parameters and an agreement factor of 0·21.

FIG. 1. *Structure viewed down the c axis. To the left, electron-density map with contour interval 2·6 e/Å² (5·2 e/Å² for the Ni + NH₃ peak). Negative regions dotted. Atomic positions indicated by crosses and by circles in the mirror image, right half.*

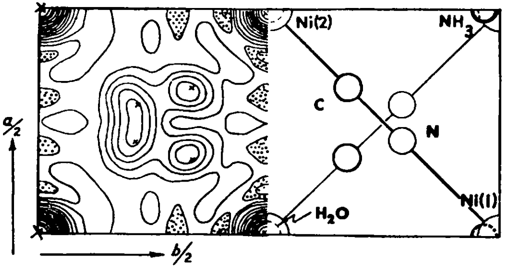
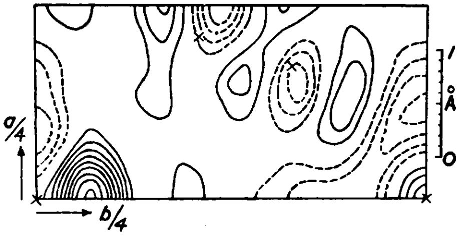


FIG. 2. *F_{hk0} difference synthesis. Crosses show atomic positions used for $F_{calc.}$, contour interval 0·7 e/Å². Negative contours broken. Zero contour omitted.*



Further refinement of this structure involves a mixed set of variables, some atomic positions, some temperature factors, and one parameter to take account of a deficiency in water content of the structure. For this refinement a least-squares method was found convenient. The rigid planar structure of the complex suggests that an anisotropic temperature factor ought to be introduced especially for the nickel atoms. In the least-squares method as first applied, only the temperature factors of the nickel atoms and the Ni(2) z parameter were considered; the process gave $\Delta B_y = -0{\cdot}34$, $\Delta B_z = +1{\cdot}09$, $\Delta z = -0{\cdot}001$, where the structure factor is represented by:

$$F_{(0kl)} = \sum_j f_j \exp\{-B_{jy}Y^2 - B_{jz}Z^2\} \cos 2\pi ky \cos 2\pi lz$$

The negative value of ΔB_y would require the nickel atoms to be more firmly held in this direction than in metallic nickel. Although this might be so it was considered sufficient to use $B_y = 0$; B_z was taken $= 1{\cdot}0$ and $\Delta z = -0{\cdot}001$, hence $z = 0{\cdot}046$, and the structure factors, recalculated on this basis, gave an improved value for R of 0·18. A least-squares process was then applied to the y and z co-ordinates of all atoms. Eight parameters are involved, yz for C, N, and N of NH_3, and z only for Ni(2) and H_2O. The modified co-ordinates deduced from this resulted in an agreement factor $R = 0{\cdot}136$. A least-squares method then applied to the x and y co-ordinates reduced the agreement factor for $F(hk0)$'s from 0·14 to 0·114. The F synthesis computed as a result of these refinements is shown as Fig. 4.

Chemical analysis and the density both suggested that the crystals contained less than $\frac{1}{2}H_2O$ per nickel atom. If the composition is $Ni(CN)_2,NH_3,nH_2O$, and there is a randomly distributed set of vacant spaces, then for $0kl$ we have:

$$\partial F/\partial n = f_{H_2O} \cos 2\pi ky \cos 2\pi lz$$

and a similar equation holds for F_{hk0}. Up to this point n had been taken as 0·5 as required by the symmetry of space group I*mma*. By applying these equations the values for Δn were obtained. F_{0kl} gave $\Delta n = -0{\cdot}18$, $\sigma = 0{\cdot}06$; F_{hk0} gave $\Delta n = -0{\cdot}26$, $\sigma = 0{\cdot}02$ (σ = standard deviation). From this it was concluded that the most probable value of n was $\frac{1}{4}$. Structure factors were recalculated with this value and for F_{hk0} the agreement factor R was reduced from 0·114 to 0·085. This value of n, giving the water content, leads to a calculated density of 1·94 g./c.c. (observed 1·98 g./c.c.). Nast [5] has state that in analyses of the substance the value of n was never found greater than 0·37. The symmetry of space group I*mma* requires at least four equivalent water molecules and hence $n = 0{\cdot}5$. The deficiency could explain the weak reflexions 110 and 130 observed although incompatible with this space group. This would involve some departure from a random distribution of vacant spaces which in turn might lead to some modification of the value deduced above for n. Aynsley and Campbell [6] give a composition corresponding to a monohydrate for material prepared by the decomposition of $Ni(CN)_2,4NH_3,2H_2O$, and a similar analysis for a blue gelatinous precipitate obtained by Hofmann and Höchtlen's method.[1] These materials may not be the same as the crystalline substance described here.

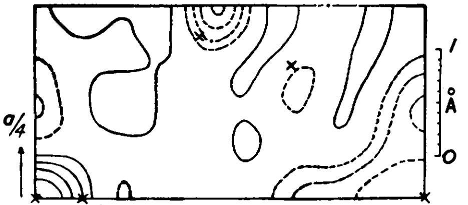
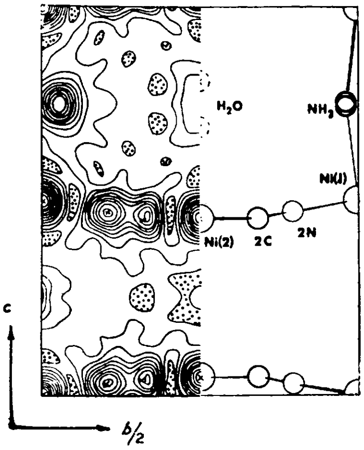


FIG. 3. *Second difference synthesis. Crosses show revised atomic positions. Contour intervals as Fig. 2.*

FIG. 4. *The structure viewed along the a axis. To the left electron-density map with contour interval* 2 e/Å² (4 e/Å² *for* Ni *atoms*). *Negative regions dotted. Atomic positions indicated by crosses and by circles in the mirror image, right half.*



The co-ordinates found for the atoms in the two projections do not completely determine the positions of the atoms in three dimensions. The three-dimensional co-ordinates for the two types of nickel atom and for the carbon and nitrogen atoms of the cyanide groups follow directly from the two projections, but the ammonia groups could be at either (0, 0·028, 0·764; $\frac{1}{2}$, 0·028, 0·736) or (0, 0·028, 0·736; $\frac{1}{2}$, 0·028, 0·764) with in each case the other six related positions of type I*mma* (h). In the first set they would be at 2·10 Å from Ni(1) atoms and in the second at 2·34 Å. The Ni–NH_3 distance found in the benzene compound was 2·06 Å and the nickel–nitrogen distance found by Driel and Verweel [7] in $K_2Ca[Ni(NO_2)_6]$ was 2·15 ± 0·03 Å. It is therefore probable that the first set of positions is correct.

A similar difficulty arises in the case of the water molecules but it is complicated both by the

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[5] R. Nast, personal communication.

[6] Aynsley and Campbell, *J.*, 1957, 4137.

[7] Driel and Verweel, *Z. Krist.*, 1936, **95**, 308.

deficiency in water content already mentioned and by the uncertainty whether the water molecules are distributed evenly over four positions as is required by the space group *Imma*, or are concentrated at two of these positions giving a structure of lower symmetry. The two projections could be explained if the space group is *Imma* and the water molecules have the co-ordinates (0, ¼, 0·809; ½, ¼, 0·691; 0, ¾, 0·191; ½, ¾, 0·309) or (½, ¼, 0·809; 0, ¼, 0·691; ½, ¾, 0·191; 0, ¾, 0·309). The first of these positions is 3·10 Å and the second 2·07 Å from Ni(2). The non-bonded radius of nickel is about 2·0 Å and so the expected distance between a nickel atom and water molecule not bonded to it is about 3 Å. If the complex is to take the same form as in the benzene compound with Ni(2) in square planar co-ordination and forming no fifth bond, then the second set of positions is too close to nickel atoms. If, as is possible, the water is co-ordinated to nickel, the second set provides sites for it at a reasonable distance.

TABLE 1. *Final atomic co-ordinates in* $Ni(CN)_2,NH_3,\frac{1}{4}H_2O$ *positions* (*a*), *etc., named as in International Tables.*

			x	*y*	*z*				*x*	*y*	*z*
4	Ni(1)	(a)	0	0	0	16	N	(j)	0·292	0·102	0·028
4	Ni(2)	(e)	½	¼	0·046	8	NH_3	(h)	0	0·028	0·764
16	C	(j)	0·319	0·158	0·045	4	($\frac{1}{4}H_2O$)	(e)	0	¼	0·809 or 0·691

TABLE 2. *Interatomic distances in* $Ni(CN)_2,NH_3,\frac{1}{4}H_2O$.

Atoms	Length (Å)	Standard deviation (Å)	Atoms	Length (Å)	Standard deviation (Å)
Ni(1)–N (of NH_3) ...	2·10	0·04	C–N (of CN)	1·15	0·05
Ni(1)–N (of CN) ...	2·11	0·04	Ni(2)–H_2O	3·10 or 2·07	0·06
Ni(2)–C (of CN) ...	1·86	0·04	H_2O–NH_3	3·22, 3·19	—

TABLE 3. *Observed and calculated structure factors.* (*hk*0 *and* 0*kl listed separately. Minor disparities between* 0*k*0 *which appear twice arise because two zones of reflexions were observed and used independently*.)

F_{hk0} *hk*	Obs.	Calc.	F_{hk0} *hk*	Obs.	Calc.	F_{0kl} *kl*	Obs.	Calc.	F_{0kl} *kl*	Obs.	Calc.	F_{0kl} *kl*	Obs.	Calc.	F_{0kl} *kl*	Obs.	Calc.
0 2	10·8	9·3	4 10	2·9	2·7	10 0	—	0·5	18 2	4·6	4·7	5 5	3·2	−2·1	0 8	4·2	1·6
0 4	24·5	23·7	4 12	17·0	14·5	12 0	22·2	23·6				7 5	14·8	15·6	2 8	11·5	15·9
0 6	2·9	−1·6	4 14	4·0	−4·3	14 0	6·1	−6·4	1 3	32·1	−29·3	9 5	6·2	−6·1	4 8	4·7	4·2
0 8	31·1	35·1	4 16	8·2	8·5	16 0	5·3	4·5	3 3	1·4	1·5	11 5	11·1	11·6	6 8	7·6	8·8
0 10	—	0·5				18 0	2·7	2·8	5 3	12·1	−11·2	13 5	10·5	−9·6	8 8	3·2	2·2
0 12	22·0	23·6	6 0	29·5	29·7				7 3	10·1	7·2	15 5	4·6	4·2	10 8	8·0	11·0
0 14	6·2	−6·4	6 2	—	0	1 1	6·4	−7·8	9 3	14·2	−13·0				12 8	1·2	0·9
0 16	4·9	4·5	6 4	18·8	18·2	3 1	4·5	5·0	11 3	7·8	6·8	0 6	9·9	9·4			
0 18	2·5	2·8	6 6	5·3	5·3	5 1	10·2	7·1	13 3	12·4	−11·5	2 6	9·6	10·0	1 9	5·4	−7·7
			6 8	16·6	15·9	7 1	9·8	9·7	15 3	3·4	2·7	4 6	3·9	4·0	3 9	0·8	−0·3
2 0	26·3	26·4	6 10	3·4	−4·6	9 1	2·8	2·3	17 3	0·7	−0·9	6 6	8·4	5·8	5 9	1·5	−0·1
2 2	8·6	6·1	6 12	14·8	14·1	11 1	5·9	6·4				8 6	8·4	8·1	7 9	4·6	6·2
2 4	58·0	61·1				13 1	1·7	−1·4	0 4	41·0	43·9	10 6	10·2	11·2	9 9	1·2	−0·6
2 6	5·0	5·1	8 0	9·0	8·2	15 1	2·6	1·9	2 4	16·7	16·6	12 6	7·1	6·3	11 9	1·9	2·7
2 8	28·5	25·0	8 2	3·3	2·3	17 1	1·7	0·3	4 4	16·7	15·2	14 6	5·5	5·3			
2 10	4·9	−5·5	8 4	18·9	19·1				6 4	8·7	7·0				0 10	2·9	−4·4
2 12	15·0	13·7	8 6	1·7	−1·7	0 2	47·9	58·7	8 4	20·2	18·2	1 7	14·4	−15·9	2 10	5·6	8·6
2 14	1·6	1·3	8 8	10·6	10·4	2 2	7·3	−5·0	10 4	8·3	8·0	3 7	1·1	−0·5	4 10	2·2	2·2
2 16	16·7	16·7				4 2	3·1	5·5	12 4	14·4	12·6	5 7	4·0	−4·0	6 10	3·8	4·9
			F_{0kl} *kl*			6 2	1·5	−1·6	14 4	1·0	0·1	7 7	6·1	6·2	8 10	1·2	0·4
4 0	40·0	41·4				8 2	25·7	25·6	16 4	3·6	3·2	9 7	6·9	−6·6			
4 2	7·5	6·1	2 0	9·7	9·3	10 2	6·2	6·1				11 7	5·0	4·3	1 11	1·6	−1·4
4 4	32·0	28·1	4 0	23·8	23·7	12 2	23·3	23·0	1 5	21·8	−23·9	13 7	7·9	−8·6	3 11	1·9	−3·1
4 6	3·9	−3·2	6 0	2·1	−1·6	14 2	1·2	0·1	3 5	6·0	7·0						
4 8	28·8	24·4	8 0	35·0	35·1	16 2	7·0	7·2									

The numerical results of the structure analysis are collected in Tables 1—3. The standard deviations in Table 2 are from the least-squares refinement.

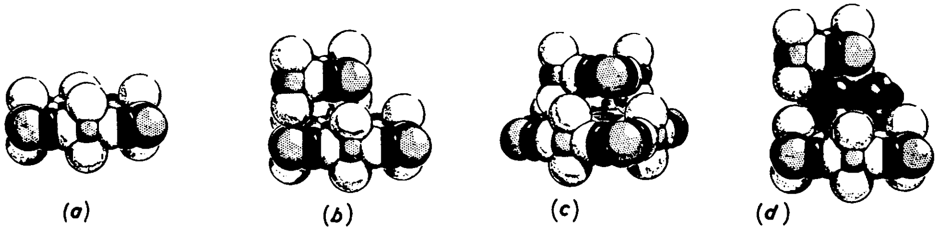
DISCUSSION

The layers of the complex found in the structure are a slightly distorted form of those in the benzene compound. The bond lengths in the two are very similar. The nickel–carbon bond, 1·86, is slightly longer than that in the benzene compound, 1·76 Å, and so approaches nearer to a single bond. The carbon–nitrogen distance, 1·15 (cf. 1·22 Å), appears to be nearer to a triple bond value than in the benzene compound but its significance is doubtful in view of the estimated errors.

The planar arrangement of four bonds at right angles around Ni(2) and the regular octahedral bonds around Ni(1) are preserved but the layers as a whole are puckered (Fig. 4). This puckering appears to be brought about entirely by a departure of the Ni–C–N–Ni sequence of atoms from linearity at the carbon atom. The angle Ni–C–N is 173°. The Ni(2) atom and its four attached carbon atoms lie in a plane parallel to (001), *i.e.*, parallel to the mean plane of the complex. The octahedron of Ni(1) is tilted so that the plane of the four cyanide nitrogen atoms makes an angle of seven degrees to (001), and the bonds of the ammonia groups are tilted in the (100) plane through a corresponding angle away from the *c* axis.

In the benzene complex the presence of molecules between the layers contributes to the stability. This is apparent from the very close packing of the structure as a whole. By contrast any structure consisting of parallel layers of the complex only is bound to be an open one owing to the manner in which the projecting ammonia groups hold the layers apart in certain places and thus produce unoccupied spaces in others. In the present structure, the layers are arranged as closely as possible with the projections of one fitting into the spaces of the other. This may be seen from Fig. 5(*c*). Although this brings the layers much closer together than in the benzene complex, it leaves considerable space, part of which is occupied by water molecules. Puckering of the layers shows that the van der Waals interaction is, in these giant molecules, great enough to cause this distortion from normal bond-angles.

FIG. 5. (*a*) *Approximate perspective drawing of part of the nickel cyanide ammonia complex layer. Nitrogen atoms white; carbon, black; nickel, dotted.* (*b*) *One method of interleaving layers.* (*c*) *Interleaving of layers as adopted in the hydrate.* (*d*) *Superposition of layers as in* (*a*), *showing the included benzene molecules of the* $Ni(CN)_2,NH_3,C_6H_6$ *structure. Note the greater inter-layer spacing than with* (*c*).



The elucidation of this crystal structure makes it possible to explain some observations made on the benzene complex. Crystals of this compound used for *X*-ray photography were found at the end of a month to be opaque. This change did not take place when the crystals were kept in a desiccator for the same length of time. *X*-Ray photographs of crystals which had not been preserved in a desiccator showed a number of diffuse spots in addition to the normal diffraction pattern. These occurred in positions corresponding to the strongest reflexions in the diffraction pattern of the hydrate. In particular, when an undecomposed crystal of the benzene complex had given a Weissenberg photograph (zero layer) on rotation about [100], and was then photographed again after exposure to the air for a few weeks, the original diffraction pattern had superposed on it a number of diffuse spots which coincided with the positions of diffraction spots that would be given by a single crystal of the hydrate rotating about its *a* axis. The *a*,*b*,*c* of the hydrate coincide with *a*,*a'*,*c* of the tetragonal benzene compound. From this it is concluded that the decomposition, which occurs in the presence of water vapour, takes place by the escape of benzene and the displacement and puckering of layers into the positions corresponding to the hydrate structure. In this process the mean plane of the puckered layers remains parallel to the original plane of the complex in the benzene compound, and the orthorhombic axes *a* and *b* in the plane emerge parallel to the *a* and *b* tetragonal axes of the original crystal. The decomposition is observed as a white surface opacity. The observed

X-ray reflexions on the Weissenberg photographs which are elongated in the direction of movement of the film suggest that the decomposed mass consists of crystallites in nearly parallel orientation, with axial directions distributed over a few degrees. It has recently been reported [8] that on removal of benzene from the complex by evacuation the cell dimensions show a continuous variation. This is presumed to be a different mode of decomposition of the compound.

The present results agree best with the formula $Ni(CN)_2,NH_3,\frac{1}{4}H_2O$, but do not remove uncertainties regarding other reported hydrates. Materials analysed by Nast [5] ($0{\cdot}37H_2O$) and by Cambi, Cagnass, and Tremolada [9] ($0{\cdot}2H_2O$) could be the same as that described here. Aynsley, Campbell, and Dodd [8] mention that their dehydrated monohydrate reabsorbs water from the atmosphere, but that the product resulting from removal of benzene from the clathrate $Ni(CN)_2,NH_3,C_6H_6$ shows no tendency to absorb water, although, as shown above, water can be absorbed while benzene is removed. It is already clear that layers of the complex may be arranged relatively to each other in more than one way, and that " single " crystals may have complex intermediate structures. It is possible therefore that a number of hydrates, perhaps including non-stoicheiometric forms, may exist.

Experimental.—Hydrated nickel cyanide–ammonia complex. The original substance was crystallised during the course of a year as described above [Found: C, 18·5; H, 2·9; N, 30·6. Calc. for $Ni(CN)_2,NH_3,\frac{1}{4}H_2O$: C, 18·2; H, 2·7; N, 31·8%]. A few crystals from this batch were added as seeds to a similar solution which then deposited a compound in about a month (Found: C, 18·5; H, 2·7; N, 31·0%).

We thank Mr. D. V. Jones for drawing Fig. 5.

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[8] Aynsley, Campbell, and Dodd, *Proc. Chem. Soc.*, 1957, 210.

[9] Cambi, Cagnass, and Tremoloda, *Gazzetta*, 1934, **64**, 758.