67. *Structure of Molecular Compounds. Part X.* Crystal Structure of the Compound of Benzene with an Ammonia–Nickel Cyanide Complex.*

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The compound $Ni(CN)_2,NH_3,C_6H_6$ has a tetragonal unit cell, $a = 7{\cdot}24$, $c = 8{\cdot}28$ Å, which contains atoms corresponding to twice this formula. Covalencies link nickel atoms through CN groups to form an extended flat network. Half the nickel atoms have four cyanide carbon atoms attached by square bonds. The metal-to-carbon distance indicates some double bonding between these atoms. The other nickel atoms are linked to four nitrogen atoms of CN groups in the form of a square, and to two ammonia groups which complete an approximately regular octahedron of nitrogen atoms. The distances nickel-to-nitrogen correspond to single bonds. Layers of this structure are arranged parallel to each other and between them are benzene molecules with their planes at right angles to that of the layers. Each benzene molecule is comparatively remote from nickel atoms. It is contained in a cavity where it makes contacts at van der Waals distances with other benzene molecules and with atoms of cyanide and ammonia groups. It is not linked by chemical bonds to the nickel complex. Some observations on related compounds are recorded.

WHEN benzene is added to a solution of nickel cyanide in aqueous ammonia a precipitate of the composition $Ni(CN)_2,NH_3,C_6H_6$ is formed (Hofmann and Küspert, *Z. anorg. Chem.*, 1897, **15**, 204). Similar compounds are formed by such other aromatic substances as pyrrole, furan, thiophen, pyridine, phenol, and aniline. Hofmann and Arnoldi (*Ber.*, 1906, **39**, 339) pointed out the comparatively small molecular volumes of these aromatic substances and found that similar compounds are not formed by fluorobenzene or other aromatic compounds of molecular volumes above a certain value.

The benzene in the compound is very firmly retained, there being no detectable pressure at room temperature. Some of it may be removed by repeated washing with ether and it is evolved when the compound is heated to 120°.

Speculations such as those of Pfeiffer ("Organische Molekülverbindungen," 2nd edn., Stuttgart, 1927, p. 213) and of Feigl (*Anais Assoc. Quim. Brasil*, 1944, **3**, 72) in which benzene molecules are supposed to occupy positions in the co-ordination sphere of the nickel atom do not provide a satisfactory formulation for the compound. Reasons for supposing that it might be a molecular compound have already been given and a preliminary account of the structure has appeared (Powell and Rayner, *Nature*, 1949, **163**, 566).

A detailed *X*-ray structural investigation requires single crystals much larger than any present in the microcrystalline substance obtained by the method mentioned above or by the modified procedure due to Hofmann and Höchtlen (*Ber.*, 1903, **36**, 1149), in which acetic acid is added to the ammoniacal nickel cyanide solution. Ordinary methods of recrystallisation are inapplicable but the formation of larger crystals might be achieved by slowing down the precipitation process. Omission of acetic acid from a solution otherwise the same as that used by Hofmann and Höchtlen has the desired effect. Such a solution left in contact with a layer of benzene deposits in a few days crystals which are recognisable under the microscope as square plates with bevelled edges. The speed of formation of crystals may be further reduced by dilution of the ammoniacal nickel cyanide solution with its own volume of water and of the benzene with its own volume of xylene. Xylene can be used because it does not replace benzene in the compound. One such preparation extending over 75 days gave crystals in the form of square plates with sides of up to 0·5 mm. and of thickness up to 0·12 mm. Some of these were used for the *X*-ray examination.

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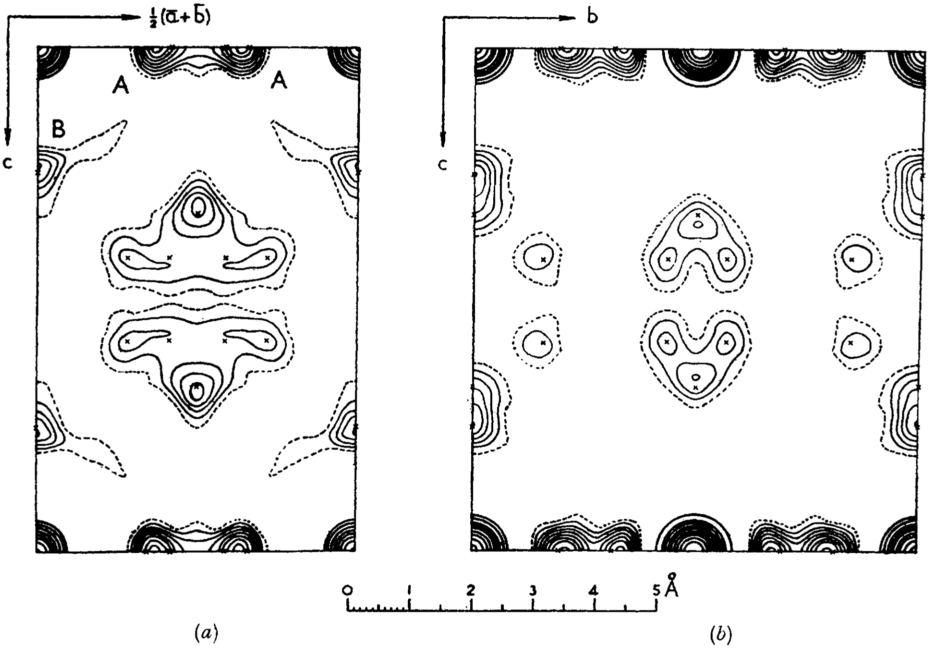
* Part IX, *J.*, 1950, 468.

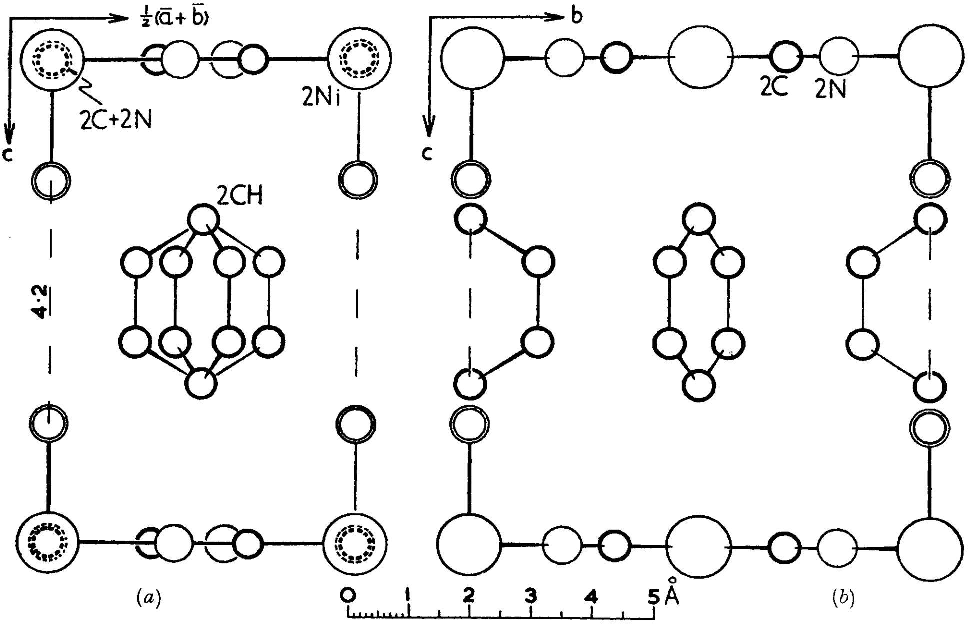
FIG. 1. *Electron-density projections on* (*a*) (110) *and* (*b*) (100).



(*a*) (*b*)

In (*a*) *the highest peaks, which represent* 2Ni + 2C + 2N, *have contours at* 20, 40, *etc., electrons*/Å^2. *In* (*b*) *the highest peaks, which represent nickel atoms, have contours at* 5, 10, *etc., electrons*/Å^2. *In other parts of both projections contours are drawn at intervals of* 2 *electrons*/Å^2. *The lowest shown is at* 4 *electrons*/Å^2. *Crosses indicate the positions of atoms determined after corrections for effects due to non-termination of Fourier series.*

FIG. 2. *Positions of atoms corresponding to Figs.* 1(*a*) *and* (*b*).



(*a*) (*b*)

[*The atoms are represented as in Fig.* 4. *In* (*a*) *two benzene molecules overlap in the centre.*]

The crystals which appear mauve to the eye are tetragonal, tabular on (001) with cleavages parallel to (001) and (110). Other faces for which approximate interfacial angles are observable under the microscope are {110} and {111}. The crystals are optically uniaxial with negative birefringence. They are pleochroic: when the electric vector is parallel to c the light transmitted is green; when it is at right angles to c the light is purple. No pyroelectric effect was observed. The density by flotation is 1·58 g./c.c.

For X-ray examination the radiation from a copper target was filtered through nickel foil. Single-crystal oscillation photographs were obtained by both the stationary-film and the Weissenberg method. In the Weissenberg procedure zero layers were photographed for oscillation about the [110] and [100] axes. Exposure times were varied and in each exposure three films were loaded together in the camera so that an intensity range of 1—2000 could be covered.

The intensities of the reflections were measured by visual comparison with a scale of spots of known exposure. Because the crystal was a flat plate the reflected spots varied in size and shape on different parts of the film, and in the case of the *hhl* reflections a correction for this was made in the way used by Broomhead (*Acta Cryst.*, 1948, **1**, 324) for a crystal of similar shape.

The film is divided into strips in which the spots are all of about equal size. Spots which by tetragonal symmetry must have equal intensity (*i.e.*, $I_{hhl} = I_{\bar{h}\bar{h}l}$) are found in different strips, so that all the strips can be compared. The factors relating intensities in one strip to those in another had values between 1 and 1·8.

These X-ray measurements confirm that the crystals belong to the tetragonal system. The cell dimensions are $a = 7{\cdot}242 \pm 0{\cdot}007$, $c = 8{\cdot}277 \pm 0{\cdot}008$ Å, and the calculated mass of the unit cell corresponds to 1·98 times the formula $\mathrm{Ni(CN)_2,NH_3,C_6H_6}$. Since no class of reflections is found to be systematically absent the space group must be $P\bar{4}$, $P4$, $P4/m$, $P\bar{4}2m$, $P4mm$, $P42$, or $P4/mmm$. The last four are excluded by intensity relations among the observed reflections, which show that there are no vertical planes of symmetry or horizontal two-fold axes. Thus for a few pairs of reflections, the intensities of hkl and $\bar{h}kl$ are clearly unequal. This may be seen most readily by a comparison of spots related symmetrically to each other above and below the zero layer line on oscillation photographs taken with [100] as oscillation axis. Although the structure as a whole lacks this symmetry many of the atoms must lie in special positions which conform to it, because for many such pairs of reflections no difference is observable. If the crystals are centrosymmetric, as is suggested by the pyroelectric test, the space groups must be $P4/m$. The structure was developed in the first place on this assumption, but, if any other of the seven space groups enumerated above is taken as a basis, either the atomic positions deduced are the same as those in $P4/m$, or a too high symmetry such as that of $P4/mmm$ restricts the position of the benzene and makes it impossible to obtain agreement between observed and calculated intensities of reflection.

The two nickel atoms in each unit cell must occupy special positions on four-fold or two-fold axes of symmetry. Odd-layer lines of oscillation photographs about [110] are weaker than even-layer lines. This suggests that the nickel atoms, which represent about a quarter of the scattering power of the cell contents, are disposed so that, as far as they are concerned, the (001) face is centred. For any such arrangement the nickel atoms must be in symmetry centres. It is therefore possible to select a unit-cell origin at the centre of a nickel atom and to evaluate Fourier series for electron density. This was done for the *hhl* structure factors and a projection on (110) was thus obtained. All the structure factors were given positive signs as though they were due to the nickel contributions alone.

In the projection [Fig. 1(a)] two peaks A are found between each pair of nickel atoms. They are in positions consistent with a structure made up of a square network parallel to (001), having nickel atoms at the corners and CN groups along the sides. In the view provided by this projection each of these peaks represents the overlap of a carbon and a nitrogen atom. The side of the square network is 5·1 Å, a distance appropriate to a linear Ni–CN–Ni arrangement. The carbon and the nitrogen atoms occupy special four-fold positions $xy0$, and for the arrangement described x and y are equal.

Peaks *B*, lying along the *c* direction about 2 Å above and below the nickel peaks, suggest that ammonia groups are attached to the nickel atoms in some way. Since there are only two of these groups per unit cell, they can only occupy the positions $00z$, $00z$ or $\frac{1}{2}\frac{1}{2}z$, $\frac{1}{2}\frac{1}{2}\bar{z}$, and the line parallel to *c* on which they lie must be a four-fold axis. It follows that the unit-cell origin (selected at a nickel atom) must also lie on a four-fold axis. The nickel atoms therefore occupy two non-equivalent special positions 000 and $\frac{1}{2}\frac{1}{2}0$ and one of these must have two attached ammonia groups. Equivalent structures result from either choice and the nickel atom at 000 has been selected as the one having attached ammonia groups.

The two benzene groups must lie in special positions and of these only $0\frac{1}{2}0$, $\frac{1}{2}00$ and $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ are possible on symmetry grounds. The remaining well-defined areas of electron density in the projection can only be explained if the benzene molecules have their centres at $0\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$. Benzene molecules are thus shown to be in these positions, with a two-fold symmetry axis parallel to [001], and a plane of symmetry perpendicular to this axis. Of the three ways in which this could be achieved by a regular hexagon, that with two carbon atoms on the two-fold axis is seen directly from the projection to be correct. Two carbon atoms of each benzene ring are on the two-fold axes at $0\frac{1}{2}z$ and its equivalents, and the remaining carbon atoms in general positions *xyz*. The values of *x* and *y* cannot be determined from the (110) projection since the tetragonal symmetry brings about an overlap of two benzene molecules in different orientations and with centres at $0\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$. This overlap is avoided in the projection on (100).

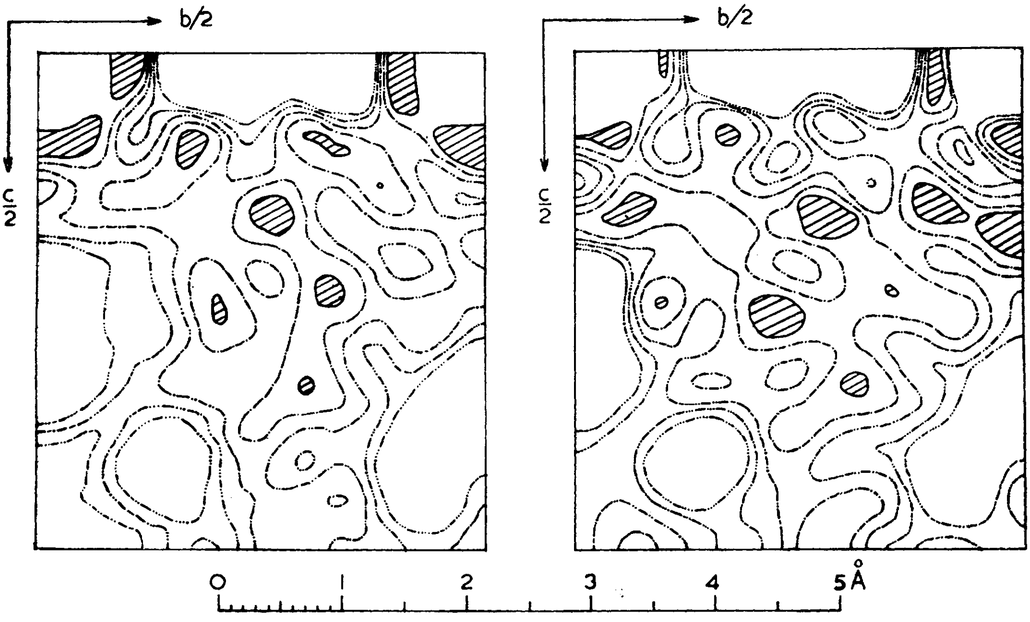
The 0*kl* structure factors were obtained from approximate co-ordinates that could now be deduced, the chief uncertainty being in the *xy* co-ordinates of the carbon atoms in general positions. In this and later structure factor calculations the atomic scattering curve used for nickel was that given by Robertson for nickel phthalocyanine (*J.*, 1936, 1195) which was investigated with Cu-K_α radiation. For the benzene carbon atoms scattering factors were taken from Robertson's values for hydrocarbons (*Proc. Roy. Soc.*, 1935, *A*, **150**, 106), but for the carbon and nitrogen atoms which are very tightly bound in the cyanide complex James and Brindley's curves (*Phil. Mag.*, 1931, **12**, 81) were employed. This choice resulted from trials with the 00*l* series of reflections.

The signs thus obtained were used in the F0*kl* electron-density synthesis. The resulting projection [Fig. 1(*b*)] confirmed the general structure proposed, showed separately the nitrogen and carbon atoms which overlapped in the (110) projection, and gave the *y* co-ordinates of the eight carbon atoms in the general positions It failed through imperfect resolution to give their *x* values and, owing to overlap with NH_3 groups, did not resolve the benzene carbon atoms on the two-fold symmetry axes. Since some changes of parameters are suggested by the projection, signs were recalculated to allow for this, and the synthesis was repeated with the inclusion of ten small terms which had previously been omitted owing to uncertainty in their signs. The general appearance of the projection was not changed but improved values of some of the parameters could be obtained. The atomic positions corresponding to the projections 1(*a*) and (*b*) are shown in Figs. 2(*a*) and 2(*b*) which are based on the final corrected parameters given below.

Since reflections at high angles are very strong it seemed probable that the calculated electron-density maps would show errors due to non-convergence of the Fourier series, and this was confirmed by a Fourier synthesis carried out with the calculated structure factors as coefficients. The results of the summations with observed and with calculated coefficients are shown in Figs. 3(*a*) and 3(*b*). In these, contours are given only for the areas of low electron density which do not correspond to atoms. They have the same general form in both and may therefore be ignored in the projection derived from the observed structure factors. The positions of the atomic peaks are however affected by these diffraction effects and a comparison of the peak positions in the two permits correction in the manner suggested by Booth (*Proc. Roy. Soc.*, 1946, *A*, **188**, 77).

With the best parameters now available the structure factors were recalculated. Improvements in the agreement between the observed and calculated structure factors were found. The sign of the calculated F_{081} had changed and this was allowed for, but all F_{hhl} remained positive as they had been taken in the first projection. The newly calculated structure factors were used for further Fourier synthesis of F_{hhl} and F_{0kl}. The F_{hhl} synthesis was compared with that calculated from the observed values, and corrections were made to the atomic co-ordinates. The F_{0kl} synthesis was similarly used to make a more accurate correction than that based on the synthesis with the former set of calculated F_{0kl}. The small changes in co-ordinates resulted in a change of sign in the small term F_{030} and so the process of correction was repeated for this projection. The parameters derived by consideration of both projections are listed in Table 1. These lead to the interatomic distances of Table 2. These are not all of the same probable accuracy.

FIG. 3. *The lower contours in the electron-density projection on* (100).



Part (*a*) *shows the contours derived from observed* F's *and corresponds to Fig.* 1(*b*). *The higher contours are omitted, the highest shown being identical with the lowest of Fig.* 1(*b*). *Contours are at intervals of* 1 *electron*/Å^2 *and the shaded areas show negative regions.*

Part (*b*) *is the similar projection derived from the calculated* F *values. Negative regions and areas of appreciable electron density not attributable to atoms occur in approximately the same positions in* (*a*) *and* (*b*).

TABLE 1. *Atomic co-ordinates.*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0	0	0	C(1)	0·328(5)	0·328(5)	0
Ni(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	C(2)	0	$\frac{1}{2}$	0·330
N(1)	0·209(6)	0·209(6)	0	C(3)	0·153	0·435	0·417
N(2)	0	0	0·249				

In Figs. 1(*a*) and 2(*a*) the peak at the origin represents 2Ni + 2C + 2N. The Ni–N (of NH_3) bond length is given by the distance from the origin to a small peak representing a single NH_3 group. The position of the small peak is subject to a large diffraction correction (0·07 Å) compared with those in the (100) projection. In this projection [Figs. 1(*b*) and 2(*b*)] the larger peaks represent single nickel atoms and carbon atoms of CN appear as peaks due to the overlap of two C atoms with the same projected co-ordinates. The nitrogen atoms of CN similarly overlap. For Ni–N (of CN) and Ni–C the probable error is ±0·03 Å while for N–C it is ±0·04 Å. The benzene C–C distances are less accurate since separate determinations of all the co-ordinates are impossible owing to over-lapping.

The most reliable of these distances is 1·38 Å for C(3)–C(3) which can be measured directly in the (100) projection. The Ni–NH_3 distance is considered the least reliable since the differences in shape and position of the NH_3 peak in the " observed " and " calculated " syntheses are greater than for any other peak.

Calculated structure factors and the observed values adjusted to the same scale are given in Table 3.

The value of

$$R = \frac{\Sigma\left||F_{\text{obs.}}| - |F_{\text{calc.}}|\right|}{\Sigma|F_{\text{obs.}}|}$$

TABLE 2. *Interatomic distances.*

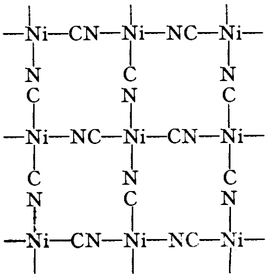
Bond lengths		*Non-bonded distances*	
Atoms	Å	Atoms	Å
Ni(1)–N(1) of CN	2·15	C(2)–N(2)	3·7
Ni(1)–N(2) of NH_3	2·06	C(2)–N(1)	3·8
Ni(2)–C(1) of CN	1·76	C(2)–C(1)	3·8
C(1)–N(1)	1·22	C(3)–N(2)	3·6
C(2)–C(3)	1·41	C(3)–C(3)	3·6
C(3)–C(3)	1·38	C(3)–C(1)	3·75
		C(3)–N(1)	3·8
		N(2)–N(2)	4·2

TABLE 3. *Observed and calculated structure factors.*

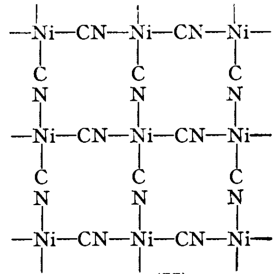
hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$
001	34	45	040	35	37	080	12	10	330	51	43
002	54	73	041	35	36	081	8	4	331	49	48
003	71	81	042	21	16	082	<2	−1	332	48	36
004	55	53	043	36	34	083	10	6	333	35	32
005	60	57	044	30	31	084	8	5	334	38	46
006	36	29	045	17	15				335	33	34
007	39	41	046	24	24	090	8	13	336	20	21
008	28	32	047	14	12	091	6	10	337	29	26
009	29	30	048	17	18	092	4	6	338	29	30
0.0.10	17	21	049	12	14				339	15	17
						110	28	27			
010	7	4	050	13	14	111	62	72	440	41	41
011	6	2	051	<2	1	112	31	29	441	29	16
012	18	−14	052	<2	1	113	30	27	442	24	17
013	<2	1	053	<3	4	114	41	55	443	27	25
014	12	8	054	6	7	115	27	26	444	23	22
015	8	−2	055	<3	5	116	24	19	445	18	20
016	7	−4	056	<3	2	117	24	20	446	19	10
017	<3	−2	057	<3	4	118	25	27	447	17	15
018	<3	3	058	<2	5	119	12	13	448	12	14
019	<3	−2	059	2	2	1.1.10	11	10			
0.1.10	<2	2							550	29	28
			060	32	36	220	70	74	551	31	30
020	48	45	061	26	26	221	56	47	552	26	22
021	<1	3	062	23	20	222	37	31	553	22	23
022	6	1	063	29	29	223	46	51	554	26	31
023	25	25	064	24	27	224	37	44	555	23	23
024	14	14	065	20	20	225	26	30	556	17	15
025	12	10	066	22	20	226	30	29			
026	13	9	067	16	17	227	23	24	660	18	22
027	9	6	068	12	18	228	25	26	661	18	18
028	7	7				229	22	22	662	12	10
029	8	6	070	4	4	2.2.10	9	11	663	19	18
0.2.10	3	−2	071	12	−11				664	15	20
			072	6	−7						
030	6	−4	073	6	−5						
031	12	10	074	4	−4						
032	15	−13	075	<2	−1						
033	<2	0	076	11	−12						
034	10	10									
035	7	−4									
036	<3	2									
037	<3	−3									
038	<3	7									
039	<2	2									

is 0·20 for 0*kl* and 0·13 for *hhl* reflections. In addition to the agreement between calculated values of the structure factors used in Fourier syntheses, confirmation of the structure as a whole was obtained by the calculation of a number of *hkl* structure factors. For all the following pairs of reflections, observed on one oscillation photograph, the calculated intensity of the first was greater than that of the second, and in every case this was also true of the observed intensities: 131, $\bar{1}31$; $\bar{2}44$, 244; $\bar{1}55$, 155; $\bar{2}46$, 246; 245, $\bar{2}45$; $\bar{3}22$, 322; 232, $\bar{2}32$; $\bar{1}44$, 144; $\bar{1}42$, 142. The reflections from the planes 243 and $\bar{2}43$ were calculated to be very nearly equal and no difference could be detected in their photographed intensities.

Nickel atoms are linked by cyanide groups in an extended two-dimensional array to form a flat network. There is no great difference in peak heights for the carbon and the nitrogen atoms of the cyanide group. There is a similar lack of any striking distinction between these atoms in the electron-density map obtained from the calculated structure factors, but in both cases the peaks near to Ni(2) are lower than those near to Ni(1). Thus the observed structure factors agree with the supposition that four cyanide carbon atoms are attached to Ni(2). The distinction between these atoms and the four cyanide nitrogen atoms attached to Ni(1) is shown more clearly by the interatomic distances. The observed distances Ni–N = 2·15 and Ni–C = 1·76 Å are explained only if the links are between the atoms named. A difference in length would not appear if the symmetry resulted from some other ordered or disordered arrangement of layers such as (I) or (II) in which the corresponding peaks would be equal.


(I)

or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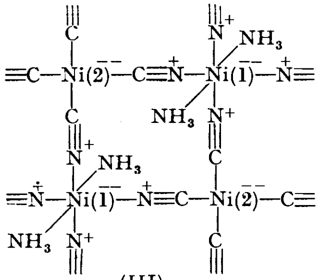

(III)

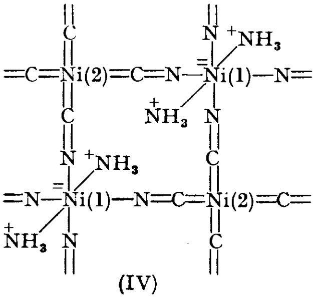
In the structure deduced the nickel atoms are of two kinds: half are bonded to four cyanide carbon atoms in the plane of the network, the others form six octahedral bonds, four to cyanide nitrogen atoms and two, projecting above and below the network, to ammonia groups. A simple formulation of this complex is (III).

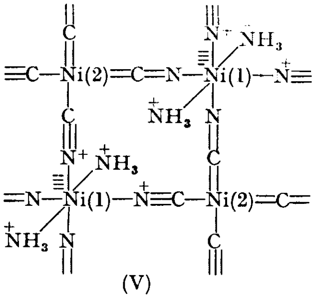
In various analogous complexes, such as nickel carbonyl (Brockway and Cross, *J. Chem. Physics*, 1935, **3**, 828), the hexamethyl*iso*cyanidoferrous ion (Powell and Bartindale, *J.*, 1945, 799), and the tetracyanonickelate ion (Brasseur and Rassenfosse, *Mem. Soc. Roy. Sci. Liège*, 1941, [2], **4**, 397; Lambot, *Bull. Soc. Roy Sci. Liège*, 1943, **12**, 522), there is evidence that the metal-to-carbon distances are shorter than might be expected for single bonds. There is no record of the nickel-to-carbon distance in any compound of planar four-covalent nickel in which there is no doubt of the single-bond character of the Ni–C link, but possible values may be estimated from bond lengths in other nickel compounds. Subtraction of the sulphur radius 1·04 from the nickel-to-sulphur distance 2·30 Å in potassium nickelodithio-oxalate (Cox, Wardlaw, and Webster, *J.*, 1935, 1475) gives a radius for nickel of 1·26 Å. Pauling obtained a similar value (1·22 Å) for the nickel radius ("Nature of the Chemical Bond," 2nd edn., Ithaca, New York, 1945, p. 251) by a more complex route, and though the derivation has been criticised (Wells, *J.*, 1949, 66) the radius obtained is not likely to be as much as 0·1 Å in error. These nickel radii require nickel-to-carbon distances of 1·99 or 2·03 Å. The observed value, 1·76, is less by 0·23, an amount so large compared with the possible errors that some multiple-bond character must be assumed.

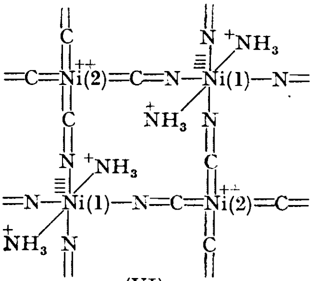
The distance may be further considered in relation to the nickel-to-carbon distance in compounds where, although the bond multiplicity may not be known, there is no doubt that at least a single bond is present. The work of Brasseur and others on the salts of the tetracyanonickelate ion indicates nickel-to-carbon distances of 1·85—1·9 Å. This length which must be less than, or equal to, the single-bond distance provides a check that the observed distance 1·76 Å is shorter than a single bond.

No similar shortening is found in the nickel-to-nitrogen distances which have been observed for octahedral nickel in $K_2Ca[Ni(NO_2)_6]$ (Driel and Verweel, *Z. Kryst.*, 1936, **95**, 308) as 2·15 ± 0·03 Å. Alternatively Pauling's single-bond radii (*op. cit.*, pp. 182, 164) lead to 2·09 Å. The distances Ni–N 2·15 and Ni–NH_3 2·06 observed are both close to these values, and their difference from each other is not regarded as significant in view of larger probable error in the Ni–NH_3 distance.

The complex may be formulated in a number of ways consistent with these conclusions on bond multiplicity, for example, (IV), (V), and (VI). In (IV), every nickel atom has the effective atomic number of krypton; Ni(2) is isoelectronic with the nickel atom in $Ni(CO)_4$ and has zero valency, and Ni(1) has a valency of four. However this arrangement of bonds cannot be the principal one in this compound which is paramagnetic. It has a moment of 2·32 Bohr magnetons per nickel atom (Craig, Thesis, Univ. Sydney, 1942), which requires some nickel electrons with unpaired spins.


(IV)


(V)


(VI)

In both (V) and (VI), Ni(1) has the effective atomic number 38. Its two " surplus " electrons must be in 5*s* or 4*d* orbitals. The paramagnetism of the isoelectronic nickel atom in $[Ni(NH_3)_6]Cl_2$ is evidence that 4*d* is preferred and, if the same is true in this compound, it should be paramagnetic, as observed. If the only restrictions on possible bond orbitals are those summarised by Kimball (*J. Chem. Physics*, 1940, **8**, 188) then in (VI) and in some other arrangements, but not in (V), Ni(2) might also contribute to the paramagnetism.

Layers of the form described are arranged parallel to each other. As shown in Fig. 4, the ammonia groups projecting from one layer, imagined as horizontal, are vertically above and below those from the adjacent layers. This packing of the layers leaves a series of cavities each containing a benzene molecule.

The benzene carbon atom C(2) which lies on the two-fold symmetry axis is surrounded by two ammonia nitrogen atoms at 3·7 and by four cyanide carbon atoms C(1) at 3·8 and four cyanide nitrogen atoms also at 3·8 Å. Of these ten contacts those to one side of the atom are shown in Fig. 5. The symmetry permits any orientation of the molecule consistent with the two-fold axis, and that adopted gives the largest possible distances between the carbon atoms of the benzene and their surroundings. The benzene carbon atom C(3) in the general position has for neighbours two C(3) atoms of other molecules at 3·6, an ammonia nitrogen atom at 3·6, a cyanide carbon atom at 3·75, and a cyanide nitrogen atom at 3·8 Å. These large distances show that there is no chemical bond between the benzene molecules and the nickel complex. The substance must be described as a crystalline molecular compound.

In this it differs from the complex of benzene with silver perchlorate described by Rundle and Goring (*J. Amer. Chem. Soc.*, 1950, **72**, 5337). Short distances 2·6 Å from silver ions to carbon atoms are interpreted in terms of bonds of very low order.

Each layer of the structure has ammonia groups projecting above and below. To form a crystal these layers can only be packed parallel to each other, but the projecting ammonia groups restrict their approach. If the projecting groups were staggered so that, as far as possible, they fitted between each other and not end to end, the layers could pack closer to each other, but the packing would still be poor. In the compound as formed with more widely separated layers, and benzene molecules occupying the cavities, there is very efficient space filling.

FIG. 4. *Part of structure to show surroundings of one benzene molecule.*

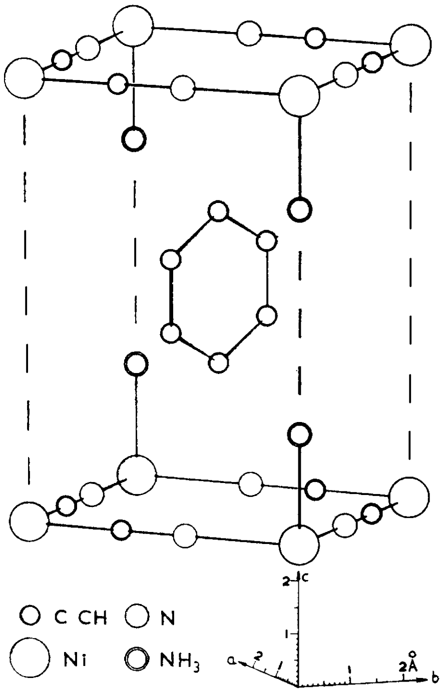
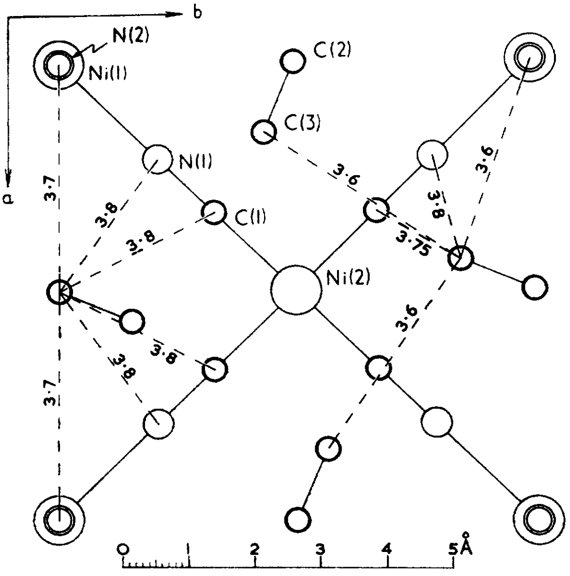


FIG. 5. *Structure projected on* (001) *to show non-bonded interatomic distances.*



Thiophen, pyrrole, furan, and pyridine, which form similar compounds, have molecules which are all somewhat similar in shape to that of benzene, but of slightly smaller volume. These substances, therefore, should replace benzene without enlargement of the layer spacing. Crystals of the thiophen compound decompose fairly readily but have been examined, and within 1% have the same *c* spacing as the benzene compound. With the observed arrangement of layers, little contraction of *c* is possible since the ammonia groups of adjacent layers are nearly in contact.

The action of the complex structure in accepting for enclosure in its cavities only those molecules of suitable size and shape explains why xylene does not form a similar compound. It has been applied to prepare quantities of benzene of exceptionally high purity (Evans, Ormrod, Goalby, and Staveley, *J.*, 1950, 3346). This selectivity resembles that in the clathrate compounds of quinol, where small atoms or molecules are completely encaged; but since the nickel cyanide complex is linked only in two dimensions, there is the possibility of enlargement of the cavities by wider separation of the layers. If molecules of substituted benzene derivatives were contained in such cavities, the substituents would have to be linked to benzene C(2) atoms by bonds parallel to the *c* axis. Since the other benzene CH groups are already in contact with others of their own kind in neighbouring molecules, there is clearly no space for substituents on them.

In the case of the aniline compound such an enlargement of the interlayer spacing has been found. For this compound $c = 9{\cdot}29 \pm 0{\cdot}05$ Å, greater by about 1 Å than the corresponding distance in the benzene compound. There will be a limit to this expansion process since it creates fresh empty spaces between the ammonia groups which are no longer nearly in contact. In conditions comparable with those used for benzene it is found that toluene does not form a compound. It is possible that the amino-group of aniline, which might interact with nickel, influences the formation of its compound, but in any case the toluene molecule would require more space since the C–C is slightly longer than C–N link and there are the additional hydrogen atoms of the methyl group. The limit of extensibility may therefore lie below that required to accommodate this molecule.

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