The Crystal Structure of Hexamminecobalt(III) Hexacyanocobaltate(III): An Accurate Determination

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The crystal structure of [Co(NH$_3$)$_6$] [Co(CN)$_6$] has been determined by three-dimensional X-ray data in an attempt to study the charge distribution in complexes. The crystals conform to the space group $R\bar{3}$ with one formula unit in a cell of dimensions $a_r = 7\cdot255(3)$ Å and $\alpha_r = 97\cdot65(2)°$ at 25·5 °C. Intensity data were collected with Mo $K\alpha$ radiation up to sin $\theta/\lambda = 1\cdot3$ Å^{-1} on an automated four-circle diffractometer. Positional and anisotropic thermal parameters for all atoms were refined by full-matrix least-squares methods. A correction for anisotropic extinction effects was included in the least-squares refinement. The conventional R index is 0·028 for 2205 independent reflexions. The complex ions are packed in much the same way as the ions in caesium chloride. Both complex ions possess the rigorous crystallographic symmetry $\bar{3}$. The coordination around the metal atoms is remarkably regular octahedral. The Co–N distance is 1·972(1) Å and Co–C is 1·894(1) Å; the angles NCoN and CCoC are 89·78(5) and 90·25(6)°, respectively. The C–N distance is 1·157(2) Å. The direct integration of the electron density around the central cobalt atom within a sphere of radius 1·22 Å showed that each metal atom has largely neutralized resultant charges: [Co(NH$_3$)$_6$]$^{3+}$, 26·3 ± 0·3 e and [Co(CN)$_6$]$^{3-}$, 26·8 ± 0·3 e.

Introduction

When chemical bonds are formed there is a change in the electron distribution of the participating atoms. Attempts have been made to obtain a picture of these changes from direct experimental information (for example, Verschoor & Keulen, 1971; Coppens, Sabine, Delaplane & Ibers, 1969; Coppens, Paulter & Griffin, 1971). The study of hexamminecobalt(III) hexacyanocobaltate(III), [Co(NH$_3$)$_6$] [Co(CN)$_6$], described in this paper was undertaken to determine with what accuracy the electron density distribution in a complex ion could be obtained. This compound was selected for the following reasons: The crystal contains two types of the most familiar and fundamental complex ions of cobalt(III); this will enable us to compare the numbers of electrons around the two cobalt atoms with the same accuracy. The crystal is rhombohedral and has a small number of atomic parameters to be determined. The crystal is stable in air and under X-irradiation.

Experimental

Crystals of [Co(NH$_3$)$_6$] [Co(CN)$_6$] were grown by the diffusion method. Two small beakers, one containing a solution of [Co(NH$_3$)$_6$]Br$_3$ and the other a solution of K$_3$[Co(CN)$_6$], were placed side by side in a large beaker and distilled water was poured very carefully down the walls of the beakers until the level was about 3 cm above the tops of the two small beakers. After about two weeks, orange-red crystals in the form of hexagonal needles grew on the upper part of the wall of the beaker containing the [Co(NH$_3$)$_6$]Br$_3$ solution.

The unit-cell dimensions were determined on the diffractometer at 25·5 °C with Mo $K\alpha$ radiation mono-

chromated by a graphite crystal ($K\alpha_1$, $\lambda = 0\cdot70926$; $K\alpha_2$, $\lambda = 0\cdot71354$ Å). ω values of 26 higher order reflexions were measured on both sides of the incident beam with the detector aperture wide open (Arndt & Willis, 1966). The cell dimensions were then refined by least-squares methods. The density of the crystal was determined by flotation in a mixture of methyl iodide, carbon tetrachloride and ethanol.

Weissenberg photographs taken with Fe $K\alpha$ radiation showed the diffraction symmetry $\bar{3}$. The only systematic absence, hkl with $-h+k+l \neq 3n$, indicated that the possible space group is $R\bar{3}$ or $R3$. However, Weissenberg photographs taken with Cu $K\alpha$ radiation, where Cu $K\alpha$ radiation is scattered anomalously by the cobalt atoms, still indicated the same diffraction symmetry. Consequently, the space group was uniquely determined as $R\bar{3}$. The crystal data are C$_6$H$_{18}$N$_{12}$Co$_2$, M.W. 376·2, hexagonal; $a = 10\cdot921$ (3), $c = 10\cdot765$ (5) Å, $Z = 3$; in rhombohedral setting, $a_r = 7\cdot255$ (3) Å, $\alpha_r = 97\cdot65$ (2)°, $U = 370\cdot6$ Å^3, $D_m = 1\cdot689$ g cm^{-3} (18 °C), $Z = 1$, $D_x = 1\cdot685$ g cm^{-3}, μ(Mo $K\alpha$) = 24·8 cm^{-1}, space group $R\bar{3}$.

The initial intensity data (hereafter called data set 1), from which the structure was solved and preliminarily refined, were collected on a Rigaku automated four-circle diffractometer at Hokkaido University. The intensity data on which the final atomic parameters are based (hereafter called data set 2) were collected on a Rigaku automated four-circle diffractometer at this Institute. The experimental conditions for the two data collections were broadly similar. The differences in experimental conditions for these measurements are summarized in Table 1. Accordingly, the experimental procedure for the second data collection will be described in some detail. In order to observe higher

order reflexions molybdenum radiation from a fine-focus Philips tube was used, a graphite monochromator being employed. The output of the tube in combination with a Rigaku generator 4053A3 appeared to be stable after a warm-up period of an hour. The long-period (three weeks) and the fast fluctuation appeared to be about 0·2% and 0·1% respectively. The angular width of the incident beam profile was 0·9°. The crystals were ground into spheres of radius about 0·1 mm. A specimen was mounted on the goniostat with its c axis nearly but not exactly parallel to the φ axis. The intensity data were collected at a take-off angle of 6°. The scintillation counter was placed 20·5 cm from the crystal with a receiving aperture of 7 mm in diameter. The linear response of the counter was 10^4 counts sec^{-1}. Integrated intensities were collected using an ω-2θ continuous scan technique. The scanning range was determined according to the formula: $1·5° + 0·6° \times \tan \theta$ and the scanning rate was 2° per min in ω when

Fig. 1. A packing diagram of [Co(NH₃)₆] [Co(CN)₆].

$2\theta \le 90°$ and 1° per min otherwise. Background counts were taken at both limits of the scanning range. Counting time was automatically varied from 15 sec to 120 sec according to the peak counts and 2θ values. Nickel-foil attenuators were automatically inserted when the intensity of the diffracted beam exceeded 5000 counts per sec during the scanning. Thus the error due to counting loss could be suppressed to less than 1%, since the dead time of the counting circuit was 2μsec. The pulse height analyser was set to accept about a 95% window centred on the molybdenum peak.

If the value of $\sigma(F)/|F|$ was larger than 0·03, the measurement was repeated until $\sigma(F)/|F|$ became less than 0·03. The maximum number of repetitions was limited to three. For those reflexions with $2\theta \le 90°$, the intensities of three equivalent members $(hk.l, ih.l, ki.l)$ of the form $\{hkl\}$ were measured. The intensities of the three standard reflexions were measured every fifty reflexions during the data collection to check the electronic stability of the instrument and any crystal deterioration. Fluctuations in the intensities of the standard reflexions over a period of three weeks were within 1·5% of $|F|$. Reflexions were measured up to a 2θ value of 130°. The raw intensities were corrected for background according to the formula,

$$I = P - (t_p/2t_b)(B_1 + B_2),$$

where P is the total integrated peak count measured in time t_p and B_1 and B_2 are background counts, each measured in time t_b. Standard deviations were assigned to the corrected intensities I by the expression:

$$\sigma(I) = [P + (t_p/2t_b)^2(B_1 + B_2)]^{1/2}.$$

The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Absorption corrections were made assuming the crystal to be a sphere (International Tables for X-ray Crystallography, 1959). An extinction correction was applied according to Coppens & Hamilton (1970) at a later stage of the refinement. Intensities of about 300 reflexions were remeasured to check the accuracy and new values were substituted in the data
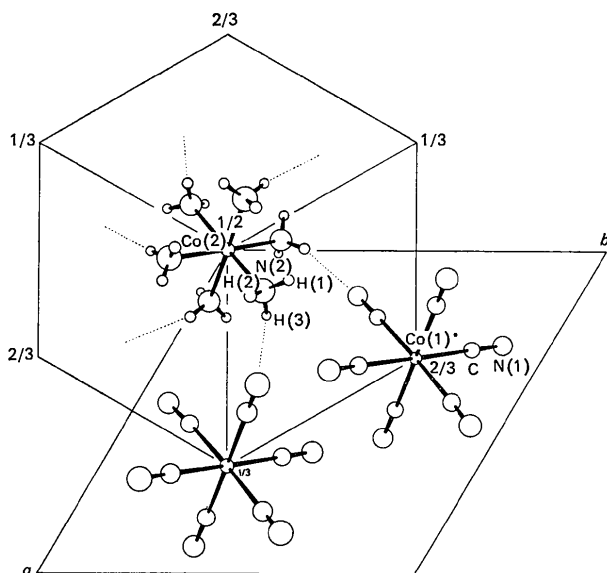
Table 1. Experimental conditions

	Data set 1	Data set 2
Monochromator	LiF (200)	Graphite (002)
Collimator	0·5 mm ⌀ × 90 mm	0·5 mm ⌀ × 150 mm
Detector aperture	3·5 mm ⌀	7·0 mm ⌀
$2\theta_{max}$	120°	130°
Scanning rate	$\frac{1}{2}$°/min ($2\theta \le 80°$) 1°/min ($2\theta > 80°$)	2°/min ($2\theta \le 90°$) 1°/min ($2\theta > 90°$)
Background counting	10 sec	15 ~ 70 sec ($2\theta \le 90°$) 15 ~ 120 sec ($2\theta > 90°$)
Radius of crystal specimen	0·115 mm	0·105 mm
Variation of standard reflexions over a period of 3 weeks	< 3·8%	< 1·5%

sets, if necessary. The intensities of 4280 reflexions were measured on the diffractometer at Hokkaido University, among which 1935 were independent and had non-zero values. Data set 1 consists of these 1935 intensities. Data set 2 collected by the diffractometer at this Institute consists of 4761 reflexions (including symmetry-related reflexions) whose $|F|$ values are greater than 3σ, of which 2205 are independent. In collecting these data, a total of 8200 reflexions were carefully measured. Standard deviations of $|F|$ were estimated from the average of the individual standard deviations and from the range of $|F|$ values of the equivalent members of the form, after the anisotropic extinction correction had been applied. If $\sigma(F)$ is assumed to be a measure of $||F_o| - |F_c||$, a predicted R index may be computed from the values of $|F|$ and $\sigma(F)$. The predicted R index on $|F|$ was 0·024.

The intensities were also measured on a manual diffractometer by the balanced filter method, using a different crystal specimen. The main purpose of this measurement was to check the experimental conditions. 851 reflexions were collected. The inter-experimental agreement factor between this set and data set 1 was 2·9% and that between this and data set 2 was 2·7%. The inter-experimental agreement between data

sets 1 and 2, computed using these 851 reflexions common to the three data sets, was 1·5%.

Absolute measurement on powdered specimen

Scale factors for the structure amplitudes were obtained by comparison with the calculated values. These were checked by absolute measurement of two reflexions from the powdered specimen. The crystals were carefully ground in an agate mortar for about half a day to free them from texture. About 0·2 g of the powder was pressed into a disk of diameter 2 cm under a pressure of about 1000 kg cm^{-2}. The experimental procedure for the absolute measurement is similar to that described by Kuriyama & Hosoya (1963). The only difference is that the transmission geometry was adopted instead of the reflexion geometry (Compton & Allison, 1935); Mo $K\alpha$ radiation was used. Two slightly overlapping reflexions, 012 and 110, were counted together and the intensity of each reflexion was obtained by a graphical method. The intensity of the transmitted primary beam was also measured. The structure amplitudes on an absolute scale are listed in Table 2, together with those obtained by the least-squares method at the final stage of refinement. Values of $|F(110)|$ in data sets 1 and 2 and $|F(012)|$ in data set 1 agree very well with the respective absolute values. Only $|F(012)|$ in data set 2 is larger by about 4·7% than the absolute value. The errors in the observed structure amplitudes from single-crystal measurements are estimated to be 2 ~ 3%, as will be discussed in the following section. Thus the agreement shown in Table 2 was considered to be reasonably good and the scale factors in both data sets were not modified.

Table 2. *Absolute measurement by powdered specimen*

	Absolute measurement	Data set 2*	Data set 1*
$|F(110)|$	196·1 ± 2·0	195·3	193·3
$|F(012)|$	162·0 ± 1·7	170·4	165·9

* Corrected for extinction

Table 3. *Final atomic parameters*

The anisotropic thermal parameters are of the form: exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.
All the parameters have been multiplied by 10^5 except those of hydrogen atoms which have been multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	0	0	0	338 (2)	338 (2)	247 (2)	338 (2)	0	0
Co(2)	0	0	50000	302 (2)	302 (2)	240 (2)	302 (2)	0	0
N(1)	20586 (6)	24119 (6)	16555 (6)	898 (7)	516 (6)	592 (5)	527 (11)	−474 (11)	−284 (9)
C	13039 (8)	15112 (7)	10154 (7)	531 (8)	448 (7)	347 (6)	530 (13)	39 (11)	74 (11)
N(2)	13129 (8)	15817 (8)	60565 (8)	468 (7)	438 (7)	377 (6)	299 (12)	−101 (11)	−142 (11)
H(1)	1029 (13)	2163 (12)	6214 (13)	185 (23)	48 (17)	137 (18)	−35 (31)	−239 (34)	−22 (29)
H(2)	1451 (13)	1251 (12)	6747 (13)	114 (19)	74 (18)	118 (18)	22 (29)	−122 (32)	−112 (29)
H(3)	2165 (14)	2083 (13)	5704 (10)	242 (24)	193 (22)	28 (12)	337 (40)	−125 (28)	−193 (27)

	α^*
Co(1)	0·854 (28)
Co(2)	0·746 (27)

* See text.

Atomic parameters obtained by special refinement (see text)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	0	0	0	339 (3)	339 (3)	250 (3)	339(3)	0	0
Co(2)	0	0	50000	311 (3)	311 (3)	248 (3)	311 (3)	0	0
N(1)	20600 (10)	24140 (8)	16634 (9)	924 (7)	508 (5)	608 (5)	487 (9)	−520 (10)	−329 (8)
C	13022 (17)	15062 (16)	10114 (14)	524 (10)	440 (9)	359 (7)	459 (15)	−45 (13)	−23 (12)
N(2)	13155 (15)	15842 (15)	60599 (14)	471 (9)	425 (8)	359 (7)	325 (13)	−64 (12)	−104 (11)
H(1)	975 (76)	2183 (47)	6256 (61)	263 (92)	92 (36)	142 (63)	−105 (96)	−218 (131)	−215 (88)
H(2)	1674 (96)	1112 (78)	6689 (105)	121 (78)	115 (54)	81 (89)	−92 (99)	61 (138)	75 (124)
H(3)	2191 (98)	2079 (86)	5698 (43)	415 (137)	269 (108)	17 (27)	550 (233)	−125 (108)	−187 (104)

Estimation of errors in the structure amplitudes

The possible errors in the observed structure amplitudes may be: (i) statistical fluctuation, (ii) instrumental errors and (iii) errors due to extinction and absorption effects. The first two can be suppressed to well below 2% if all the instruments are operated in good conditions. This can be ascertained from the variation of the standard reflexions and inter-experimental agreement factors between different sets of intensity data. The third effect can be evaluated from the intensities of symmetry related reflexions and also by measuring the intensity of a reflexion by rotating the crystal around the scattering vector. The variations of the intensities of symmetry-related reflexions seriously affected by extinction were 3·5% (110 in data set 1) and 0·5% (122 in data set 2). The intensity of the latter reflexion was found to change by about 2·5% under rotation by 360° about the scattering vector. However, these discrepancies among symmetry-related reflexions could be brought to coincide with each other within 1%, by applying an anisotropic extinction correction. Thus the errors in the observed structure amplitudes in the present investigation may be in the range 2·0~3·0% at most.

Determination and refinement of the structure

The general position of space group $R\bar{3}$ is eighteenfold. The two cobalt atoms of the complex cation and anion are required to lie on the special positions: (a) 000 and (b) 00½, since there are only three formula units in the unit cell. The site symmetry of the two cobalt atoms is $\bar{3}$. Since the shape and size of the two complex ions are well known (for example, Meek & Ibers, 1970; Muto, Marumo & Saito, 1970), the azimuthal orientation of both complex ions around the threefold axis could be easily determined by trial calculation of the structure amplitudes. The coordinates of all the atoms thus obtained, except those of hydrogen, were refined by a block-diagonal least-squares method, in which individual isotropic thermal parameters were used. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. In the calculation of the structure factors the atomic scattering factors tabulated in *International Tables for X-ray Crystallography* (1959) were used. Corrections for anomalous dispersion were also included. After six cycles the R value had been reduced to 0·065. The difference synthesis at this stage clearly revealed the positions of hydrogen atoms. After inclusion of the hydrogen atoms two further cycles of least-squares refinements were performed in anisotropic modes, but the thermal parameters of the hydrogen atoms were assumed to be isotropic. The R value decreased to 0·052. At this stage the isotropic extinction parameter g was introduced (Coppens & Hamilton, 1970). Positional and thermal parameters as well as the extinction parameter were refined for two cycles of full-matrix least-squares calculations, yielding values of 0·038 and 0·032 for R and R_2. Then g was converted into the six components G_{ij} of the tensor describing a three-dimensional Gaussian distribution of mosaic spread for a type I crystal. These components and usual structural parameters were refined. The isotropic g value was also converted to the six components of the tensor describing the ellipsoidal shape of an average mosaic particle which characterizes the anisotropic extinction in a type II crystal. Both types of refinement gave the same R and R_2 values of 0·038 and 0·030. The atomic parameters obtained agreed within their standard deviations. However, some G_{ij}'s for a type I crystal became non-positive definite after two cycles. The structure was then refined by using the expression $\alpha f_{Co} + (1-\alpha) f_{Co^{3+}}$ for the scattering factor of the cobalt atoms, the α's being included as unknown parameters. The atomic parameters as well as the R value did not change in this refinement. The final type II refinement based on data set 1 with 1648 selected reflexions reduced R and R_2 to 0·035 and 0·027, respectively. The positional and thermal parameters were then refined on the basis of data set 2. In this refinement the anisotropic extinction parameters in a type II crystal were introduced.

Fig. 2. Number of electrons in a sphere of radius R.
———————— Observed value for [Co(NH₃)₆]³⁺.
---------- Calculated value for [Co(NH₃)₆]³⁺.
— — — — — Observed value for [Co(CN)₆]³⁻.

Table 4. *Extinction parameters for the specimen used to collect data set 2*

	Anisotropic crystal type II
G_{11}	122 (13)
G_{22}	233 (31)
G_{33}	1318 (190)
G_{12}	−48 (21)
G_{13}	296 (50)
G_{23}	85 (77)

The values of G_{ij} have been multiplied by 10^4.

After two cycles the R and R_2 values became 0·029 and 0·021, respectively. Then all the atoms were refined by two further cycles of full-matrix least-squares calculations. The final R and R_2 values are 0·028 and 0·019 for the 2205 independent reflexions. The positional and thermal parameters and the values of α are listed in Table 3. The positional parameters agreed with those based on data set 1 to within 3σ and the thermal

Table 5. *Observed and calculated structure amplitudes* ($\times 10$)

Table 5 (*cont.*)

H	K	L	FO	FC
4	-18	10	117	123
7	-18	10	98	108
10	-18	10	112	124
13	-18	10	152	154
16	-18	10	145	154
22	-18	10	105	113
25	-18	10	66	53
2	-17	10	141	148
5	-17	10	138	142
8	-17	10	85	96
11	-17	10	110	134
14	-17	10	100	108
17	-17	10	109	121
20	-17	10	113	113
23	-17	10	84	85
3	-16	10	257	255
6	-16	10	147	148
9	-16	10	184	194
12	-16	10	110	118
15	-16	10	104	103
18	-16	10	80	96
1	-15	10	255	255
4	-15	10	277	281
7	-15	10	209	203
10	-15	10	318	321
13	-15	10	115	120
16	-15	10	157	154
19	-15	10	85	79
22	-15	10	79	76
2	-14	10	310	311
5	-14	10	197	200
8	-14	10	405	409
11	-14	10	232	229
14	-14	10	235	235
17	-14	10	181	[illegible]
23	-14	10	53	[illegible]
3	-13	10	234	245
6	-13	10	252	261
9	-13	10	352	366
12	-13	10	217	217
15	-13	10	299	304
18	-13	10	133	131
21	-13	10	173	134
24	-13	10	62	68
1	-12	10	252	261
4	-12	10	210	223
7	-12	10	325	346
10	-12	10	229	225
13	-12	10	268	270
16	-12	10	253	242
19	-12	10	247	228
22	-12	10	134	136
2	-11	10	239	241
5	-11	10	347	342
8	-11	10	289	302
11	-11	10	204	213
14	-11	10	279	292
17	-11	10	139	134
20	-11	10	168	167
3	-10	10	399	401
6	-10	10	210	206
9	-10	10	340	346
12	-10	10	252	255
15	-10	10	127	140
18	-10	10	142	145
24	-10	10	75	63
1	-9	10	403	399
4	-9	10	321	319
7	-9	10	287	295
10	-9	10	292	288
13	-9	10	222	216
16	-9	10	189	189
19	-9	10	122	131
22	-9	10	96	91
25	-9	10	61	62
2	-8	10	639	638
5	-8	10	209	203
8	-8	10	465	470
11	-8	10	210	214
14	-8	10	197	196
17	-8	10	167	160
20	-8	10	110	112
3	-7	10	511	504
6	-7	10	474	478
9	-7	10	501	497
12	-7	10	157	159
15	-7	10	286	281
18	-7	10	89	90
21	-7	10	98	107
1	-6	10	677	665
4	-6	10	552	554
7	-6	10	778	781
10	-6	10	295	294
13	-6	10	380	367
16	-6	10	193	192
19	-6	10	169	162
22	-6	10	83	95
2	-5	10	480	479
5	-5	10	549	530
8	-5	10	672	667
11	-5	10	345	332
14	-5	10	377	377
17	-5	10	131	132
20	-5	10	155	151
3	-4	10	415	412
6	-4	10	548	534
9	-4	10	255	275
12	-4	10	431	433
15	-4	10	252	247
18	-4	10	144	146
21	-4	10	136	126
1	-3	10	500	496
4	-3	10	379	369
7	-3	10	328	321
10	-3	10	305	295
13	-3	10	270	243
16	-3	10	158	157
19	-3	10	170	165
2	-2	10	694	695
5	-2	10	268	249
8	-2	10	414	409
11	-2	10	205	200
14	-2	10	182	198
17	-2	10	140	129
20	-2	10	110	107
3	-1	10	652	651
6	-1	10	472	468
9	-1	10	331	323
12	-1	10	194	189
15	-1	10	167	162
18	-1	10	81	102
21	-1	10	75	68
1	0	10	942	936
4	0	10	330	314
7	0	10	774	771
10	0	10	192	195
13	0	10	226	228
16	0	10	130	134
19	0	10	61	83
22	0	10	67	57
6	-14	11	49	19
12	-14	11	54	27
4	-13	11	63	73
7	-13	11	48	3
2	-12	11	50	38
5	-12	11	57	38
8	-12	11	70	79
14	-12	11	40	9
6	-11	11	45	61
12	-11	11	22	72
15	-11	11	58	43
1	-10	11	58	60
10	-10	11	58	42
13	-10	11	50	26
16	-10	11	52	43
2	-9	11	54	44
5	-9	11	49	25
8	-9	11	56	52
3	-8	11	68	42
6	-8	11	22	12
7	-7	11	61	57
22	-7	11	48	8
14	-6	11	58	7
20	-6	11	48	9
9	-5	11	52	17
12	-5	11	49	24
2	-3	11	186	179
3	-2	11	52	49
6	-2	11	142	120
12	-2	11	45	5
1	-1	11	46	46
4	-1	11	36	37
7	-1	11	53	49
10	-1	11	49	49
2	0	11	37	41
5	0	11	45	41
6	-24	12	42	43
12	-24	12	[illegible]	70
15	-24	12	46	45
18	-24	12	73	71
4	-23	12	58	[illegible]
7	-23	12	46	54
19	-23	12	74	63
2	-22	12	60	67
4	-22	12	74	76
[illegible]	-21	12	66	74
[illegible]	-21	12	[illegible]	102
[illegible]	-21	12	76	87
21	-21	12	48	53
1	-20	12		[illegible]
4	-20	12	117	118
7	-20	12	148	124
10	-20	12	98	103
13	-20	12	95	112
16	-20	12	92	84
19	-20	12	79	70
22	-20	12	62	62
5	-19	12	161	163
8	-19	12	130	123
11	-19	12	102	159
14	-19	12	121	118
17	-19	12	101	96
20	-19	12	71	76
3	-18	12	124	132
6	-18	12	140	147
9	-18	12	137	140
12	-18	12	194	202
15	-18	12	104	118
18	-18	12	120	126
21	-18	12	79	74
24	-18	12	55	58
1	-17	12	73	77
4	-17	12	135	142
7	-17	12	61	74
10	-17	12	172	212
13	-17	12	132	153
16	-17	12	[illegible]	155
19	-17	12	142	127
22	-17	12	77	75
2	-16	12	129	132
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10	0	16	266	269
13	0	16	[illegible]	[illegible]
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19	0	16	[illegible]	[illegible]
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15	-12	18	138	134
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9	-9	18	[illegible]	[illegible]
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13	-5	18	[illegible]	154
16	-5	18	[illegible]	97
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12	-3	18	[illegible]	159
15	-3	18	[illegible]	75
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10	-2	18	[illegible]	[illegible]
13	-2	18	104	[illegible]
16	-2	18	[illegible]	[illegible]
2	-1	18	255	[illegible]
5	-1	18	233	[illegible]
8	-1	18	[illegible]	[illegible]
11	-1	18	[illegible]	[illegible]
14	-1	18	[illegible]	[illegible]
0	0	18	342	[illegible]
3	0	18	[illegible]	[illegible]
6	0	18	231	[illegible]
9	0	18	[illegible]	[illegible]
12	0	18	[illegible]	[illegible]
15	0	18	[illegible]	[illegible]
18	0	18	[illegible]	63
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	-17	20	56	[illegible]
[illegible]	-17	20	[illegible]	92
1	-16	20	[illegible]	[illegible]
4	-16	20	[illegible]	81
7	-16	20	[illegible]	57
[illegible]	-16	20	[illegible]	[illegible]
14	-16	20	57	59
2	-15	20	[illegible]	48
5	-15	20	66	67
11	-15	20	[illegible]	[illegible]
17	-15	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
[illegible]	[illegible]	20	[illegible]	[illegible]
1	-13	20	103	104
4	-13	20	[illegible]	105
7	-13	20	[illegible]	129
13	-13	20	92	95
16	-13	20	75	82
2	-12	20	105	98
8	-12	20	[illegible]	139
14	-12	20	[illegible]	[illegible]
17	-12	20	[illegible]	56
3	-11	20	[illegible]	106
6	-11	20	86	[illegible]
9	-11	20	95	[illegible]
12	-11	20	[illegible]	[illegible]
15	-11	20	106	98
18	-11	20	[illegible]	61
4	-10	20	[illegible]	[illegible]
7	-10	20	56	[illegible]
10	-10	20	118	[illegible]
13	-10	20	88	[illegible]
16	-10	20	[illegible]	[illegible]
19	-10	20	56	[illegible]
2	-9	20	[illegible]	[illegible]
5	-9	20	[illegible]	[illegible]
8	-9	20	[illegible]	[illegible]
[illegible]	-9	20	[illegible]	[illegible]
17	-9	20	[illegible]	[illegible]
3	-8	20	[illegible]	[illegible]
6	-8	20	[illegible]	[illegible]
9	-8	20	147	145
15	-8	20	[illegible]	64
18	-8	20	52	52
1	-7	20	213	211
4	-7	20	126	121
7	-7	20	189	200
10	-7	20	119	112
13	-7	20	88	90
2	-6	20	168	164
5	-6	20	165	161
8	-6	20	181	[illegible]
11	-6	20	106	99
14	-6	20	132	126
3	-5	20	149	140
5	-5	20	140	167
6	-5	20	183	187
9	-5	20	137	136
12	-5	20	123	121
15	-5	20	101	102
18	-5	20	62	54
1	-4	20	141	139
4	-4	20	147	146
7	-4	20	152	149
10	-4	20	[illegible]	[illegible]
13	-4	20	130	129
2	-3	20	195	190
5	-3	20	104	109
8	-3	20	130	129
11	-3	20	113	114
17	-3	20	71	65
3	-2	20	[illegible]	130
6	-2	20	111	121
9	-2	20	141	125
15	-2	20	83	77
1	-1	20	222	[illegible]
4	-1	20	81	99
7	-1	20	154	155
10	-1	20	101	89
13	-1	20	81	91
16	-1	20	50	59
2	0	20	164	[illegible]
5	0	20	144	143
8	0	20	162	154
14	0	20	94	91
10	-11	21	47	8
6	-16	22	[illegible]	47
9	-16	22	[illegible]	60
12	-16	22	43	49
4	-15	22	56	58
7	-15	22	58	54
10	-15	22	65	64
2	-14	22	[illegible]	[illegible]
5	-14	22	84	74
8	-14	22	64	69
11	-14	22	67	59
[illegible]	-14	22	[illegible]	[illegible]
3	-13	22	46	52
6	-13	22	79	85
9	-13	22	61	68
12	-13	22	63	71
15	-13	22	62	56
1	-12	22	77	70
4	-12	22	125	116
7	-12	22	88	77
10	-12	22	41	[illegible]
13	-12	22	64	68
2	-11	22	100	99
5	-11	22	115	109
8	-11	22	85	89
11	-11	22	93	107
14	-11	22	67	62
3	-10	22	121	112
6	-10	22	95	70
9	-10	22	117	123
[illegible]	[illegible]	22	62	80
[illegible]	[illegible]	22	81	72
[illegible]	[illegible]	22	[illegible]	82
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	22	[illegible]	101
[illegible]	[illegible]	[illegible]	[illegible]	63
[illegible]	-9	22	[illegible]	80
2	-8	22	[illegible]	91
5	-8	22	[illegible]	[illegible]
8	-8	22	[illegible]	[illegible]
11	-8	22	[illegible]	67
3	-7	22	107	104
6	-7	22	90	97
9	-7	22	106	86
15	-7	22	61	[illegible]
1	-6	22	107	[illegible]
4	-6	22	[illegible]	[illegible]
7	-6	22	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	-5	22	165	[illegible]
[illegible]	-5	22	125	[illegible]
8	-5	22	120	[illegible]
[illegible]	-5	22	117	[illegible]
3	-4	22	178	[illegible]
6	-4	22	[illegible]	[illegible]
9	-4	22	[illegible]	[illegible]
12	-4	22	85	[illegible]
15	-4	22	64	[illegible]
1	-3	22	137	[illegible]
4	-3	22	114	106
7	-3	22	117	[illegible]
10	-3	22	127	123
13	-3	22	[illegible]	64
2	-2	22	125	131
5	-2	22	72	74
8	-2	22	123	136
11	-2	22	73	65
14	-2	22	96	80
3	-1	22	106	103
6	-1	22	94	98
9	-1	22	97	93
12	-1	22	73	64
[illegible]	0	22	105	[illegible]
4	0	22	[illegible]	[illegible]
7	0	22	121	120
[illegible]	-15	23	38	[illegible]
[illegible]	[illegible]	23	60	[illegible]
4	-7	23	55	[illegible]
14	-3	23	67	[illegible]
4	-1	23	[illegible]	[illegible]
2	0	23	48	[illegible]
5	-13	24	51	[illegible]
3	-12	24	65	69
9	-12	24	55	55
1	-11	24	75	72
4	-11	24	70	77
7	-11	24	60	[illegible]
10	-11	24	71	[illegible]
2	-10	24	80	76
5	-10	24	87	64
8	-10	24	87	80
11	-10	24	58	74
3	-9	24	54	67
6	-9	24	53	44
9	-9	24	[illegible]	75
12	-9	24	75	58
1	-8	24	92	98
4	-8	24	94	85
7	-8	24	69	72
10	-8	24	50	73
2	-7	24	50	55
5	-7	24	90	88
11	-7	24	90	76
[illegible]	-6	24	89	97
6	-6	24	55	61
9	-6	24	64	63
12	-6	24	67	65
1	-5	24	101	97
4	-5	24	106	105
10	-5	24	84	84
2	-4	24	119	113
5	-4	24	100	95
8	-4	24	95	87
11	-4	24	64	68
3	-3	24	118	107
6	-3	24	93	93
9	-3	24	95	96
12	-3	24	76	56
[illegible]	-2	24	96	80
4	-2	24	110	104
7	-2	24	92	93
10	-2	24	61	75
2	-1	24	[illegible]	81
5	-1	24	107	100
8	-1	24	84	69
11	-1	24	77	74
0	0	24	79	[illegible]
3	0	24	107	105
9	0	24	76	73
6	-7	25	53	5
3	-5	26	40	50
1	-4	26	72	66
4	-4	26	38	61
2	-3	26	69	61
3	-2	26	87	78
1	-1	26	62	63
[illegible]	0	26	82	72

parameters were smaller by $1\sigma \sim 5\sigma$ than those based on data set 1. The values of G_{ij} are given in Table 4. These values are about 20 times larger than those for data set 1. The values of y $(\equiv F_o^2/F_c^2)$ for the worst extinction are 0·72 and 0·91 for data sets 1 and 2, respectively. The crystal used for collecting data set 2 was much less affected by extinction than that for data set 1. The observed and calculated structure amplitudes are compared in Table 5.

Special refinement of the atomic coordinates

The atomic coordinates were refined by using 800 high-order reflexions with $1{\cdot}0 \geq \sin\theta/\lambda \geq 0{\cdot}6$, in an attempt to reduce the effect of asphericity of the electron clouds. The interatomic distances and bond angles based on the coordinates thus obtained are listed in the third column of Table 6.

Description of the structure and discussion

The crystal structure contains discrete $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ ions. They are arranged in much the same way as the ions in caesium chloride. A packing diagram is shown in Fig. 1. This agrees with the result

Table 6. *Interatomic distances and bond angles*

All values are corrected for thermal vibrations.

Co(1)–C	1·900 (1) Å	1·894 (1)* Å
Co(2)–N(2)	1·968 (1)	1·972 (1)
C——N(1)	1·146 (1)	1·157 (2)
N(2)—H(1)	0·85 (2)	0·93 (8)
N(2)—H(2)	0·88 (2)	1·04 (12)
N(2)—H(3)	0·90 (1)	0·92 (8)
C——Co–C't	90·10 (3)°	90·25 (6)°
N(2)—Co–N'(2)	89·84 (3)	89·78 (5)
Co(1)–C—N(1)	177·88 (5)	177·43 (9)
Co(2)–N(2)–H(1)	113·2 (7)	112 (4)
Co(2)–N(2)–H(2)	109·4 (9)	103 (5)
Co(2)–N(2)–H(3)	111·9 (8)	111 (5)
H(1)–N(2)–H(2)	110 (1)	126 (7)
H(1)–N(2)–H(3)	107 (1)	110 (7)
H(2)–N(2)–H(3)	106 (1)	91 (8)
H(1)···H(2)	1·41 (2) Å	1·75 (14) Å
H(1)···H(3)	1·40 (2)	1·52 (14)
H(2)···H(3)	1·41 (2)	1·41 (12)

N–H···N hydrogen bond

N(2)···N(1)	3·006 (2) Å
H(3)···N(1)	2·12 (2)
N(2)–H(3)–N(1)	170 (1)°

* Based on high-angle data.

† Atoms with a prime are related by a threefold axis of rotation.

previously reported by Hassel & Salvesen (1927). Interatomic distances and bond angles in both complex ions based on the final set of coordinates are listed in Table 6, together with their estimated standard deviations. In the last column of the Table are shown those interatomic distances and bond angles based on the set of coordinates obtained from the high-angle reflexions. The site symmetry of both complex ions is $\bar{3}$. The coordination geometry around the cobalt atoms in both complex ions is very close to octahedral, as can be discerned from the data listed in Table 6. The complex cations and anions are linked by a weak N–H···N hydrogen bond of 3·006 (2) Å as shown in Fig. 1 by broken lines. Details of this hydrogen bond are also included in Table 6.

The N(2)···N(1) distances are 3·144 (2), 3·251 (2) and 3·298 (2) Å and N···H–N angles are in the range 124~170°. Generally speaking, the interatomic distances based on the high-angle data seem to give more reasonable values, free from the asphericity of the electron clouds, except for the bonds involving hydrogen atoms. The Co–N bond distance is 1·972 (1) Å and is in agreement with the values 1·968 (11), 1·968 (10), 1·968 (8) and 1·960 (6) Å in [Co(NH$_3$)$_6$] [ZnCl$_4$]Cl (Meek & Ibers, 1970), [CoCl(NH$_3$)$_5$]Cl$_2$ (Messmer & Amma, 1968), [Co(NH$_3$)$_5$N$_3$] (N$_3$)$_2$ (Palenik, 1964) and [Co(NH$_3$)$_6$] [CdCl$_5$] (Long, Herlinger, Epstein & Bernal, 1970), respectively. The Co–C distance of 1·894 Å (1) in [Co(CN)$_6$]$^{3-}$ may be compared with that of 1·89 Å and 1·883 (9) Å from neutron diffraction studies of K$_3$[Co(CN)$_6$] (Kohn & Townes, 1961) and D$_3$[Co(CN)$_6$] (Güdel, Ludi, Fischer & Hälg, 1970). It also agrees

with those observed in other structures containing [Co(CN)$_6$]$^{3+}$ (for example, Muto, Marumo & Saito, 1970; Konno, Marumo & Saito, 1973; Haser, de Broin & Pierrot, 1972). The C–N distance of 1·157 (2) Å may be compared with the value of 1·156 (4) Å obtained from the mean value of ten independent C–N distances in the [Ni(CN)$_5$]$^{3-}$ salt (Raymond, Corfield & Ibers, 1968) and with the value 1·154 (4) Å in H$_3$[Co(CN)$_6$] (Haser *et al.*, 1972). As can be seen from Table 6, all the interatomic distances except Co–C, based on high-angle data increased in length, while Co–C decreased. The shortening of the Co–N bond by 0·004 Å, based on the complete set of intensity data, could be caused by a shift of the lone pair electrons of the ammonia molecule towards the cobalt atom. Three N–H distances increased consider-
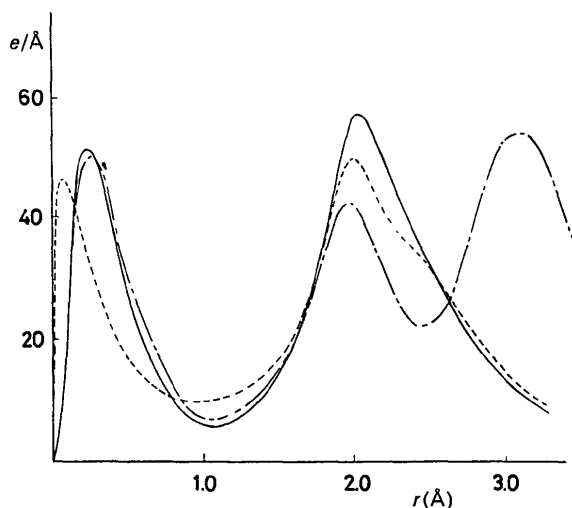
Fig. 3. Radial distribution of electron density in the complex ions:
——————— Observed value for [Co(NH$_3$)$_6$]$^{3+}$.
– – – – – – – Calculated value for [Co(NH$_3$)$_6$]$^{3+}$.
—–—–—– Observed value for [Co(CN)$_6$]$^{3-}$.
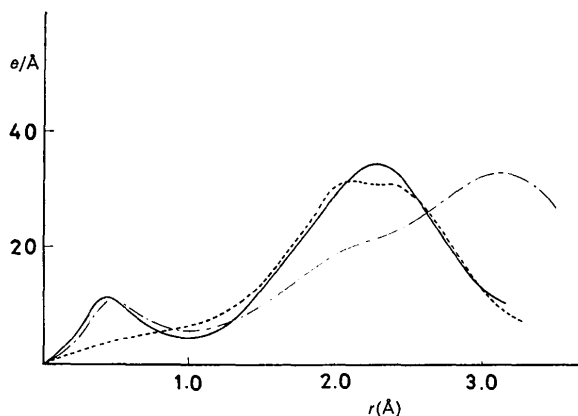
Fig. 4. Radial density of valence electrons in the complex ions.
——————— Observed value for [Co(NH$_3$)$_6$]$^{3+}$.
– – – – – – – Calculated value for [Co(NH$_3$)$_6$]$^{3+}$.
—–—–—– Observed value for [Co(CN)$_6$]$^{3-}$.

ably and came closer to the value of 1·005 (23) Å determined by neutron diffraction (Reed & Harris, 1961). However, trigonal symmetry of the NH_3 molecule was considerably disturbed. This is certainly due to the smaller contribution of hydrogen atoms to the high-angle reflexions. In the Co–C–N group, the increase in the CoC distance of 0·006 Å, based on the complete data set, appears to be due to an accumulation of electron density between the carbon and nitrogen atoms.

Thermal parameters

Since both complex ions (disregarding the hydrogen atoms) were expected to behave as a rigid body a least-squares analysis (Cruickshank, 1956) was carried out to obtain two tensors to describe the translational

Table 7. *Molecular vibrational tensors*

$[Co(NH_3)_6]^{3+}$

R.m.s. amplitude of translational motion	Components of principal axes with respect to the crystal axes ($\times 10^4$)		
0·118 Å	1021	274	0
0·118	274	1021	0
0·120	0	0	929
R.m.s. amplitude of librational motion			
2·99°	−34	−931	−46
3·02	−1056	−500	34
3·61	37	−28	927

$[Co(CN)_6]^{3-}$

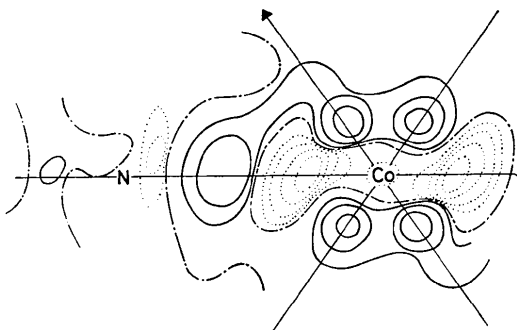| R.m.s. amplitude of translational motion			
0·122 Å	−57	−368	861
0·126	−1053	−570	−66
0·127	78	−808	−345
R.m.s. amplitude of librational motion			
2·87°	−154	−620	736
3·02	−1045	−474	−131
3·22	45	−713	−552

Fig. 5. Section of final difference Fourier synthesis through a Co–N bond and a threefold axis. An arrow indicates the threefold axis. The solid contours are at intervals of 0·1 $eÅ^{-3}$. Negative contours are dotted, zero being chain-dotted.

vibration and libration of the rigid body. The coordinates of the centre of vibration were fixed at the cobalt atoms. The results are given in Tables 7 and 8. Inclusion of the hydrogen atoms did not alter the result greatly. The rigid-body motions are similar in the two complex ions and are strikingly isotropic. The results based on the high-angle data are not very different from those based on all the data, except for an increase in some vibrational amplitudes by about a few per cent.

Number of electrons around the cobalt atom

An attempt was made to estimate the number of electrons around the central cobalt atom by direct integration of the electron density. The electron density at a point r in the unit cell is given by

$$\varrho(\mathbf{r}) = 1/V \sum \sum \sum F(hkl) \exp[-2\pi i(\mathbf{S}.\mathbf{r})] \quad (1)$$

where

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* .$$

Let $C(R)$ be the number of electrons in a sphere of radius R with its centre at r. This can be obtained by integrating equation (1) (Sakurai, 1967):

$$C(R) = 1/V\{4\pi/3 R^3 F(000)$$
$$+ \tfrac{1}{2}\pi^2 \sum \sum \sum 1/S^3 F(hkl) \exp[-2\pi i(\mathbf{S}.\mathbf{r})]$$
$$\times(-2\pi SR \cos 2\pi SR + \sin 2\pi SR)\} . \quad (2)$$

$C(R)$ was calculated according to equation (2) by using the observed $F(hkl)$'s for which the effects of anomalous dispersion were corrected. The termination effect in the Fourier series was corrected as described in the previous paper (Kobayashi, Marumo & Saito, 1972). The correction was about one half of the standard deviations. $C(R)$ for $[Co(NH_3)_6]^{3+}$ gives rise to the full line in Fig. 2. The dotted line is the calculated value obtained by means of the Thomas–Fermi method (Kamimura, Koide, Sugano & Tanabe, 1958). The original result was modified by taking an isotropic temperature factor of 1·2 $Å^2$ into account. The agreement is very good. $C(R)$ for $[Co(CN)_6]^{3-}$ is also presented in Fig. 2. The number of electrons around the cobalt atom in $[Co(NH_3)_6]^{3+}$ in a sphere of radius 1·22 Å (covalent radius of cobalt) is 26·3 ± 0·3 e. The error in the number of electrons was estimated from the error in the observed electron density distribution (Cruickshank & Rollett, 1953) and the latter is 0·06 $eÅ^{-3}$ in the general positions.

In Table 9 the numbers of electrons determined from $C(R)$ for the two complex ions and from the values of α obtained at the final stage of the refinement are compared with the calculated values. The number of electrons around the cobalt atom in the complex ion, $[Co(NH_3)_6]^{3+}$, is in good agreement with the calculated values (Kalman & Richardson, 1971). This result shows that the cobalt atom has a largely neutralized resultant charge by donation of electrons from the six ligand atoms. The positive charge is mainly distributed

on the eighteen hydrogen atoms of the six ammonia molecules. In fact, a final difference synthesis indicated the deficiency of electrons around each hydrogen atom. One hydrogen atom is bonded to the nitrogen atom of the cyano group of the complex anion. Likewise, the negative charge on $[Co(CN)_6]^{3-}$ is distributed on the six cyano groups and the metal atom is almost neutralized. The mean resultant charge on the cobalt atom is $26\cdot7 \pm 0\cdot3$ e. A recent electron population analysis for [N,N'-di-(2-aminomethyl)malondiamidato]nickel-(II) trihydrate has shown that the nickel atom has a small positive charge of about 0·5 (Coppens, Paulter & Griffin, 1971). This is in excellent agreement with the present result. These results indeed verify Pauling's electroneutrality principle (Pauling, 1960).

In Fig. 3 the observed radial distribution of electron density of $[Co(NH_3)_6]^{3+}$ is compared with that calculated by Kamimura *et al.* (1958). They agree qualitatively except for the inner region. The observed radial distribution for $[Co(CN)_6]^{3-}$ is also presented in Fig. 3. Fig. 4 shows the radial density of valence electrons in both complex ions together with the calculated value for the complex cation. These curves were calculated from the observed radial electron density by subtracting the contribution of the inner shell electrons. Mean scattering factors of the inner shell electrons were those listed in Fukamachi's (1971) Table. A small peak which appeared at about 0·5 Å from the cobalt atom apparently corresponds to the one due to $3d^6$ electrons in the t_{2g} orbitals. A similar peak with a half peak height was also observed for $[Cr(CN)_6]^{3-}$ ($3d^3$) in $[Co(NH_3)_6]$ $[Cr(CN)_6]$ (Iwata & Saito, 1972). This will be discussed in the next section.

Residual electron density

At the final stage of refinement a three-dimensional difference synthesis with all the atoms included was calculated in order to detect any asphericity of electron density distribution due to bond formation. The atomic coordinates based on high-angle reflexions

were used in this calculation. $\sigma(\varrho)$ was reduced to $0\cdot06$ e Å^{-3} at the final stage. Fig. 5 shows a section containing a threefold axis and a Co-N bond of the complex ion $[Co(NH_3)_6]^{3+}$. A maximum appears between the cobalt and nitrogen atoms, while there are minima on either side of the bond. The height of the positive region between the cobalt and nitrogen atoms is approximately $0\cdot30$ e Å^{-3} and the minima range from $-0\cdot20$ to $-0\cdot40$ e Å^{-3}. This arrangement of maximum and minima suggests that the electron density has moved to the centre of bond due to donation of the lone pair electrons from an ammonia molecule. The four maxima around the cobalt atom will be discussed below. The corresponding section of the difference synthesis for $[Co(CN)_6]^{3-}$ is presented in Fig. 6.

The arrangement of the maxima and minima is much the same as that observed for the $[Co(NH_3)_6]^{3+}$ ion. However, the residual electron densities between Co and C and between C and N are much more elongated perpendicularly to the bonds, than is observed for Co-N bond. The difference Fourier sections bisecting the bonds are presented in Fig. 7. We are inclined to ascribe the elongations to d_π–p_π and p_π–p_π
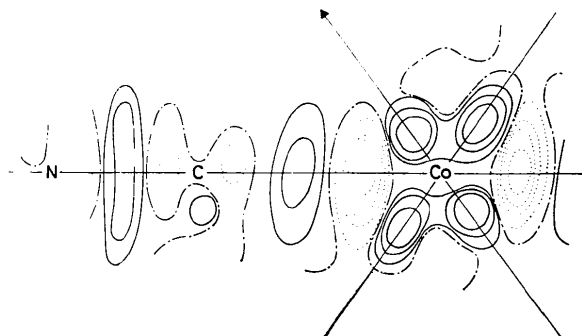

Fig. 6. Section of final difference Fourier synthesis through a Co-C-N bond and a threefold axis. An arrow indicates the threefold axis. The scale is the same as in Fig. 5.

Table 8. *Observed and calculated tensor elements of thermal vibration,* $U_{ij}(\text{Å}^2 \times 10^4)$

	Co(2)		N(2)		Co(1)		N(1)		C	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
U_{11}	137	139	182	177	153	157	294	250	228	192
U_{22}	137	139	275	273	153	159	402	396	205	252
U_{33}	141	145	221	215	145	151	347	328	203	221
U_{12}	0	0	8	17	0	-1	100	11	22	4
U_{13}	0	0	-36	-50	0	2	-133	-123	16	-46
U_{23}	0	0	11	7	0	-3	-49	25	-9	7

Table 9. *Number of electrons around the cobalt atom*

	Direct integration of electron density	Least-squares fitting of scattering factor curves	Calculated values Kalman & Richardson (1971)	Kamimura *et al.* (1958)
$[Co(NH_3)_6]^{3+}$	$26\cdot3 \pm 0\cdot3$*	$26\cdot2 \pm 0\cdot1$	$26\cdot4$	$25\cdot9$*
$[Co(CN)_6]^{3-}$	$26\cdot8 \pm 0\cdot3$*	$26\cdot6 \pm 0\cdot1$	–	–

* Within a sphere of radius 1·22 Å.

overlap respectively. Similar features in the C–N bond have been observed in the residual electron density maps of 1,2,4,5-tetracyanobenzene complexes (Tsuchiya, Marumo & Saito, 1972, 1973) and of tetracyanoethylene oxide (Mathiews & Stucky, 1971).

Another interesting feature is observed in the section through C, N(1) and N(3), shown in Fig. 8. A small peak indicated as A lies at 0·75 Å from N(1) and is slightly off the line through the C–N(1) bond. Though not significant this small peak appears to be due to the localized nitrogen lone pair directed towards H(3). A well defined maximum is observed on the threefold axis of the complex ions at 0·45 Å from the cobalt atom. Similar peaks are observed in all the chemically equivalent directions at the same distance, which correspond to a peak in radial density of valence electrons (see Figs. 5 and 6). The peak height is 0·3 e Å^{-3}.

In all, eight peaks are arranged at the corners of a cube around the cobalt atom. It is interesting that the positions of these maximum densities apparently correspond to what is expected for six $3d$ electrons in t_{2g} orbitals (Weiss, 1966). The positions of the maximum density of $d^2_{xy}+d^2_{yz}+d^2_{xz}$ for a free cobalt atom lie at distances of 0·35 Å from the nucleus (Clementi, 1965). This distance generally increases when the atom is placed in an octahedral crystal field. For example, in NiO this distance becomes 0·6 Å (Watson & Freeman, 1960). Shull & Yamada (1962) showed that the maxima due to $3d$ electrons are located at 0·5 Å from the nucleus in Fe (by neutron diffraction), in agreement with the calculated value of 0·4 Å (Weiss & Freeman, 1959). The contribution of the $3d$ electrons, though small, would be appreciable to $(|F_o|-|F_c|)$ (not to $|F_o|$). These considerations lead us to suspect that these

eight peaks are an indication of $3d$ electrons in the t_{2g} orbitals of cobalt. However, this point must be more carefully examined with reference to other cobalt(III) complexes.

Verschoor & Keulen (1971) showed that restriction of the reflexions to the copper sphere caused the residual electron density to diminish drastically. This is certainly true because the inclusion of higher order reflexions will improve the resolution of Fourier maps. On the other hand, bonding electrons as well as $3d$ electrons in t_{2g} orbitals, will contribute more to lower order reflexions than to higher order reflexions. It was thought worth while to see whether omission of those reflexions having sin $\theta \geq 0·62$ Å^{-1} would cause the general features of the final difference synthesis to be retained. Thus, two difference syntheses were calculated. In one, F_c's based on the atomic parameters obtained by using all the data were used (hereafter called D_1) and in the other F_c's based on the atomic coordinates obtained by special refinement were used (hereafter called D_2). When D_1 and D_2 were compared with the final difference synthesis, all peaks but one due to bonding effects were found to be diminished to about one half in peak heights and to be shifted by about 0·1 Å. General features were, however, retained. Only one peak between Co(2) and N(2) disappeared in D_1 but it appeared in D_2 with a peak height of 0·13 e Å^{-3}, peak position being shifted by 0·15 Å towards N(2). The eight peaks around the cobalt atoms still appeared in D_1 and D_2 with one exception. A peak on the threefold axis of Co(1) disappeared in D_2, although the corresponding peak was observed in D_1. All the peak heights were diminished to about one half and the positions were slightly shifted.
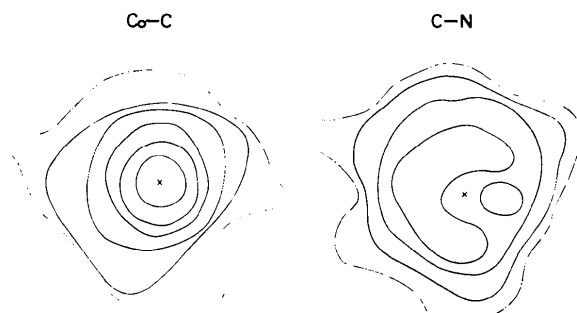
Fig. 7. Difference Fourier sections bisecting the bond. The contours are at intervals of 0·05 eÅ^{-3}.

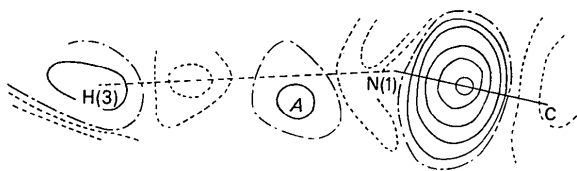Fig. 8. Section of difference Fourier synthesis through C, N(1) and H(3). The contours are at intervals of 0·05 eÅ^{-3}. Negative contours are broken, zero being chain-dotted.

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The Crystal Structure of Barium Diferrite

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A new barium ferrite, $BaO.2Fe_2O_3$, has been synthesized hydrothermally. It is hexagonal, space group $P6_3/m$, with lattice dimensions $a = 5.160$ and $c = 13.811$ Å; $Z = 2$. The structure has been determined by the heavy-atom method and refined by least-squares methods using the block-diagonal approximation to a final R of 0.08. The hexagonal unit cell consists of six layers of large ions. There are two successive layers of three oxygen ions, but the third layer contains only one oxygen ion and one barium ion. Thus an open space is formed at the third level. The basal plane containing the barium ion is a mirror plane of the structure. Ferric ions are distributed equally into two different sites: one surrounded tetrahedrally and the other octahedrally by oxygen ions.

Introduction

Because of the practical importance of $BaO.6Fe_2O_3$ as a permanent magnet (Went, Rathenau, Goter and van Oosterhaut, 1951, 1952), the system $BaO-Fe_2O_3$ has been investigated by many workers (Goto & Takada, 1960; Batti, 1960; van Hook, 1964). The phase diagram of this system contained $BaO.6Fe_2O_3$, $BaO.Fe_2O_3$ and $2BaO.Fe_2O_3(BaFeO_{2.5})$. Recently, a new metastable compound, $2BaO.3Fe_2O_3$, has been reported (Shirk, 1970). These compounds were synthesized by either powder reactions or flux techniques, mostly at temperatures higher than 700°C.

Barium hexaferrite, $BaO.6Fe_2O_3$, has the magnetoplumbite structure (hexagonal, $P6_3/mmc$) with cell dimensions $a = 5.888$ and $c = 23.22$ Å (Adelsköld, 1938). Barium monoferrite, $BaO.Fe_2O_3$, is orthorhombic with $a = 19.074$ Å, $b = 5.372$ Å and $c = 8.450$ Å, and has a