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**The Co(III)–N bond-length in relation to the Co(II)–N bond-length. The crystal structure of hexaamminecobalt(III) iodide [Co(NH<sub>3</sub>)<sub>6</sub>]I<sub>3</sub>\*.** By N. E. KIME and JAMES A. IBERS, *Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.*

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Hexaamminecobalt(III) iodide, [Co(NH<sub>3</sub>)<sub>6</sub>]I<sub>3</sub>, crystallizes in the (NH<sub>4</sub>)<sub>3</sub>FeF<sub>6</sub> structure type with four formula units in the cubic space group *Fm3m* with  $a = 10.82(2)$  Å. The atoms are in the following positions: Co in 4(*a*); I<sub>1</sub> in 4(*b*); I<sub>2</sub> in 8(*c*); N in 24(*e*) with  $x = 0.1789(14)$ ; H apparently disordered. The Co–N distance, uncorrected for the effects of thermal motion, is 1.936(15) Å, some 0.18 Å shorter than the corresponding distance in the Co(II) complex.

The lengths of the Co(II)–N and Co(III)–N bonds have often been quoted (Basolo & Pearson, 1960; Emeleus & Anderson, 1960) as 2.5 and 1.9 Å, respectively. These values are based on early structure determinations from powder samples (Biltz, 1927). This difference of 0.6 Å has been used to explain the slow rate of electron transfer reactions for Co(II)–Co(III) systems compared with other systems [*e.g.* Fe(II)–Fe(III)]. In an earlier report (Barnet, Craven, Freeman, Kime & Ibers, 1966) we showed that the Co(II)–N and Co(III)–N distances in the hexaamminecobalt complexes differ by only 0.16 Å. Here we document the structure determination of [Co(NH<sub>3</sub>)<sub>6</sub>]I<sub>3</sub>.

The iodide salt was chosen for this study since it is cubic with *m3m* site symmetry imposed on the hexaamminecobalt(III) cation, whereas the chloride and bromide salts were found to crystallize in the monoclinic system, with no symmetry conditions imposed on the cation. The chloride salt was prepared by the method of Bjerrum & McReynolds (1946). The iodide salt was prepared by passing the chloride salt through an anion exchange column with the iodide ion occupying the active sites. The salt was recrystallized from water. Analyses for [Co(NH<sub>3</sub>)<sub>6</sub>]I<sub>3</sub>: calculated: C, 0.0; H, 3.35; N, 15.51. Found: C, <0.3; H, 3.2; N, 15.45.

A series of precession photographs taken with Mo *K* $\alpha$  radiation ( $\lambda = 0.7107$  Å) at 25°C confirmed that the material crystallizes with four formula units in a cubic cell of edge 10.82(2) Å. Laue symmetry *m3m* and the observed extinctions (*hkl* absent for *h+k* odd or *k+l* odd) are compatible with space groups *Fm3m*, *F432* and *F43m*. The placement of 72 hydrogen atoms in ordered positions in any of these groups requires that 24 of these be in a special 24-fold position. All such 24-fold positions lead to impossible N–H distances. Since there are no violations of the space group extinctions on overexposed photographs, we conclude that the hydrogen atoms are not ordered in the structure. Conditions imposed on the anisotropic thermal vibrations of the nitrogen atom were used to distinguish between the possible space groups. For *Fm3m* and *F432* the aniso-

tropic temperature factor on the nitrogen atom is of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}(k^2 + l^2))]$  whereas in *F43m* the form is  $\exp[-\beta_{11}h^2 + \beta_{22}(k^2 + l^2) + 2\beta_{23}kl]$ . Refinement in space group *F43m* gives worse agreement with the data and a non-positive definite temperature factor for the nitrogen atom. For these reasons, and since the positions eventually assigned to Co, I, and N are the same special ones in all of these groups, we assign the material to the space group *O<sub>h</sub><sup>5</sup>–Fm3m*.

A spherical crystal of radius 0.085 mm was prepared by grinding. This crystal was mounted parallel to its [011] axis and eleven layers of data were collected at room temperature by the equi-inclination Weissenberg method. Intensities of 361 reflections were estimated visually against a calibrated intensity strip. After correction for Lorentz and polarization effects and for absorption (linear absorption coefficient for Mo *K* $\alpha$  is calculated to be 87.5 cm<sup>-1</sup>) the data were interscaled, by comparison of common reflections, to yield structure amplitudes for 105 independent reflections.

The structure was refined by standard least-squares procedures (The programs for the CDC 3400 used in this work include local modifications of Zalkin's *FORDAP*, and the Busing-Levy *ORFLS* and *ORFFE* programs.) In these calculations the function  $\sum w(|F_o| - |F_c|)^2$  was minimized where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and where the weights *w* were taken as  $I^2/4F_o^2$  for  $I < 20$  and as  $100/F_o^2$  for  $I \geq 20$  (*I* is the raw intensity). The atomic scattering factors for Co, I, and N were taken from the usual tabulation (Ibers, 1962), while those for hydrogen were taken from the calculations of Stewart, Davidson & Simpson (1965). The effects of anomalous dispersion were included in  $F_c$  (Ibers & Hamilton, 1964). The values of  $\Delta f'$  and  $\Delta f''$  for Co and I were those computed by Cromer (1965). A trial structure based on the earlier model (Biltz, 1927) converged rapidly. In this trial model Co is in position 4(*a*) 000; I<sub>1</sub> is in 4(*b*),  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ; I<sub>2</sub> is in 8(*c*),  $\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ; and N is in 24(*e*),  $x, 0, 0$  of *Fm3m*. Initial refinement without inclusion of the hydrogen atoms and with all atoms restricted to isotropic thermal motion converged to values of  $R_1$  and  $R_2$  of 6.7 and 8.5%, where  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and where the weighted *R* value or  $R_2$  is  $(\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$ . A difference-Fourier synthesis computed at

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Table 1. Final parameters for [Co(NH<sub>3</sub>)<sub>6</sub>]I<sub>3</sub>

	Position	Site symmetry	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	100 $\beta_{11}$ <sup>b</sup>	100 $\beta_{22}$
Co	4( <i>a</i> )	<i>m3m</i>	0	0	0	1.71 (9) <sup>a</sup>		
I <sub>1</sub>	4( <i>b</i> )	<i>m3m</i>	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.77 (7)		
I <sub>2</sub>	8( <i>c</i> )	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.69 (6)		
N	24( <i>e</i> )	<i>4mm</i>	0.1789 (14)	0	0		0.42 (13)	0.80 (10)

<sup>a</sup> The estimated standard deviation of the least significant digits is given in parentheses.

<sup>b</sup> The form of the thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}(k^2 + l^2))]$ .

this point provided no indication of localized positions for the hydrogen atoms, but did exhibit high electron density in the general region expected. Accordingly, the  $\text{NH}_3$  ligand was assumed to be rotating freely around the Co-N bond and the appropriate contributions of the hydrogen atoms to the structure factors were computed (Zachariasen, 1945). In this calculation the following quantities were assumed:  $\text{N-H} = 1.008 \text{ \AA}$ ;  $\text{Co-N-H angle} = 109.5^\circ$ ;  $\text{B(H)} = 3.5 \text{ \AA}^2$ . Inclusion of these contributions reduced  $R_1$  and  $R_2$  to 6.5 and 8.2%. In a final calculation the nitrogen atom was permitted to vibrate anisotropically. (The Co and I atoms are restricted by symmetry to isotropic vibrations.) This calculation converged to the values of  $R_1$  and  $R_2$  of 6.3 and 8.0% and to the parameters listed in Table 1. Table 2 lists the final values of  $|F_o|$  and  $|F_c|$  in electrons.

Table 2. Observed and calculated structure amplitudes for  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$

K	L	PO	FO	FC	K	L	PO	FC	K	L	PO	FC	K	L	PO	FC
0	0	1058	1058	1058	0	0	1058	1058	0	0	1058	1058	0	0	1058	1058
0	8	715	684	684	0	8	715	684	0	8	715	684	0	8	715	684
0	16	169	154	154	0	16	169	154	0	16	169	154	0	16	169	154
0	24	85	75	75	0	24	85	75	0	24	85	75	0	24	85	75
2	8	880	880	880	2	8	880	880	2	8	880	880	2	8	880	880
2	16	470	465	465	2	16	470	465	2	16	470	465	2	16	470	465
2	24	211	204	204	2	24	211	204	2	24	211	204	2	24	211	204
2	32	100	95	95	2	32	100	95	2	32	100	95	2	32	100	95
4	8	816	828	828	4	8	816	828	4	8	816	828	4	8	816	828
4	16	406	400	400	4	16	406	400	4	16	406	400	4	16	406	400
4	24	202	201	201	4	24	202	201	4	24	202	201	4	24	202	201
4	32	101	100	100	4	32	101	100	4	32	101	100	4	32	101	100
6	8	628	608	608	6	8	628	608	6	8	628	608	6	8	628	608
6	16	314	304	304	6	16	314	304	6	16	314	304	6	16	314	304
6	24	157	154	154	6	24	157	154	6	24	157	154	6	24	157	154
6	32	78	75	75	6	32	78	75	6	32	78	75	6	32	78	75
8	8	514	514	514	8	8	514	514	8	8	514	514	8	8	514	514

It is interesting that no evidence for localized hydrogen positions could be found in this structure, whereas the hydrogen positions are localized in  $[\text{Cr}(\text{NH}_3)_6][\text{CuCl}_2]$  (Raymond, Meek & Ibers, 1968). In the latter case, of course, the hydrogen atoms are in a less symmetrical environment and moreover some  $\text{N-H} \cdots \text{Cl}$  bonding occurs. There is no evidence of  $\text{N-H} \cdots \text{I}$  bonding in the present compound, nor does one expect such bonds to be effective in stabilizing hydrogen atom positions. Thus it is only at  $-42.5^\circ$  that the  $\text{NH}_4\text{I}$  structure is ordered (Simon, Simon & Ruhemann, 1927) by the formation of  $\text{N-H} \cdots \text{I}$  bonds.

The crystal structure of  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$  is of the  $(\text{NH}_4)_3[\text{FeF}_6]$  structure type (Wyckoff, 1965). Since the hexaaminocobalt (III) ion is restricted crystallographically to have  $m\bar{3}m$  symmetry, the only structural parameter of interest is the Co-N distance. This distance, uncorrected for thermal motion, is found to be  $1.936(15) \text{ \AA}$ . The values of this distance under various assumptions for thermal motion (Busing & Levy, 1964) are: minimum,  $1.939$ ; riding,

$1.950$ ; independent,  $1.972$ ; maximum,  $2.005 \text{ \AA}$ . The Co-N distance in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  is  $2.114(9) \text{ \AA}$ , uncorrected for thermal motion. The difference between the Co(II)-N and Co(III)-N distances is therefore  $0.18 \text{ \AA}$ .\* Since one expects the principal motions of the atoms in the  $[\text{Co}(\text{NH}_3)_6]^{2+}$  ion to be similar, this difference should be essentially independent of the effects of thermal motion. Thus arguments based on changes in the Co-N distances used to explain the slow rates of electron transfer in these systems do not appear to be valid. More important, there is evidence that the effect of the change of spin type on the radius of cobalt is small.

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\* This differs by  $0.02 \text{ \AA}$  from the result given previously by Barnett *et al.* (1966) owing to the change in the Co(III)-N distance in the present structure as a result of the inclusion of the hydrogen atom contribution in subsequent calculations.