the *LASL* system of crystallographic programs developed primarily by A. C. Larson.

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Hexaamminecobalt(III) Chloride

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Abstract. $Co(NH_3)_6Cl_3$, $M_r = 267.5$, monoclinic, $C2/m$, $a = 12.46$ (1), $b = 21.30$ (2), $c = 12.74$ (1) Å, $\beta = 112.96$ (8)°, $Z = 12$, $D_m = 1.74$ (flotation), $D_c = 1.75$ g cm^{-3}, 20°C. The four independent and very regular $Co(NH_3)_6^{3+}$ octahedra are each surrounded by 14 nearest-neighbour Cl atoms. Only one of the Cl polyhedra is severely distorted.

Introduction. Gimènez-Huguet (1961) reported the cell dimensions of $Co(NH_3)_6Cl_3$ as $a = 12.50$, $b = 12.29$, $c = 21.68$ Å, $\gamma = 113.63°$, and the space group as $P2_1/m$. The twelve Co atoms were distributed at two 4(f) and two 2(e) sites and six N atoms surrounding each Co atom occupied four positions in a plane parallel to (001) and two other positions above and below this plane such that the remaining two Co–N bonds were perpendicular to (001).

A great deal of interest in hexaamminecobalt(III) complexes was initiated amongst workers in NMR (Reynhardt, 1974a,b; Kim, 1960; Ito & Chiba, 1969) by the reportedly unusual broad linewidth transitions (Murray & Waugh, 1958) and the phase transitions observed in specific-heat experiments (Ziegler, 1941; Matsuo, Tatsumi, Suga & Seki, 1973). A recent NMR investigation of the ^{59}Co quadrupole parameters (Reynhardt, 1974a) revealed a marked difference between the quadrupole coupling constant at one Co site and those at the other three sites. The quadrupole coupling constant, which is expected to be mainly of intramolecular origin, is 17 MHz at one Co site while the corresponding values at the other sites vary from 1 to 3 MHz.

Although the ratio of the number of Co atoms occupying twofold and fourfold positions is in agreement with the results of an NMR study of $Co(ND_3)Cl_3$ by Ito & Chiba (1969), the Co–N bond directions obtained from the experimental deuteron electric field gradient tensors do not agree with those reported by Gimènez-Huguet (1961).

Crystals were obtained by slow evaporation of a saturated aqueous solution. Rotation, Weissenberg and precession photographs showed that the crystals belong to the monoclinic system and systematic absences were observed for general reflections hkl: $h + k = 2n + 1$, allowing three possible space groups, viz $C2$, Cm or $C2/m$. No trace could be found of the 13 weak reflections among $0kl$, $hk0$ and $h0l$ which, according to Gimènez-Huguet (1961), indicated a primitive lattice.

Accurate cell dimensions were obtained on the diffractometer by least-squares refinement of 25 reflections. Extremely carefully executed recorder traces showed that reflections with $h + k = 2n + 1$ were

Table 1. *Experimental conditions*

Instrument: Philips PW 1100 diffractometer
Source: Mo $K\alpha$, $\lambda = 0.7107$ Å, graphite monochromator
Crystal size: $0.22 \times 0.22 \times 0.28$ mm
$\omega–2\theta$ scan; scan width $= 1.2°$ (θ), scan speed $= 0.02°$ s^{-1}
$\theta_{max} = 22°$, confidence level $= 2.0$
Total number of independent reflections $= 1973$
Total observed $= 1714$

Table 2. *Fractional atomic coordinates of the atoms in the asymmetric unit*

The number of positions and the Wyckoff notation are given in column 2.

	N	x	y	z
Co(1)	4(g)	0.0	0.1662 (1)	0.0
Co(2)	4(h)	0.5	0.1713 (1)	0.5
Co(3)	2(b)	0.5	0.0	0.0
Co(4)	2(c)	0.0	0.0	0.5
Cl(1)	8(j)	0.7394 (2)	0.1369 (1)	0.2477 (2)
Cl(2)	8(j)	0.1314 (2)	0.1721 (1)	0.3649 (2)
Cl(3)	8(j)	0.3711 (2)	0.1867 (1)	0.1417 (2)
Cl(4)	4(i)	0.3069 (2)	0.0	0.1963 (2)
Cl(5)	4(i)	0.6342 (2)	0.0	0.4388 (2)
Cl(6)	4(i)	0.9061 (3)	0.0	0.1265 (2)
N(11)	8(j)	0.0967 (6)	0.1013 (3)	0.1030 (6)
N(12)	8(j)	0.0968 (6)	0.2323 (3)	0.1017 (5)
N(13)	8(j)	0.8959 (6)	0.1645 (3)	0.0832 (5)
N(21)	8(j)	0.5996 (5)	0.1701 (4)	0.4122 (5)
N(22)	8(j)	0.4024 (6)	0.1068 (3)	0.3968 (5)
N(23)	8(j)	0.4014 (6)	0.2371 (3)	0.3983 (5)
N(31)	4(i)	0.5588 (8)	0.0	0.1670 (7)
N(32)	8(j)	0.6130 (7)	0.0643 (4)	0.0020 (7)
N(41)	4(i)	0.0885 (7)	0.0	0.4001 (7)
N(42)	4(i)	0.8544 (7)	0.0	0.3641 (7)
N(43)	4(h)	0.0	0.0918 (4)	0.5

definitely absent. The experimental conditions used for data collection are given in Table 1. Lp corrections were applied but no absorption corrections were made.

The correct space group could not be assigned uniquely from the systematic absences but available single-crystal NMR information (Reynhardt, 1974a) could be used to determine the space group unambiguously. An extensive room-temperature study of the angular dependence of the electric quadrupole splitting of the ^{59}Co NMR lines showed that there are four nonequivalent Co sites in the unit cell. Since the NMR spectra of all the symmetry-related positions of each of these four Co sites coincide for rotations about the crystallographic axes, each of these unique sites must be a crystallographically special position. To accommodate 12 Co atoms in four different special positions, twofold as well as fourfold special positions must be available. Thus $C2$ and Cm, which have only twofold special positions, are eliminated. With $C2/m$ left, eight Co atoms can be placed at two fourfold special positions and four Co atoms at two twofold special positions. With the 12 Co atoms per unit cell distributed amongst four special positions the symmetry-related sites appear identical for all rotations about the crystallographic axes in the NMR experiment.

Atomic positions were obtained from Patterson and Fourier maps. Full-matrix least-squares refinement with anisotropic temperature factors gave a conventional R of 0.038. H atoms could not be located in a difference Fourier map. The fractional atomic parameters are listed in Table 2.* All the calculations were performed with the computer programs of the XRAY system (1972).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33092 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
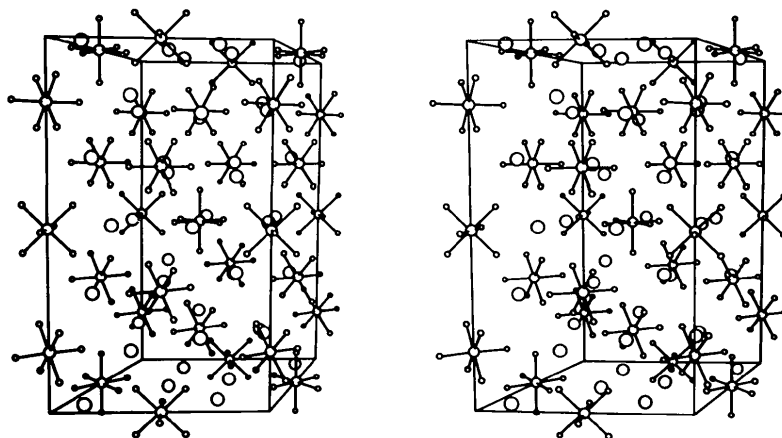

Fig. 1. Stereoscopic drawing of the Co(NH$_3$)$_6$Cl$_3$ unit cell and contents. The atoms Cl, Co and N are represented by spheres of decreasing radii. The a axis is horizontal and the b axis vertical in the plane of the paper.
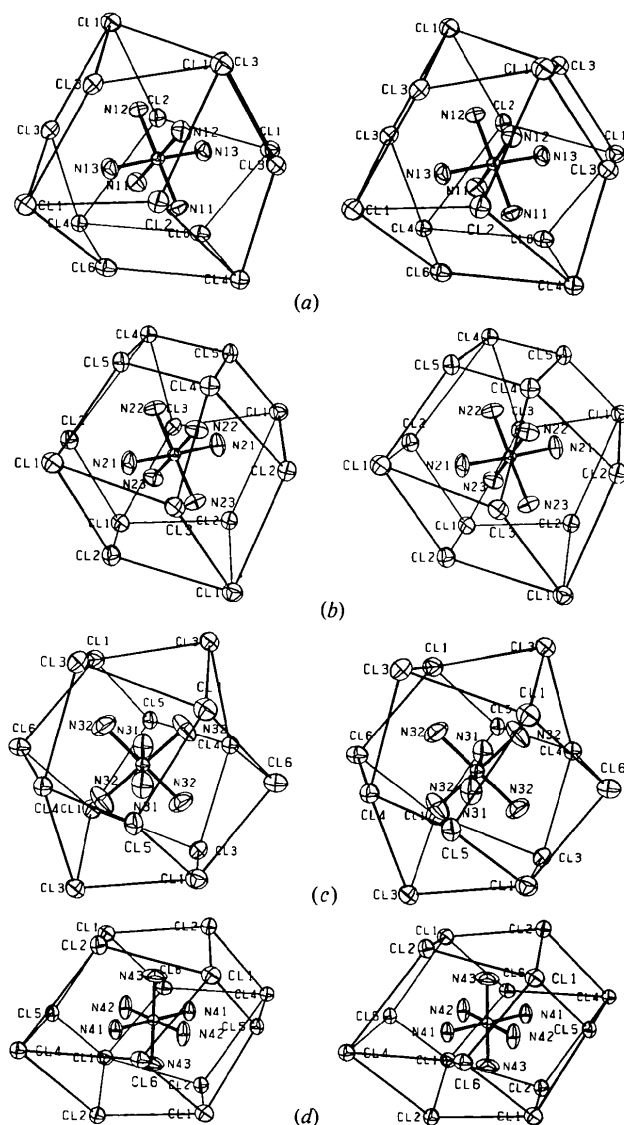
Fig. 2. Stereoviews of the distorted dodecahedral Cl environments of the $Co(NH_3)_6^{3+}$ octahedra. (a) Co(1). (b) Co(2). (c) Co(3). (d) Co(4).

Table 3. *Interatomic distances* (Å)

Co(1)–N(11)	1·963 (6)	Co(2)–N(21)	1·968 (8)
Co(1)–N(12)	1·974 (6)	Co(2)–N(22)	1·961 (6)
Co(1)–N(13)	1·970 (8)	Co(2)–N(23)	1·978 (6)
Co(3)–N(31)	1·962 (9)	Co(4)–N(41)	1·983 (11)
Co(3)–N(32)	1·957 (9)	Co(4)–N(42)	1·959 (8)
Average Co–N	1·963	Co(4)–N(43)	1·955 (9)
Co(1)–Cl(1)	5·374	Co(2)–Cl(1)	5·424
Co(1)–Cl(1)	5·394	Co(2)–Cl(1)	5·220
Co(1)–Cl(2)	4·287	Co(2)–Cl(2)	4·228
Co(1)–Cl(3)	4·233	Co(2)–Cl(2)	4·355
Co(1)–Cl(3)	4·278	Co(2)–Cl(3)	4·221
Co(1)–Cl(4)	5·093	Co(2)–Cl(4)	5·178
Co(1)–Cl(6)	4·239	Co(2)–Cl(5)	4·211
Co(3)–Cl(1)	4·474	Co(4)–Cl(1)	4·608
Co(3)–Cl(3)	4·890	Co(4)–Cl(2)	4·613
Co(3)–Cl(4)	4·091	Co(4)–Cl(4)	6·413
Co(3)–Cl(5)	5·174	Co(4)–Cl(5)	4·312
Co(3)–Cl(6)	4·671	Co(4)–Cl(6)	4·430
Average Co–Cl	4·714		

at the corners of distorted rhombic dodecahedra, illustrated in Fig. 2.

The average Co—Cl distance is 4·714 Å. The two Co(4)—Cl(4) distances are considerably longer at 6·413 Å, resulting in the severe elongation of the Cl cage around Co(4) and hence causing the one large quadrupole coupling constant. The orientations of the $Co(NH_3)_6^{3+}$ octahedra in the Cl dodecahedra also differ. For Co(1) and Co(2) all the Co—N bonds point at vertices of the Cl cage, i.e. directly at Cl atoms. For Co(3) and Co(4) four of the Co—N bonds point at faces of the dodecahedra and only two point directly at vertices. These differences between orientations are reflected in the differences in Co—Cl distances.

The influence of the distortion of the dodecahedra on the observed NMR results is discussed in detail elsewhere (Reynhardt, 1977).

Discussion. The contents of the unit cell are shown in Fig. 1. The Co positions are in agreement with those suggested by Gimènez-Huguet (1961), but the N positions differ completely. In accordance with the NMR results, there are four crystallographically distinct but chemically similar $Co(NH_3)_6^{3+}$ octahedra in the asymmetric unit. As seen from the bond lengths in Table 3, these four octahedra have very similar geometries. The average Co—N distance is 1·963 Å and the maximum deviation of the N—Co—N angles from their ideal values is 2·1° with a standard deviation of 0·7°.

The differing Cl environments of the $Co(NH_3)_6^{3+}$ octahedra explain the NMR results. Each Co atom is surrounded by 14 nearest-neighbour Cl atoms situated

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