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Electron-Density Distribution in Crystals of 1,4,7,10,13,16-Hexaazacyclooctadecane-cobalt(III) Trichloride, *meso*-[Co(hexaen)]Cl_3 at 106 K

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Abstract

Charge asphericity around the Co^{III} atom in the title complex has been determined by single-crystal X-ray diffraction. $[Co(C_{12}H_{30}N_6)]Cl_3$, $M_r = 423.7$, rhombohedral, $R\bar{3}$, cell dimensions in hexagonal setting $a = 9.2536\,(1)$, $c = 16.7028\,(5)$ Å, $V = 1238.63\,(4)$ Å^3, $D_x = 1.70$ Mg m^{-3}, $Z = 3$, Mo $K\alpha_1$, $\lambda = 0.70926$ Å, $\mu = 1.532$ mm^{-1}, $F(000) = 666$, $T = 106\,(1)$ K, $R = 0.020$ for 4631 observed unique reflections after multipole refinement. The Co atom is surrounded by six equivalent N atoms of the cyclic hexadentate ligand hexaen (1,4,7,10,13,16-hexaazacyclooctadecane) at a distance of 1.9963 (2) Å, and the CoN_6 octahedron is trigonally compressed along the threefold axis. The aspherical 3*d*-electron distribution is typical of octahedral cobalt(III) complexes in a low-spin state. The numbers of *d* electrons in the a_{1g}, e_g and e_g' orbitals were estimated to be 1.76 (3), 3.16 (4) and 1.10 (4), respectively. The C—N bonding electron in the ligand was analyzed based on the oriented-atom model.

Introduction

The electron-density distribution in transition-metal complexes has been examined in order to elucidate the charge asphericity due to the *d* electrons in the ligand field (for a recent review, see Saito, 1989). The study of chelate compounds is one area in which we are currently interested and we have therefore investigated *lel*$_3$- and *ob*$_3$-$[Co(chxn)_3]^{3+}$ complexes (chxn = 1,2-diaminocyclohexane; Morooka, Ohba, Saito & Miyamae, 1991). The crystals are noncentrosymmetric and phase improvement was achieved by the multipole-expansion method (Hansen & Coppens, 1978). The charge asphericity around the Co^{III} atom is essentially that of the octahedral complex and the chirality of the *d*-electron distribution in these optically active complexes was not significant. In order to further investigate the effect that the chelate rings have on the *d*-electron distribution, the title complex, which has a hexaaza macrocyclic ligand, hexaen, was examined. The crystals are centrosymmetric and the phase error is expected to be negligible. The preparation of this compound and its crystal structure at room temperature have already been reported (Yoshikawa, Toriumi, Ito & Yamatera, 1982).

Experimental

A spherically shaped crystal 0.364 (8) mm in diameter was cooled to 106 (1) K in a cold nitrogen gas stream. X-ray intensities were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode with scan rate 2° min^{-1} in θ and scan range $(1.6 + 0.8\tan\theta)$°. Cell parameters were refined by least-squares fitting of 31 2θ values ($70 < 2\theta < 80$°). Reflections were measured for a hemisphere of reciprocal space in the range $2 \leq 2\theta \leq 80$°, and for an asymmetric unit in the high-order region ($80 \leq 2\theta \leq 135$°). Six standard reflections were monitored every 50 measurements. During data collection (23 days), $|F_o|$'s of the standard reflections decreased by 2.31% and the time dependence could be expressed as $|F_o| = |F_o|_{\rm initial}(1 - at - bt^2)$. Intensity data were corrected according to the equation by using the coefficients *a* and *b* obtained by least-squares fitting. 10057 reflections were measured, of which 8305 reflections were observed with $|F_o| > 3\sigma(|F_o|)$; 4631 unique reflections ($R_{\rm int} = 0.015$). An absorption correction was applied with $\mu r = 0.28$ assuming a spherical crystal shape (transmission factor, $0.66 < A < 0.68$).

Atomic coordinates at room temperature (Yoshikawa *et al.*, 1982) were utilized as initial parameters. The positional, thermal and multipole

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parameters were refined with the program *MOLLY* (Hansen & Coppens, 1978). Multipoles were included up to the hexadecapole level for Co, Cl, N and C atoms. Core-scattering factors and anomalous-scattering terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The 4*s* and 4*p* orbitals of the Co atom were assumed to be unoccupied. When the κ parameters were refined, the monopole populations became unreasonable. Therefore, screening parameters ζ were fixed at the theoretical values for isolated atoms (Clementi & Raimondi, 1963). For H atoms, scattering factors were those of Stewart, Davidson & Simpson (1965) and monopole populations were refined with positional and isotropic thermal parameters. The total charge of the unit cell was constrained to be neutral. An isotropic secondary-extinction parameter of type I (Becker & Coppens, 1975) was introduced, $g = 0.37\ (2) \times 10^4$ and $y_{\min}(= F_o^2/F_c^2) = 0.75$ for 300. Final discrepancy indices were $R(F) = 0.020$, $wR(F) = 0.024$, $S = 1.05$ for 4631 unique reflections. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ by a full-matrix least-squares method. The number of parameters refined was 149, $\Delta/\sigma < 0.008$ for non-H atoms. Atomic coordinates are listed in Table 1, bond lengths, bond angles and torsion angles in Table 2.* The electron populations of the cobalt *d* orbitals listed in Table 3 were derived from the multipole coefficients (Holladay, Leung & Coppens, 1983). Computations were carried out on a MIPS RS3230 workstation.

Results and discussion

Molecular structure

The molecular structure is shown in Fig. 1. The complex cation has crystallographic $\bar{3}$ (S_6) symmetry and the CoN$_6$ octahedron is compressed along the threefold axis. The inclination angle of Co—N to the threefold axis is 59.312 (6)°, which is larger than in a regular octahedron (54.74°) and in *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ [54.23 (4)–54.55 (3)°] and *ob*$_3$-[Co(chxn)$_3$]$^{3+}$ [56.27 (8)–56.84 (6)°] complexes (Morooka *et al.*, 1991). This is due to the macrocyclic coordination of the hexaen which gives a N—Co—N chelate angle of 83.73 (1)°. Strain in the molecular structure is reflected in the unsymmetric *gauche* conformation of the five-membered chelate ring with imbalances in the N—C bond lengths of 0.0190 (5) Å, and in the

Table 1. *Positional parameters* ($\times 10^5$, $\times 10^4$ *for* H) *and equivalent isotropic temperature factors* (*Hamilton*, 1959)

	x	y	z	B_{eq}(Å$^2 \times 10$)
Co	0	0	0	4 (1)
Cl(1)	0	0	50000	10 (1)
Cl(2)	0	0	22379 (1)	8 (1)
N	21367 (3)	12017 (3)	6100 (1)	6 (1)
C(1)	29173 (3)	1357 (3)	6045 (2)	8 (1)
C(2)	33030 (3)	28851 (3)	2538 (2)	8 (1)
H(1)	1903 (13)	1303 (13)	1129 (7)	10 (2)
H(2)	2281 (15)	−834 (15)	973 (7)	9 (2)
H(3)	4103 (16)	767 (15)	820 (8)	22 (3)
H(4)	4511 (15)	3142 (14)	272 (7)	15 (2)
H(5)	3265 (14)	3796 (15)	564 (7)	15 (2)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

Co—N	1.9963 (2)	C(1)—C(2^i)	1.5177 (5)
N—C(1)	1.4857 (5)	Cl(2)···N	3.2157 (2)
N—C(2)	1.5047 (3)		
N—Co—N^i	83.73 (1)	C(1)—N—C(2)	110.47 (2)
Co—N—C(1)	107.57 (2)	N—C(1)—C(2^i)	107.21 (3)
Co—N—C(2)	111.89 (2)	N^i—C(2)—C(1)	108.86 (3)

Co—N—C(1)—C(2^i)	48.26 (2)
Co—N^i—C(2^i)—C(1)	19.49 (4)
C(2)—N—C(1)—C(2^i)	− 74.13 (2)
C(1^i)—N^i—C(2^i)—C(1)	− 100.33 (4)
N—C(1)—C(2^i)—N^i	− 43.86 (4)

Symmetry code: (i) y, $-x+y$, $-z$.

Table 3. *d-Electron populations of the* Co *atom*

Total	6.02 (3)
a_{1g}	1.76 (3)
e_g	3.16 (4)
e'_g	1.10 (4)
$e_{g+}e'_{g+} + e_g\ e'_g$	−0.07 (6)

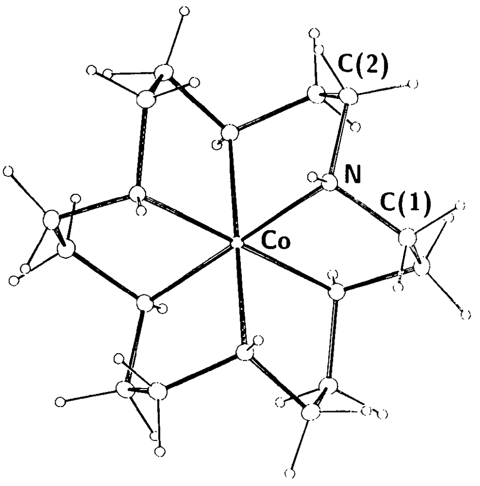

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the complex cation along the threefold axis. Thermal ellipsoids are scaled at the 50% probability level. H atoms are represented as spheres of radius 0.08 Å.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and multipole parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55008 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0590]

Co—N—C bond angles of 4.32 (2)°. Similar structural features have already been observed in room-temperature X-ray work and investigated by conformational analysis (Yoshikawa *et al.*, 1982). The conformation of the complex cation in the nitrate crystal, [Co(hexaen)]$(NO_3)_3.H_2O$ (Searle & Tiekink, 1989), is essentially the same as that in the present chloride crystal.

Charge asphericity

Deformation densities were calculated as the difference between the observed electron-density distribution and the superposition of spherical atoms with refined effective charges in order to show the charge asphericity around the metal atom clearly. A section of the observed deformation densities in the plane containing the Co—N bond axis and the threefold axis is shown in Fig. 2(*a*). The observed asphericity around the Co atom was well reproduced by the multipole functions as can be seen in Fig. 2(*b*), where the contributions of the unobserved weak reflections $[|F_o| < 3\sigma(|F_o|)]$ have been supplemented. Four positive peaks around the Co atom indicate excess 3*d*-electron populations in the a_{1g} and e_g orbitals, and the troughs on the Co—N bond axes are attributed to the electron deficiency of the e_g' orbitals. The positive peaks on the threefold axis are higher than the others. This accords with the higher electron population of the a_{1g} [88 (2)%] than that of the e_g orbitals [79 (1)%], and suggests that the ligand-field strength along the threefold axis becomes weaker after trigonal compression of the CoN_6 octahedron.

The deformation density of the t_{2g} orbitals in the octahedral ligand field has eight maxima around the metal atom arranged like the apices of a cube (Ohba, Toriumi, Sato & Saito, 1978). In the course of this study, the authors thought it unusual that the $(a_{1g})^2(e_g)^4$ electron configuration in the trigonal ligand field should give the same peak height, although two of the eight positive peaks correspond to a_{1g} and six peaks to e_g orbitals, and the number of *d* electrons/number of positive peaks = 1 and $\frac{2}{3}$ for $(a_{1g})^2$ and $(e_g)^4$ configurations, respectively. Accordingly, hypothetical deformation densities for the $(a_{1g})^2$, $(e_g)^4$ and $(a_{1g})^2(e_g)^4$ configurations were calculated for this complex using the refined thermal parameters of the Co atom. As shown in Fig. 5, the positive and negative deformation densities of the a_{1g} and e_g orbitals cancel each other out so as to give the same peak height for the $(a_{1g})^2(e_g)^4$ configuration.

In Fig. 2(*a*), the lone-pair electrons of the N atom appear as split peaks, which may indicate a series-termination error in the observed electron densities. The bias due to series-termination error can also be seen in the multipole model deformation map, *i.e.* the lone-pair peak in Fig. 2(*b*) is disturbed by the ripple around the Co atom. When high-order reflections are included up to $(\sin\theta/\lambda)_{\max} = 1.8$ Å^{-1}, the series-termination effect in the model map becomes

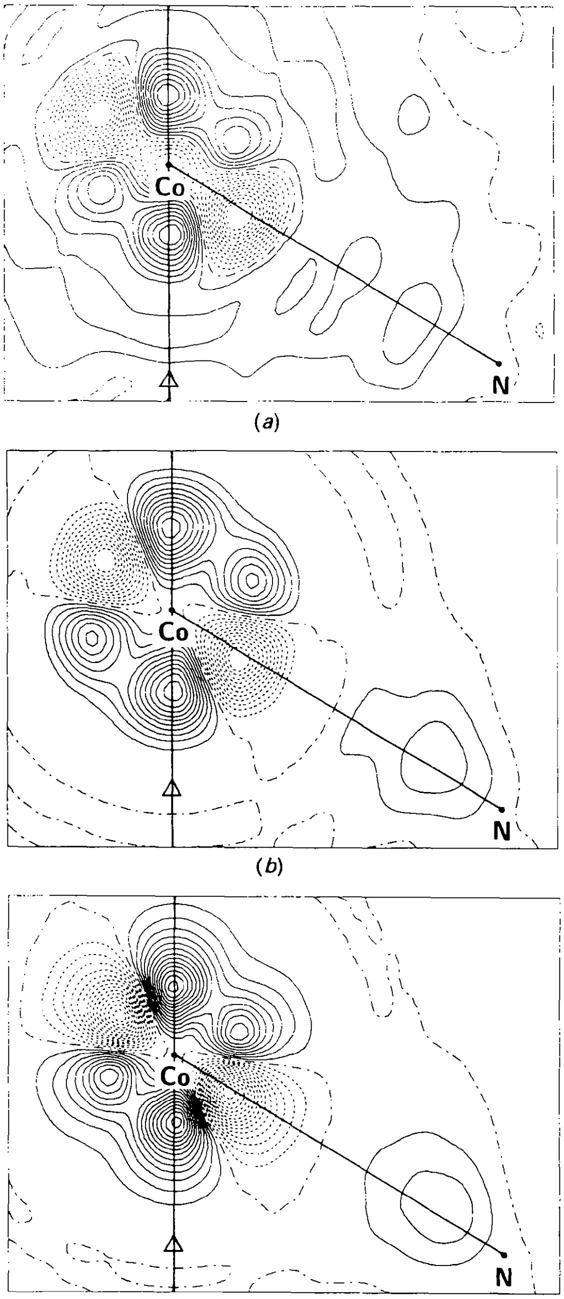


Fig. 2. Deformation density in the plane containing a Co—N bond axis and the threefold axis. (*a*) Observed deformation density based on the 4631 reflections with $(\sin\theta/\lambda)_{\max} = 1.3$ Å^{-1}. (*b*) Multipole model density with $(\sin\theta/\lambda)_{\max} = 1.3$ Å^{-1} (5067 reflections). (*c*) Multipole model density with $(\sin\theta/\lambda)_{\max} = 1.8$ Å^{-1} (13477 reflections). Contour intervals are at 0.2 e Å^{-3}. The standard deviation of electron density in (*a*) is 0.08 e Å^{-3} in a general position.

negligible (see Fig. 2*c*). Fig. 3 is the model deformation density in the plane containing the Co—N bond axis and the Cl(2) ion on the threefold axis. Three hydrogen bonds exist between the Cl(2) ion and three equivalent N atoms of a complex cation with an N···Cl(2) distance of 3.2157 (2) Å. A positive peak on the threefold axis near the Cl(2) atom suggests a weak polarization of the electron cloud of Cl^- by the hydrogen bonds.

Model deformation densities on the C—C and C—N bond axes of the ligand are shown in Fig. 4(*a*), where the subtracted promolecule is the independent atom model (IAM) with neutral atomic charges. The peak height of the C—N bond (0.32 e Å^{-3}) is smaller than that of the C—C bond (0.54 e Å^{-3}). This accords with the fact that the bonding electron around a valence-electron-rich atom tends to exhibit a lower density than that around a C—C bond (Moeckli, Schwarzenbach, Bürgi, Hauser & Delley, 1988). That is, electron accumulation between the atoms due to covalent-bond formation is estimated as being lower for valence-electron-rich atoms

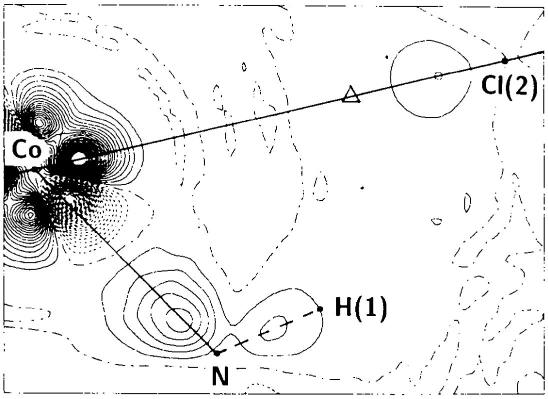
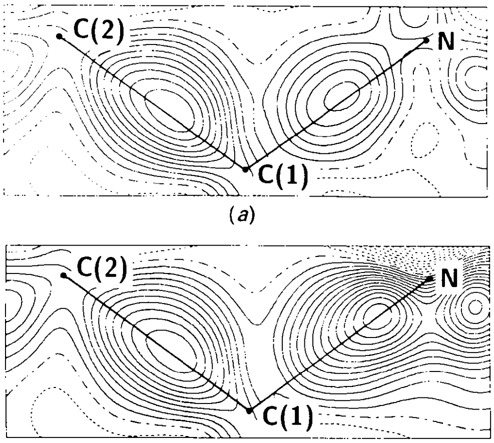


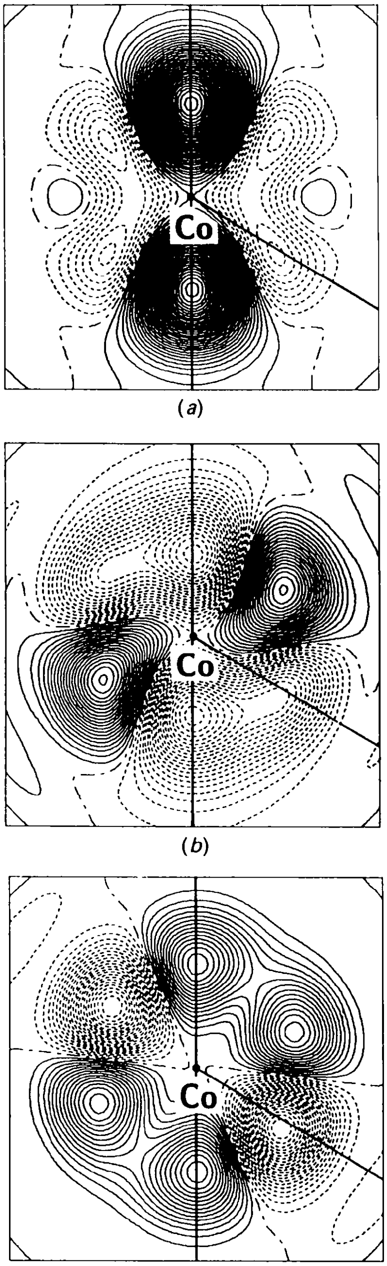
Fig. 3. Model deformation density in the plane containing the Cl(2) atom on the threefold axis and a Co—N bond axis. The H(1) atom is shifted from the plane by 0.21 Å. $(\sin\theta/\lambda)_{max}$ = 1.8 Å^{-1} (13477 reflections). Contour intervals are at 0.1 e Å^{-3}.



(*a*)

(*b*)

Fig. 4. Model deformation density in the plane containing the C—N and C—C bonds. (*a*) Based on the independent atom model (IAM). (*b*) Based on the oriented-atom model (OAM). $(\sin\theta/\lambda)_{max}$ = 1.3 Å^{-1}. Contour intervals are at 0.05 e Å^{-3}.



(*a*)

(*b*)

(*c*)

Fig. 5. Hypothetical model deformation density in the plane containing a Co—N bond axis and the threefold axis for (*a*) $(a_{1g})^2$, (*b*) $(e_g)^4$ and (*c*) $(a_{1g})^2(e_g)^4$ configurations. $(\sin\theta/\lambda)_{max}$ = 1.3 Å^{-1} (5067 reflections). Contour intervals are at 0.2 e Å^{-3}. Coefficients of the multipole densities are as follows: (*a*) P_{20} 0.275, P_{40} 0.368, P_{43+} 0, P_{43-} 0; (*b*) P_{20} −0.275, P_{40} −0.081, P_{43+} −0.450, P_{43-} 0; (*c*) P_{20} 0, P_{40} 0.287, P_{43+} −0.450, P_{43-} 0.

(Spackman & Maslen, 1985; Hall, 1986). Because of this shortcoming of the IAM, the oriented-atom model (OAM) was proposed by Schwarz, Valtazanos & Ruedenberg (1985). The OAM can be calculated from the multiple density functions (Takazawa, Ohba & Saito, 1989). Fig. 4(*b*) shows the deformation densities based on the OAM, where the number of electrons in one of the sp^3 atomic orbitals of N along the C—N bond axis is assumed to be unity. The peak height of the C—N bond increases from 0.32 to 0.68 e Å^{-3} and balances with that of the C—C bond. The bonding electron density on the C—C axis remains unchanged because the half-filled sp^3 orbitals of the C atom give a spherical electron density, which is identical with that of IAM.

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Structure of a Cobalt Complex Capable of Multiple Electron Transfer*

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Abstract

The compound [Co($C_{26}H_{42}N_8O_2$)]Cl_3.7.5H_2O [M_r = 799.1, $P6_522$, $a = b = 13.196$ (1), $c = 74.872$ (6) Å, V = 11291 (2) Å^3, $Z = 12$, $D_m = 1.41$ g cm^{-3} (by flotation), $D_x = 1.410$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, μ = 61.38 cm^{-1}, $F(000) = 5076$] has an unusually long c axis for a coordination complex. Single-crystal X-ray diffractometer data were filtered to exclude reflections badly affected by adjacent reflections. The structure at room temperature is described as a commensurate displacive modulation of an idealized parent structure in space group $P6_422$ with axial lengths $a' = b' = a$, $c' = \frac{1}{2}c$, $Z = 6$. Some of the water molecules are disordered and ordering this disorder would further reduce the symmetry to $P3_212$. Sections of the structure perpendicular to **c** are described as strings of hydrogen-bond-connected cations propagated by 2_1 screw axes parallel to secondary crystal axes. The Cl anions are directly

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* Δ-(15,20,25,30*R*)-(1,12-Diammonio-2,11-dioxo-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.$0^{4,9}$.$0^{15,20}$.$0^{25,30}$]dotriaconta-4,6,8-trienato)cobalt(III) trichloride heptasesquihydrate.

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