shortest bond is C(*m*2)—N(*m*3). This is consistent with a lessening of double-bond character in the C—S bonds, and with the direction of bending of the C—S bonds out of their normal positions.

Table 4 shows that the pyrimidine rings are satisfactorily planar, while some of the exocyclic atoms, *e.g.* S(20), show a slight departure from the plane. The maximum distance of the Co atom from a ring plane is 0·14 Å.

Packing of the two molecular species in the unit cell is shown in Fig. 3 (Johnson, 1965). Solvate acetone molecules are only loosely held as indicated by temperature parameters which are much higher than those of atoms in the complex. The whole structure is held together by van der Waals forces. There is no possibility of hydrogen bonding between acetone and the ligands since the only potential sites on the rings, N(*m*3), are deprotonated.

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The Structure of (1,2,3-Triamino-1,3-diimino-2-methylpropane)triamminecobalt(III) Tribromide ⅔-Hydrate

BY P. A. TUCKER

Research School of Chemistry, The Australian National University, PO Box 4, *Canberra, ACT* 2600, *Australia*

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Abstract

$[C_4H_{20}CoN_8]^{3+}[Br^-]_3.\frac{2}{3}H_2O$, hexagonal, space group $P6_3/m$, $a = 14{\cdot}455$ (1), $c = 13{\cdot}300$ (1) Å, $U = 2406{\cdot}7$ Å^3, $D_m = 2{\cdot}05$ (1) by flotation, $Z = 6$, $D_c = 2{\cdot}03$ Mg m^{-3}. $R = 0{\cdot}036$ for 1661 reflections. The cation contains a tridentate bis(amidine)aminomethylmalonate cap coordinated to Co *via* two imine and one amine function.

Introduction and experimental

Acetonitrile coordinated to Co in pentaammineacetonitrilecobalt(III) ions is attacked by CN^- at the

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nitrile C atom. The reaction proceeds by further attack of CN^- and by two intramolecular additions of bound amide ion to yield the cation of the title compound (Creaser, Dyke, Sargeson & Tucker, 1978). Creaser *et al.* (1978) described the geometry of this cation; in this paper the X-ray crystal structure is reported in detail.

Orange crystals of the tribromide, commonly six-sided prisms, were thinly coated with hair lacquer to prevent efflorescence. Photographs show diffraction symmetry $6/m$ and systematic absences $00l$ $l = 2n + 1$ establish the space group as $P6_3$ or $P6_3/m$. The choice of the latter, in which the cation lies on a crystallographic mirror plane, was confirmed by the successful refinement. Twelve reflections with $2\theta > 50°$ (Mo $K\alpha$ radiation) were centred on a Picker FACS-I four-circle diffractometer. The cell dimensions and orientation matrix were derived by least-squares analysis of the optimized 2θ, ω and χ angles. Intensities for the 7974 reflections in quadrants hkl and $\bar{h}kl$ with $3 \leq 2\theta \leq 60°$ were measured with graphite-monochromated ($2\theta_m$ = 12·16°) Mo $K\alpha$ radiation. A $\theta/2\theta$ scan at 2° $\min^{-1}$ in 2θ from 0·5° below the $K\alpha_1$ to 0·5° above the $K\alpha_2$ maximum, with stationary background counts for 10 s either side of the scan range, was employed. The measurement, every 97 reflections, of three standards showed there was no significant intensity loss over the period of data collection. The intensities were corrected for absorption [μ(Mo $K\alpha$) = 8·38 mm^{-1}] (de Meulenaer & Tompa, 1965). The crystal used for data collection was bounded by the forms {001}, {100}, {010} and {1$\bar{1}$0} with perpendicular distances between pairs of faces of 0·60, 0·30, 0·33 and 0·33 mm respectively.

Table 1. *Final atomic parameters and, for* H, *isotropic temperature factors with e.s.d.'s in parentheses*

	x	*y*	*z*	*B* (Å^2)
Br(1)	0·80142 (3)	0·55388 (5)	0·02166 (3)	
Br(2)	0·23662 (6)	0·04529 (5)	0·25	
Co	0·29642 (5)	0·36231 (5)	0·25	
N(1)	0·1996 (4)	0·4205 (4)	0·25	
N(2)	0·2115 (3)	0·2579 (3)	0·3542 (4)	
N(3)	0·4098 (4)	0·3286 (4)	0·25	
N(4)	0·3872 (2)	0·4613 (2)	0·3507 (2)	
N(5)	0·5695 (2)	0·5616 (3)	0·3945 (2)	
C(1)	0·5057 (3)	0·4355 (3)	0·25	
C(2)	0·6114 (4)	0·4372 (4)	0·25	
C(3)	0·4871 (2)	0·4900 (2)	0·3402 (2)	
O(1)	0·3333	0·6667	0·1418 (8)	
H(1)	0·204 (4)	0·477 (4)	0·296 (5)	9·4 (21)
H(2)	0·133 (8)	0·392 (7)	0·25	8·2 (26)
H(3)	0·415 (3)	0·304 (3)	0·210 (3)	1·5 (8)
H(4)	0·670 (4)	0·504 (4)	0·25	2·2 (11)
H(5)	0·606 (3)	0·406 (3)	0·192 (3)	2·6 (8)
H(6)	0·203 (5)	0·186 (5)	0·349 (5)	8·4 (18)
H(7)	0·143 (4)	0·219 (4)	0·341 (4)	5·6 (14)
H(8)	0·232 (6)	0·277 (6)	0·402 (6)	9·3 (26)
H(9)	0·366 (3)	0·490 (3)	0·398 (3)	3·1 (9)
H(10)	0·559 (3)	0·610 (3)	0·433 (3)	3·1 (8)
H(11)	0·640 (3)	0·586 (3)	0·383 (3)	2·1 (8)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co–N(1)	1·961 (4)	N(1)–Co–N(2)	91·4 (2)
Co–N(2)	1·963 (4)	N(1)–Co–N(3)	170·9 (2)
Co–N(3)	1·930 (4)	N(1)–Co–N(4)	92·8 (1)
Co–N(4)	1·919 (3)	N(2)–Co–N(4)	90·7 (2)
		N(2)–Co–N(2′)	89·8 (3)
N(3)–C(1)	1·472 (6)	N(2)–Co–N(3)	95·1 (2)
		N(3)–Co–N(4)	80·7 (1)
C(1)–C(2)	1·515 (6)	N(4)–Co–N(4′)	88·5 (2)
C(1)–C(3)	1·531 (4)	Co–N(3)–C(1)	102·0 (3)
		Co–N(4)–C(3)	113·6 (2)
C(3)–N(4)	1·295 (4)	N(3)–C(1)–C(3)	103·0 (2)
C(3)–N(5)	1·334 (4)	N(4)–C(3)–C(1)	112·0 (3)
		N(4)–C(3)–N(5)	127·6 (3)
N(1)–H(1)	1·00 (6)	C(1)–C(3)–N(5)	120·3 (3)
N(1)–H(2)	0·83 (9)	N(3)–C(1)–C(2)	115·4 (4)
N(2)–H(6)	0·99 (6)	C(3)–C(1)–C(2)	115·2 (2)
N(2)–H(7)	0·88 (5)	C(3)–C(1)–C(3′)	103·2 (3)
N(2)–H(8)	0·70 (8)		
N(3)–H(3)	0·66 (3)	Co–N(4)–H(9)	125 (3)
		C(3)–N(4)–H(9)	121 (3)
N(4)–H(9)	0·88 (4)	C(3)–N(5)–H(10)	118 (3)
N(5)–H(10)	0·93 (4)	C(3)–N(5)–H(11)	127 (3)
N(5)–H(11)	0·91 (4)	H(10)–N(5)–H(11)	111 (4)
		Co–N(3)–H(3)	117 (3)
C(2)–H(4)	0·92 (4)	C(1)–N(3)–H(3)	105 (3)
C(2)–H(5)	0·88 (5)		

The intensities were reduced to $|F_o|$ (Bennett, Matheson, Robertson, Smith & Tucker, 1978), the data sorted and equivalent reflections for point group $6/m$ averaged. The statistical R factor, $\sum \sigma_s(F_o)/\sum |F_o|$, was 0·017 for the 1661 unique reflections with $I > 3\sigma(I)$.

Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Computer programs are described elsewhere (Bennett *et al.*, 1978). The positions of the Br and Co atoms were deduced from the Patterson synthesis and most of the remaining atoms were located from successive difference syntheses. Only the H atoms attached to O(1) of the water molecule could not be located. Since O(1) has site symmetry 3, the presumption was made that the H atoms were disordered. The two water H atoms were therefore omitted from the scattering model. Full-matrix least-squares refinement of positional parameters and anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for H reduced R to a final value of 0·036 $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}041\}$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0{\cdot}002F_o^4]^{-1}$.

In the final cycle no parameter shift exceeded 0·2 times its e.s.d. A final difference synthesis showed no features > |0·7| e Å^{-3}. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, was 2·18. The minimized function was essentially independent of both $\sin\theta/\lambda$ and $|F_o|$. An isotropic extinction correction was applied (Zachariasen, 1968). The refined extinction parameter was 7·6 (8) × 10^{-6}.

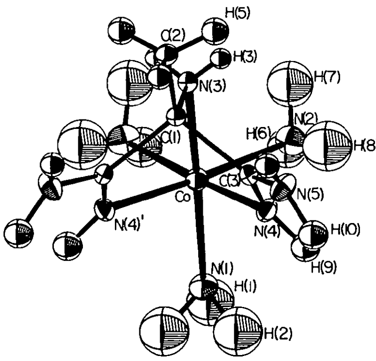
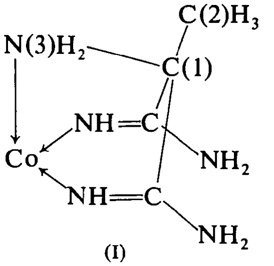


Fig. 1. Geometry and atom numbering in the cation. Ellipsoids are drawn to include 50% probability.

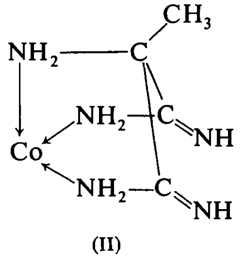
The final atomic parameters are listed in Table 1.* The geometry and atom numbering of the cation are illustrated in Fig. 1. The packing is shown in Fig. 2. Bond lengths and angles with standard deviations estimated from the full variance/covariance matrix are listed in Table 2.

Discussion

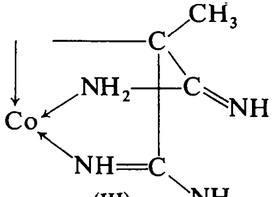
The cation (Fig. 1) has a crystallographic mirror plane passing through N(1), N(3), Co, C(1) and C(2). The Co atom is coordinated by three ammonia ligands and a tridentate bis(amidine)aminomethylmalonate cap (I) in which C(2), C(1) and N(3) derive from the coordinated acetonitrile of the precursor. One Br^- ion lies in a general position in the cell and the other on a mirror plane at $\frac{1}{4}c$. Location and refinement of the H atoms shows that the tridentate ligand is coordinated *via* both imine functions as in (I) rather than as in (II) or (III). A likely reason for this is that the coordination of an amine function would not allow delocalization over the N—C—N sections of the ligand (see below).



(I)



(II)



(III)

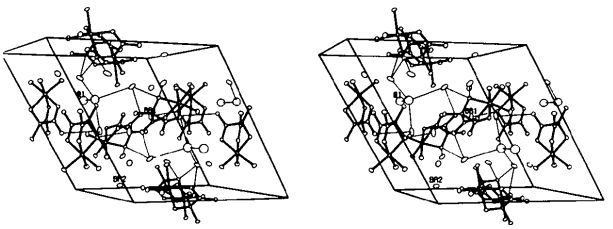


Fig. 2. Stereoscopic drawing of the unit-cell contents viewed approximately along *c*. Thin lines represent likely hydrogen-bonding interactions.

The two chemically inequivalent Co—N(amine) bond lengths [Co—N(1) 1·961, Co—N(2) 1·963 Å] do not differ significantly, suggesting no substantial difference between the *trans* influences of the amine and imine functions. The mean Co—ammine distance (1·962 Å) is similar to the mean [1·976 (15) Å] derived from different salts of the hexaamminecobalt(III) cation (Iwata & Saito, 1973; Schroeder & Jacobson, 1973*a*,*b*; Burns, Baldwin & Stokely, 1973; Epstein & Bernal, 1971; Meek & Ibers, 1970). It is also similar to the mean [1·960 (16) Å] of Co—NH_3 *cis* to the ligand *L* in cations of the type $[Co(NH_3)_5L]^{n+}$ ($L = SO_3$, $n = 1$, Elder & Trkula, 1974; L = NONOCo$(NH_3)_5$, $n = 4$, Hoskins & Whillans, 1973; L = NHCOMe, $n = 3$, Schneider, Ferguson & Balahura, 1973; L = SCN, $n = 2$, Snow & Boomsma, 1972; L = Cl, $n = 2$, Messmer & Amma, 1968; $L = N_3$, $n = 2$, Palenik, 1964).

The Co—N(3) length of 1·930 Å lies at the shorter end of the range of Co—N(tetrahedral) lengths (1·89 to 2·06 Å, mean 1·96 Å, *Molecular Structure by Diffraction Methods*, 1975). It is possible that the relative shortness of the Co—N(3) bond is a chelate effect. However, there are no available data on comparable complexes containing a Co—NH=C(NH_2)—CR_2—NH_2 ring. A close comparison, with respect to ring size and coordination geometry of the ring atoms, is with rings of type Co—O—C(:O)—CR_2—NH_2. In general where this type of ring is part of a multidentate ligand the Co—NH_2 bond is relatively short, *e.g.* 1·946 Å in the bis(*S*-methyl-L-cysteinato)cobalt(III) ion (De Meester & Hodgson, 1976), 1·943 Å in the (α-amino-γ-imino-α-methylvaleric acid)triamminecobalt(III) ion (Golding, Harrowfield, Robertson, Sargeson & Whimp, 1974), 1·925 Å in the (ethylenediaminetetraacetato)cobaltate(III) ion (Okamoto, Tsukihara, Hidaka & Shimura, 1973), 1·925 and 1·902 Å in the two isomers of the bis(L-aspartato)cobaltate ion (Oonishi, Shibata, Marumo & Saito, 1973) and 1·912 Å in the (*S*,*S*)-6,9-diaza-2,13-dithiatetradecane-5,10-dicarboxylatocobalt(III) ion (Geue & Snow, 1977). An exception is to be found in the *cis*-(sarcosinato-*N*-monopropionato)triamminecobalt(III) ion (Okamoto *et al.*, 1973) where the distance is 2·013 Å. The Co—N(4) length (1·919 Å)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33889 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is approximately the same as the mean [1·916 (9) Å] of Co–imine bonds in other structures (Harrowfield, Robertson, Sargeson & Whimp, 1975; Golding *et al.*, 1974; Kurahashi, 1974; Kistenmacher, Marzilli & Marzilli, 1974; Snow, 1974; Akatova, Tarkhova & Belov, 1973; Schneider *et al.*, 1973; Buckingham, Foxman, Sargeson & Zanella, 1972).

There is evidence of electron delocalization in the amidine sections of the chelating ligand. Co, N(4), H(9), C(3), N(5) and C(1) are roughly coplanar and the angles between the coordination planes of N(4), C(3) and N(5) are small (3–11°, Table 3). The geometry about N(5) is between tetrahedral and trigonal planar, being slightly closer to the latter. C(3)–N(5) and C(3)–N(4), 1·334 (4) and 1·295 (4) Å respectively, compare with estimates for C (sp^2)–N(sp^2) and C(sp^2)=N(sp^2) of 1·451 and 1·271 Å respectively (Nishimoto & Forster, 1966). The comparison indicates considerable double-bond character for C(3)–N(5) and possibly somewhat less than a bond order of two for C(3)–N(4). The mean values of equivalent distances in the tris(biguanide)cobalt(III) ion are 1·353 and 1·282 Å (Snow, 1974). A comparison of the latter, formally C=N length of the coordinated imine group with that of 1·284 Å in *N*,*N*-dimethylacetamide oxime (Bright, Plessius & de Boer, 1973) indicates that coordination to the metal has little effect on the C=N length. The C(1)–C(3), C(1)–C(2) and C(1)–N(3) lengths are reasonably close to their usual values of 1·510, 1·537 and 1·479 Å respectively (*Interatomic Distances and Configuration in Molecules and Ions*, 1965). Exact agreement would not, in any event, be expected because of the deviations of C(1) from ideal tetrahedral geometry.

Table 3. *Some best planes through sets of atoms and distances* (Å) *of atoms from those planes*

Plane	Defined by atoms	Distances of specified atoms from the plane
(1)	Co, C(1), C(3), N(4), N(5), H(9)	Co 0·018, C(1) 0·000, C(3) −0·024, N(4) −0·028, N(5) 0·023, H(9) 0·010, H(10) 0·305, H(11) 0·099
(2)	Co, N(4), H(9), C(3)	Co 0·005, N(4) −0·021, H(9) 0·010, C(3) 0·006
(3)	C(3), N(5), N(4), C(1)	C(3) −0·017, N(5) 0·006, N(4) 0·006, C(1) 0·005
(4)	N(5), H(10), H(11), C(3)	N(5) −0·085, H(10) 0·029, H(11) 0·033, C(3) 0·023
(5)	Co, N(1), N(2), N(3), N(4′)	Co 0·046, N(1) −0·060, N(2) 0·035, N(3) −0·065, N(4′) 0·043, N(4) −1·863, N(2′) 2·008
(6)	Co, N(2), N(2′), N(4), N(4′)	Co −0·05, N(2) 0·044, N(2′) −0·072, N(4) 0·043, N(4′) −0·072
(7)	Co, N(1), N(2′), N(3), N(4)	Co −0·046, N(1) 0·060, N(2′) 0·035, N(3) 0·065, N(4) −0·043, N(4′) 1·863, N(2) −2·008

Dihedral angles (°) between planes

(2)–(3)	2·3	(3)–(4)	10·8
(5)–(6)	90	(5)–(7)	89·2
(6)–(7)	90		

Table 4. *Interionic contacts*

The superscripts refer to atoms related to those in Table 1 by the operations:

(i) $1+x-y, x, z-\frac{1}{2}$
(ii) $1-x+y, 1-x, z$
(iii) $x, y, \frac{1}{2}-z$
(iv) $1-y, 1-x-y, \frac{1}{2}-z$
(v) $1-x, 1-y, -z$
(vi) $1-x, 1-y, z-\frac{1}{2}$
(vii) $y-x, -x, z.$

(*a*) Possible hydrogen-bonding interactions

	Br···N (Å)	Br···H (Å)	Br···H–N (°)
Br(1)···H(10)$^{\text{i}}$–N(5)$^{\text{i}}$	3·34	2·41	175
Br(1)···H(3)$^{\text{ii}}$–N(3)$^{\text{ii}}$	3·39	2·74	167
Br(2)···H(6)–N(2)	3·55	2·66	153
Br(2)···H(6)$^{\text{iii}}$–N(2)$^{\text{iii}}$	3·55	2·66	153

O(1)···O(1)$^{\text{iv}}$	2·88 Å
Br(1)···O(1)$^{\text{v}}$	3·53 Å

(*b*) Other short non-bonding contacts (Å)

Br(1)···N(5)$^{\text{i}}$	3·59	Br(1)···C(2)	3·87
Br(1)···N(4)$^{\text{vi}}$	3·47	Br(1)···C(2)$^{\text{ii}}$	3·99
Br(2)···N(1)$^{\text{vii}}$	3·43		
Br(2)···N(2)$^{\text{vii}}$	3·61		

Evidence of strain in the tridentate cap of the cation may be found from the internal angles of the ligand. Co–N(3)–C(1) (102·0), C(3)–C(1)–N(3) (103·0) and C(3)–C(1)–C(3′) (103·2°) are some 5–6° smaller than the expected tetrahedral value and Co–N(4)–C(3) (113·6) and N(4)–C(3)–C(1) (112·0°) are some 6–8° smaller than their ideal value of 120°. The N(3)–Co–N(4) angle (80·7°) is also substantially smaller than might be expected for a five-membered chelating ring.

Probable hydrogen-bonding interactions are listed in Table 4 and are marked on Fig. 2. The shorter non-bonded distances which all involve anion–cation contacts are also listed in Table 4. There are no H···H contacts, between cations, of <2·6 Å. Those short Br···N contacts listed in the second part of Table 4 are unlikely to involve hydrogen bonding because the angle at the most appropriate H atom would be small (<140°).

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The Structure of Δ-(R)-μ-Cystinato-tetrakis(ethylenediamine)dicobalt(III) Tetraperchlorate Hexahydrate

By P. A. Tucker

Research School of Chemistry, The Australian National University, PO Box 4, *Canberra, ACT* 2600, *Australia*

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Abstract

$[C_{14}H_{42}Co_2N_{10}O_4S_2]^{4+}[ClO_4^-]_4.6H_2O$, M_r = 1103, orthorhombic, space group $P2_12_12$, a = 35·708 (4), b = 8·869 (1), c = 6·847 (1) Å, U = 2168·4 Å^3, D_m = 1·74 (2) (by flotation), Z = 2, D_c = 1·69 Mg m^{-3}. R = 0·072 for 1996 reflections. The absolute configurations at Co and the asymmetric C atom are Δ and R respectively. Results of strain-energy-minimization calculations on the cation suggest that differences in energy between λ and δ conformers for the ethylenediamine rings are small and that their observed conformations are probably controlled by interionic interactions.

Introduction and experimental

Jackson, Sargeson & Tucker (1977) reported that oxidation of the N,S-bound Δ-(R)-cysteinatobis(ethylenediamine)cobalt(III) cation in DMSO/Ac$_2$O mixture yields an N,O-bound sulphenamide complex in which the cysteinato S is bound to a N atom of one of the ethylenediamine ligands. The sulphenamide complex reacts with N,O-bound cysteinatobis(ethylenediamine)cobalt(III), obtained by borohydride reduction of the sulphenamide, to give the cation of the title complex, the structure of which was briefly reported (Jackson *et al.*, 1977). In this paper the

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