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Cobalt(III) Complexes with *N*-Methylethane-1,2-diamine (meen). Crystal Structures of the Stable Isomers of $[Co(meen)_3]^{3+}$ and $[Co(meen)_2(en)]^{3+}$

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Abstract

The X-ray crystal structures of two geometric isomers–diastereoisomers of $[Co(meen)_3]^{3+}$, designated **A** and **C**, and one isomer of $[Co(meen)_2(en)]^{3+}$, designated **F**, are reported (meen = *N*-methylethane-1,2-diamine). **A**, **C** and **F** (as racemates) were isolated as their bromide salts and crystallized as di-, mono-, and mono-hydrates respectively. **A** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 8.231(2)$, $b = 8.682(1)$ and $c = 14.247(2)$ Å, $\alpha = 96.84(1)$, $\beta = 97.16(2)$ and $\gamma = 99.62(2)°$, and $Z = 2$. **C** crystallizes in the orthorhombic space group $Pna2_1$ (implying spontaneous resolution) with $a = 12.758(3)$, $b = 11.236(1)$ and $c = 13.19(1)$ Å, and $Z = 4$. Complex **F** is monoclinic, $I2/a$, with $a = 12.626(5)$, $b = 22.977(5)$ and $c = 12.619(6)$ Å, $\beta = 97.84(4)°$, and $Z = 8$. The structures were solved by direct methods and each was refined by a full-matrix least-squares procedure. Final refinement details for **A** (those for **C** and **F** follow in parentheses): R 0.044 (0.040; 0.038), R_w 0.046 (0.041; 0.041) for 2487 (1318; 1693) reflections with $I \geqslant 2.5\sigma(I)$. The complex cations feature octahedrally coordinated Co(III) centres, and they are involved in complicated hydrogen bonding networks with the bromide anions and water molecules in the crystal lattices. The stereochemistries of the complex cations are (one enantiomer specified only) **A**: Λ-*mer*-$[Co(meen)_3]^{3+}$-RRR^*-$\lambda\delta\delta^*$; **C**: Λ-*mer*-$[Co(meen)_3]^{3+}$-RSR^*-$\delta\lambda\delta^*$; **F**: Λ-*trans*-CH_3, *cis*-NH_2-$[Co(meen)_2(en)]^{3+}$-RR-$\delta\delta\delta$. *Equatorial* methyl dispositions and *lel* ring geometries predominate, although **A** has one ring which is *ob* and which also has the methyl *axial*, and **C** has one *ob* ring.

Introduction

Complexes of *N*-methylethane-1,2-diamine (meen) are of considerable stereochemical interest because this ligand may coordinate in different modes giving rise to several sources of isomerism. We recently described the isolation and characterization of several isomers for each of the complexes $[Co(meen)_3]^{3+}$, $[Co(meen)_2(en)]^{3+}$ and $[Co(meen)(en)_2]^{3+}$ [1], and the present paper reports the X-ray structural analyses of three isomers of these compounds.

For tris(meen) complexes, only the crude complexes $[Co(meen)_3]Cl_3$ and $[Ni(meen)_3]Cl_2$ had been described previously [2], and the questions of their isomeric identities, and whether other isomers might be separated chromatographically from equilibrium mixtures of these systems had remained over many years. In addition, several bis(meen) and mono(meen) complexes had been prepared in particular geometric isomers although not necessarily under equilibrium conditions [3–6], so that the relative stabilities of isomers involving different coordination modes are uncertain in these systems also.

The separation and isolation of three isomers of $[Co(meen)_3]^{3+}$, designated **A**, **B** and **C**, was achieved by using cation-exchange chromatography on SP-Sephadex [1]. These isomers were obtained from preparative mixtures not involving charcoal, or from the equilibrated mixture arising from isomerization of each isomer **A** or **C** in water or base. However, syntheses of $[Co(meen)_3]^{3+}$ in water in the presence of charcoal and oxygen at elevated temperature were accompanied by some demethylation, giving rise also to the complexes $[Co(meen)_2(en)]^{3+}$, $[Co(meen)(en)_2]^{3+}$ and $[Co(en)_3]^{3+}$. From the resulting mixtures, fractional crystallization and Sephadex chromatography have enabled the separation and characterization of some isomers for the complex systems $[Co(meen)_2(en)]^{3+}$, isomers designated **F**, **G** and **H**, and $[Co(meen)(en)_2]^{3+}$, isomer **E** [1].

The stereochemistry in each of these complex systems is complicated, involving geometric isomers and internal diastereoisomers, and the relative stabilities of the various geometrically distinct isomers cannot be simply predicted on the basis of steric interactions using molecular models. A molecular mechanics analysis including contributions to molecular potential energies from bond length deformations, valence angle deformations and torsional strains as well as non-bonded interactions (which are all interdependent) provides prospects of rationalizing the stabilities, and this analysis is proceeding [7].

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TABLE 1. Crystal Data and Refinement Details for Complexes A, C and F

	A	C	F
Formula	$C_9H_{34}Br_3CoN_6O_2$	$C_9H_{32}Br_3CoN_6O$	$C_8H_{30}Br_3CoN_6O$
Formula weight	557.1	539.1	525.0
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$ (C_i^1, no. 2)	$Pna2_1$ (C_{2v}^9, no. 33)	$I2/a$ (C_{2h}^6, no. 15)
a (Å)	8.231(2)	12.758(3)	12.626(5)
b (Å)	8.682(1)	11.236(1)	22.977(5)
c (Å)	14.247(2)	13.19(1)	12.619(6)
α (°)	96.84(1)	90	90
β (°)	97.16(2)	90	97.84(4)
γ (°)	99.62(2)	90	90
V (Å^3)	985.7	1890.8	3626.7
Z	2	4	8
ρ_c (g cm^{-3})	1.877	1.894	1.923
F(000)	550	1060	2056
μ (cm^{-1})	68.29	71.15	74.17
Crystal dimensions (mm)	$\pm(100)$ 0.62; $\pm(010)$ 0.22; $\pm(03\bar{2})$ 0.22; $\pm(001)$ 0.30.	$\pm(110)$ 0.32; $\pm(1\bar{1}0)$ 0.32; $\pm(001)$ 0.88.	$\pm(12\bar{1})$ 0.25; $\pm(1\bar{2}\bar{1})$ 0.28; $\pm(101)$ 0.42.
Max./min. transmission factors	0.2985, 0.1282	0.1769, 0.1075	0.2386, 0.1347
Theta limits	1–25	1–25	1–25
Data collected	3869	1995	3480
Unique data	3470	1808	3200
Data with $I \geqslant 2.5\ (I)$	2487	1318	1693
R	0.044	0.040	0.038
g	0.0037	0.0023	0.0033
R_w	0.046	0.041	0.041
ρ_{max} (e Å^{-3})	1.42	0.92	0.97

These various isolated complexes (as racemates) were isomerically pure as demonstrated by their ^{13}C NMR spectra. These spectra, together with considerations of facility of isomeric interconversions and steric crowding of methyl substituents in some instances, have enabled their broad geometries to be deduced. However, their diastereoisomeric arrangements could not be determined, and X-ray structure analyses were necessary therefore for assigning the full molecular configurations to the isolated complexes. We take these isolated isomers to be the most stable in their respective complexes, since they correspond to the isomers present in equilibrated solutions. Also, the isomer ratios in solution, as observed on Sephadex chromatography or by ^{13}C NMR, should reflect their relative stabilities: **C** > **A** > **B** for [Co(meen)$_3$]$^{3+}$ and **H** ≫ **F** > **G** for [Co(meen)$_2$(en)]$^{3+}$ [1]. Comparison of the predictions of relative stabilities from energy minimization with those found experimentally and identified from the present structural results should enable appraisal of the factors which influence coordination of *N*-methyl ethyleneamines like meen [7].

Of the various isomers detected over these three complex systems of meen, only **A**, **C** and **F** were obtained as the bromide salts in crystals which were suitable for X-ray diffraction studies, and the single crystal structure analyses of **A**-[Co(meen)$_3$]Br$_3$·2H$_2$O, **C**-[Co(meen)$_3$]Br$_3$·H$_2$O and **F**-[Co(meen)$_2$(en)]Br$_3$·H$_2$O are now described.

Experimental

Preparation of Crystals

Isomers **A** and **C** of [Co(meen)$_3$]$^{3+}$ were separated chromatographically on SP-Sephadex using Na_2SO_4/H_2SO_4 as eluent. They were obtained from the effluents of the Sephadex bands (1) and (2) respectively as bromide salts by using elution from Dowex cation-exchange resin with 3 M HBr, as described previously [1]. **A** crystallized first from the solution from band (1) (leaving a second, minor isomer **B** in the mother liquor), and band (2) contained C only.

Complex **F**, an isomer of [Co(meen)$_2$(en)]$^{3+}$, was obtained from a preparative mixture containing [Co(meen)$_2$(en)]$^{3+}$, [Co(meen)(en)$_2$]$^{3+}$ and [Co(en)$_3$]$^{3+}$. It occurred in a fourth band, along with a second isomer **G** of [Co(meen)$_2$(en)]$^{3+}$, from a separation on SP-Sephadex with Na_3PO_4 as eluent. This band was rechromatographed so that a slower-moving third isomer **H** was removed as a following band, and the **F** + **G** mixture was isolated as the bromide salt using Dowex/HBr. Crystals of pure **F** were obtained on recrystallization from 0.01 M HBr, leaving the minor component **G** in the mother liquor [1].

Suitable crystals of the complexes for the X-ray analyses were obtained by slow recrystallizations from warm 0.01 M HBr, aided by ethanol vapour diffusion at room temperature.

Crystallography

Intensity data sets for the three isomers were measured at room temperature on an Enraf-Nonius CAD4-F diffractometer, fitted with Mo Kα (graphite monochromator) radiation $\lambda = 0.7107$ Å, with the use of the ω:2θ scan technique. No decomposition of any crystal occurred during its respective data collection. Corrections were applied for Lorentz and polarization effects and for absorption [8a], using an analytical procedure [9]. Crystal data are listed in Table 1.

The structures of isomers **A** and **C** were solved by direct methods using the MULTAN program [10], whereas the structure of complex **F** was solved with SHELXS86 [11]. The structures were each refined by a full-matrix least-squares procedure in which the function $\Sigma w\Delta^2$ was minimized, where $\Delta = ||F_c| - |F_o||$ and w was the weight applied to each reflection [9]. For **C** which crystallized in the acentric space group $Pna2_1$, the origin was arbitrarily fixed by setting $z = 0$ for the Br(1) atom. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the models at their calculated positions. A weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]^{-1}$ was included in each refinement. Final refinement details are given in Table 1. Fractional atomic coordinates for the three complexes are listed in Tables 2–4, and the atom numbering schemes employed are shown in Figs. 1–3 which were drawn with ORTEP [12]. The scattering factors for Co(III) were from ref. 8b and those for the other atoms were as incorporated in SHELX-76 [9].

TABLE 2. Fractional Atomic Coordinates (×10^5 for Br and Co; ×10^4 for remaining atoms) for A-[Co(meen)$_3$]Br$_3$·2H$_2$O

Atom	*x*	*y*	*z*
Br(1)	75516(8)	61950(9)	3759(5)
Br(2)	71761(7)	41912(8)	49027(4)
Br(3)	25097(8)	−5377(10)	80708(5)
Co	−27244(8)	25781(8)	−22125(5)
N(1)	−1195(6)	4509(6)	−1568(3)
N(2)	−1214(5)	2714(5)	−3225(3)
N(3)	−4223(5)	709(5)	−2951(3)
N(4)	−4208(6)	3806(6)	−2907(3)
N(5)	−4091(6)	2608(6)	−1169(3)
N(6)	−1436(6)	1281(6)	−1422(3)
C(1)	−355(8)	5305(7)	−2287(5)
C(2)	217(8)	4025(8)	−2886(5)
C(3)	−638(8)	1299(8)	−3653(5)
C(4)	−5255(7)	1179(8)	−3754(4)
C(5)	−5773(7)	2688(7)	−3382(4)
C(6)	−4709(8)	5221(8)	−2402(5)
C(7)	−3606(7)	1623(8)	−448(4)
C(8)	−1749(7)	1656(8)	−413(4)
C(9)	−1781(8)	−477(8)	−1692(5)
O(1)	−72(7)	2197(7)	3961(4)
O(2)	3318(7)	2088(7)	3965(5)

TABLE 3. Fractional Atomic Coordinates (×10^5 for Br and Co; ×10^4 for remaining atoms) for C-[Co(meen)$_3$]Br$_3$·H$_2$O

Atom	*x*	*y*	*z*
Br(1)	98432(9)	−15801(11)	00000(−)
Br(2)	78048(10)	11824(10)	−20394(15)
Br(3)	−53505(10)	18289(11)	12033(15)
Co	−28952(9)	1309(11)	32497(16)
N(1)	−2950(7)	−1171(9)	4255(7)
N(2)	−1336(6)	−10(7)	3462(8)
N(3)	−2804(8)	1442(9)	2270(8)
N(4)	−2995(7)	1459(8)	4270(8)
N(5)	−2853(8)	−1010(9)	2140(8)
N(6)	−4454(6)	54(8)	3097(7)
C(1)	−1923(9)	−1401(11)	4726(11)
C(2)	−1120(10)	−1207(11)	3932(11)
C(3)	−603(10)	191(12)	2625(11)
C(4)	−2885(9)	2631(9)	2788(11)
C(5)	−2458(9)	2508(10)	3823(8)
C(6)	−2755(10)	1303(12)	5354(9)
C(7)	−3902(10)	−1136(11)	1679(11)
C(8)	−4689(9)	−1046(11)	2527(11)
C(9)	−5184(10)	173(13)	3958(11)
O(1)	−2049(7)	328(10)	369(8)

TABLE 4. Fractional Atomic Coordinates (×10^5 for Br and Co; ×10^4 for remaining atoms) for F-[Co(meen)$_2$(en)]Br$_3$·H$_2$O

Atom	*x*	*y*	*z*
Br(1)	9705(7)	37500(4)	15276(7)
Br(2)	43273(7)	2096(4)	−21227(8)
Br(3)	−46226(7)	27093(4)	18293(7)
Co(a)	25000(−)	−37282(6)	00000(−)
N(1a)	3628(5)	−4327(3)	280(5)
N(2a)	2811(5)	−3754(3)	−1513(5)
N(3a)	1445(5)	−3097(3)	−343(5)
C(1a)	4176(7)	−4397(4)	−675(7)
C(2a)	3368(7)	−4314(3)	−1659(7)
C(3a)	1951(6)	−3671(4)	−2423(7)
C(4a)	2033(6)	−2538(3)	−440(7)
Co(b)	25000(−)	37717(6)	50000(−)
N(1b)	2219(5)	3176(3)	3880(5)
N(2b)	4014(5)	3739(3)	4696(5)
N(3b)	2158(5)	4401(2)	3943(5)
C(1b)	3175(6)	3096(4)	3333(7)
C(2b)	4153(6)	3187(3)	4120(7)
C(3b)	4912(6)	3832(3)	5542(7)
C(4b)	2058(6)	4960(3)	4537(7)
O(1)	2500(−)	4549(4)	0000(−)
O(2)	2500(−)	2958(4)	0000(−)

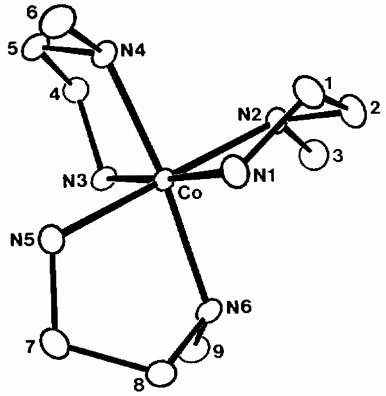


Fig. 1. Molecular structure and numbering scheme employed for $[Co(meen)_3]^{3+}$, isomer **A**. Atoms not otherwise indicated are carbons.

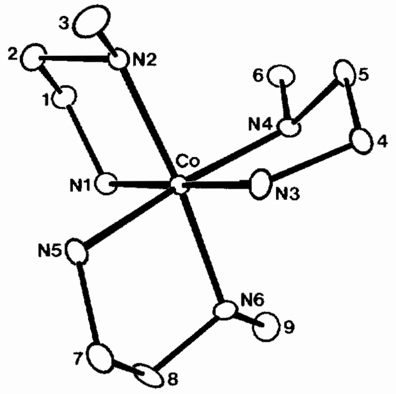


Fig. 2. Molecular structure and numbering scheme employed for $[Co(meen)_3]^{3+}$, isomer **C**. Atoms not otherwise indicated are carbons.

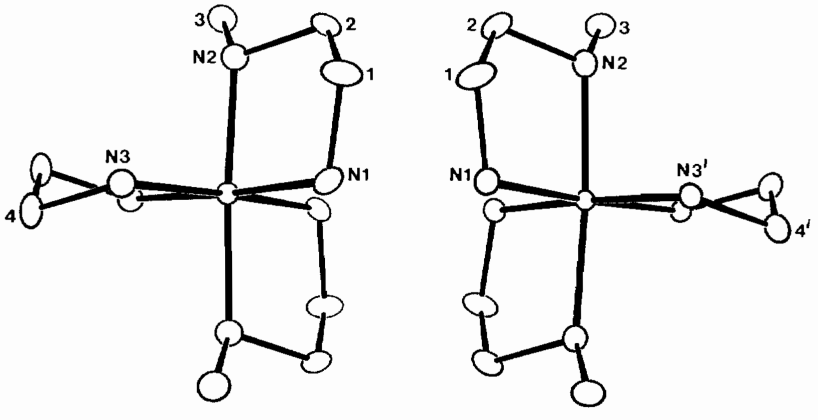
Results and Discussion

Molecular Structures

The three complexes **A**, **C** and **F** are characterized by slightly distorted octahedral Co(III) geometries each defined by six nitrogen atoms derived from three chelating ligands. The Co–N bond distances fall into two groups, the $Co-N(CH_3)$ bonds being longer than the $Co-NH_2$ bonds by an average 0.04 Å which may account, in part, for the above distortion from the ideal octahedral geometry. Bond distances and angles for the complexes are listed in Tables 5–8 and show no unusual features.

TABLE 5. Bond Distances (Å) for Isomers **A**- and **C**-$[Co(meen)_3]^{3+}$

Atoms	Isomer A	Isomer C
Co–N(1)	1.969(4)	1.98(1)
Co–N(2)	2.020(4)	2.015(8)
Co–N(3)	1.965(4)	1.96(1)
Co–N(4)	1.998(5)	2.01(1)
Co–N(5)	1.973(5)	1.95(1)
Co–N(6)	2.017(5)	2.000(8)
N(1)–C(1)	1.480(7)	1.47(1)
C(1)–C(2)	1.494(9)	1.48(2)
N(2)–C(2)	1.481(7)	1.51(1)
N(2)–C(3)	1.481(7)	1.46(2)
N(3)–C(4)	1.477(7)	1.51(2)
C(4)–C(5)	1.501(9)	1.48(2)
N(4)–C(5)	1.506(7)	1.49(1)
N(4)–C(6)	1.493(7)	1.47(2)
N(5)–C(7)	1.473(8)	1.48(2)
C(7)–C(8)	1.518(8)	1.51(2)
N(6)–C(8)	1.499(7)	1.48(2)
N(6)–C(9)	1.498(8)	1.48(2)



Molecule a, Λ Molecule b, Δ

Fig. 3. Molecular structure and numbering scheme employed for the two molecules comprising the asymmetric unit for $[Co(meen)_2(en)]^{3+}$, complex **F**. The molecules have been arbitrarily aligned to emphasise their pseudo-mirror relationship. Molecule a is that of configuration Λ on the left of the diagram. Atoms not otherwise indicated are carbons.

TABLE 6. Bond Angles (°) for Isomers A- and C-[Co-(meen)$_3$]$^{3+}$

Atoms	Isomer A	Isomer C
N(1)–Co–N(2)	83.9(2)	83.3(4)
N(1)–Co–N(3)	175.5(2)	178.3(4)
N(1)–Co–N(4)	92.4(2)	95.6(4)
N(1)–Co–N(5)	91.5(2)	91.0(4)
N(1)–Co–N(6)	89.7(2)	90.0(4)
N(2)–Co–N(3)	92.4(2)	95.3(4)
N(2)–Co–N(4)	90.4(2)	91.6(4)
N(2)–Co–N(5)	175.4(2)	91.5(4)
N(2)–Co–N(6)	95.9(2)	172.7(3)
N(3)–Co–N(4)	85.1(2)	83.6(4)
N(3)–Co–N(5)	92.2(2)	89.8(4)
N(3)–Co–N(6)	93.2(2)	91.4(4)
N(4)–Co–N(5)	89.5(2)	173.0(4)
N(4)–Co–N(6)	173.5(2)	92.1(4)
N(5)–Co–N(6)	84.3(2)	85.6(4)
Co–N(1)–C(1)	109.2(4)	112.5(7)
Co–N(2)–C(2)	108.9(3)	107.9(7)
Co–N(2)–C(3)	121.1(4)	120.9(8)
Co–N(3)–C(4)	109.9(4)	111.3(8)
Co–N(4)–C(5)	108.4(3)	107.1(7)
Co–N(4)–C(6)	121.0(4)	123.2(8)
Co–N(5)–C(7)	112.5(4)	110.3(8)
Co–N(6)–C(8)	106.7(3)	106.8(7)
Co–N(6)–C(9)	118.6(4)	123.1(8)
N(1)–C(1)–C(2)	105.1(5)	107(1)
C(1)–C(2)–N(2)	108.9(5)	107.2(9)
C(2)–N(2)–C(3)	110.5(5)	109.3(9)
N(3)–C(4)–C(5)	107.2(5)	108.1(9)
C(4)–C(5)–N(4)	106.8(4)	105.8(9)
C(5)–N(4)–C(6)	107.8(4)	112.6(9)
N(5)–C(7)–C(8)	107.1(4)	107(1)
C(7)–C(8)–N(6)	107.2(4)	107.4(9)
C(8)–N(6)–C(9)	108.5(5)	109.8(9)

TABLE 7. Bond Distances (Å) for F-[Co(meen)$_2$(en)]$^{3+}$

Atoms	Molecule a	Molecule b
Co–N(1)	1.976(6)	1.965(6)
Co–N(2)	2.001(7)	2.002(6)
Co–N(3)	1.976(6)	1.975(6)
N(1)–C(1)	1.48(1)	1.48(1)
C(1)–C(2)	1.51(1)	1.49(1)
N(2)–C(2)	1.490(9)	1.484(9)
N(2)–C(3)	1.481(9)	1.46(1)
N(3)–C(4)	1.50(1)	1.500(9)
C(4)–C(4′)	1.51(2)	1.50(2)

TABLE 8. Bond Angles (°) for F-[Co(meen)$_2$(en)]$^{3+}$

Atoms	Molecule a	Molecule b
N(1)–Co–N(2)	85.4(3)	85.4(3)
N(1)–Co–N(3)	175.7(3)	91.4(3)
N(1)–Co–N(1′)	91.8(3)	91.7(3)
N(1)–Co–N(2′)	92.3(3)	91.6(3)
N(1)–Co–N(3′)	91.4(3)	175.9(3)
N(2)–Co–N(3)	91.5(3)	91.4(3)
N(2)–Co–N(2′)	176.7(3)	175.7(3)
N(2)–Co–N(3′)	90.9(3)	91.7(3)
N(3)–Co–N(1′)	91.4(3)	175.9(3)
N(3)–Co–N(3′)	85.6(3)	85.8(3)
Co–N(1)–C(1)	109.7(5)	110.0(5)
Co–N(2)–C(2)	107.5(5)	107.8(5)
Co–N(2)–C(3)	121.2(5)	121.4(5)
Co–N(3)–C(4)	108.7(4)	108.3(4)
C(2)–N(2)–C(3)	108.9(6)	110.5(6)
N(1)–C(1)–C(2)	108.6(6)	109.0(7)
N(2)–C(2)–C(1)	106.5(6)	107.7(6)
N(3)–C(4)–C(4′)	106.8(6)	106.5(7)

In each of **A** and **C** there is no crystallographically imposed symmetry on the individual complex cations. In **F**, however, the two molecules comprising the asymmetric unit lie on crystallographic two-fold axes; the pseudo-*m* relationship between the two molecules, designated a and b, is clearly seen from Fig. 3. The asymmetric unit for **F** also contains three bromide anions in general positions and two water molecules of crystallization which each lie on a crystallographic two-fold axis; the overall stoichiometry of the asymmetric unit for **F** is [Co(meen)$_2$(en)]-Br$_3$·H$_2$O. Crystals of **A** and **F** contain both Λ and Δ enantiomers of the complex cations in their respective unit cells. However, complex **C** crystallizes in the acentric space group *Pna*2$_1$, which shows it to be an example of the less frequently observed phenomenon of spontaneous resolution by crystallization [13, 14].

Crystal Structures

The complexes **A**, **C** and **F** were crystallized as di-, mono-, and mono-hydrates respectively. These solvent molecules, along with the complex cations and bromide anions, contribute to complicated hydrogen-bonding networks in these salts. Each of the nitrogen bound hydrogen atoms in the cations participates in hydrogen bonding contacts to either bromide anions or water molecules. As a generalization, it can be stated that each N–H group interacts with one bromide anion at N...Br distances in the range 3.3–3.6 Å. Exceptions (or elaborations) to this generalization: in complex **A** there is a N(3)–H...O(2) contact with N...O of 2.82 Å (rather than a N(3)–H...Br contact), and N(5)–H interacts with two (rather than one) bromide anions at 3.53 and 3.54 Å. The water molecules are separated at 2.82 Å from each other and each participates in three other contacts. Thus O(1) is separated from N(3)–H, Br(2) and Br(2′) at 2.92, 3.39 and 3.55 Å respectively, and similarly O(2) is 3.34, 3.39 and 3.67 Å from Br(2), Br(2′) and Br(3) respectively. The bromide anion environments in complex **A** are Br(1)N$_5$, Br(2)N$_2$O$_4$

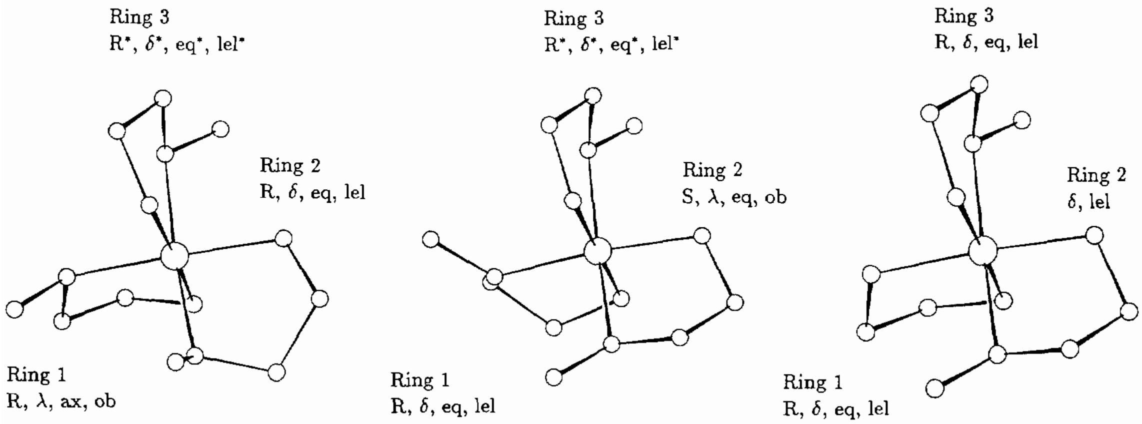


Fig. 4. Structures of complexes **A**, **C** and **F** as Λ enantiomers viewed at the same angle to the CoNN plane of their common ring (ring 3), with stereochemical parameters *R*/*S*, λ/δ, *equatorial*/*axial*, *lel*/*ob* shown.

and $Br(3)N_2O$. In complex **C** there is a contact of 2.98 Å between N(3) and O(1) and similarly a contact of 2.95 Å between N(5) and O(1); the two other contacts for O(1) are 3.32 and 3.34 Å with Br(1) and Br(2) respectively. Both the Br(1) and Br(2) atoms exist in BrN_2O geometries. In complex **F** a N(1)–H...O(1) contact of 2.96 Å is found (and similarly for molecule b). The water molecules have crystallographic two-fold symmetry and each makes four contacts, *i.e.* two with N(1)–H of 2.96 Å and two with Br(1) of 3.44 Å. There are three distinct bromide atom environments in the structure with the geometries $Br(1)N_4O_2$, $Br(2)N_2$ and $Br(3)N_2$.

Assignment of Stereochemistries

It is evident from Figs. 1–3 that the complexes have one ring of corresponding stereochemistry, this being characterized by the parameters asymmetric nitrogen configuration *R*, conformation δ, and methyl disposition equatorial. Figure 4 shows the three complexes (as their Λ enantiomers) viewed at the same angle to the CoNN plane of this common ring, which is designated ring 3.

On coordination, a meen ligand becomes asymmetric, by 'donor atom asymmetry', and the alternative ring conformations λ and δ are not equivalent because of the different dispositions equatorial or axial of the methyl substituent, and also because of different inter-ring interactions. For each complex a number of geometrically distinct isomers is possible, comprising geometric isomers and internal diastereoisomers, and these should in principle be distinguishable chromatographically and by NMR. (Ring conformational interconversions are presumed to be facile [15, 16], so that different conformations are not distinguishable by these means). These various geometric possibilities for the three complex systems of meen (along with the conformational possibilities) have been elaborated previously [1], and their numbers are as follows:

$[Co(meen)_3]^{3+}$: four for the *facial* geometry; eight for the *meridional*.

$[Co(meen)_2(en)]^{3+}$: four for the *cis*-CH_3, *cis*-NH_2 geometry; three for *cis*-CH_3, *trans*-NH_2; three for *trans*-CH_3, *cis*-NH_2.

$[Co(meen)(en)_2]^{3+}$: two diastereoisomers only.

Only three geometric isomers–diastereoisomers of $[Co(meen)_3]^{3+}$ were detected in aqueous solution, and the designations **A**, **B** and **C** refer to their chromatographic elution order down Sephadex cation-exchange resin with eluent Na_2SO_4/H^+. Their facile interconversions in neutral aqueous solution indicated them to be diastereoisomers of the one geometry, which was deduced to be *mer* from their C_1 symmetries (^{13}C NMR) and from the lesser steric crowdings of the methyls in this geometry [1]. This deduction is confirmed by the present X-ray structural results for **A** and **C**, which show the particular diastereoisomers and conformers in the solid state to be as follows (only one enantiomer of the racemate is specified):

A = Λ-*mer*-$[Co(meen)_3]Br_3 \cdot 2H_2O$-*RRR**-λδδ*

C = Λ-*mer*-$[Co(meen)_3]Br_3 \cdot H_2O$-*RSR**-δλδ*

The stereochemical parameters *R*/*S* and λ/δ have to be specified for the three rings in a particular order, which is defined to be clockwise when the molecule is viewed along the pseudo-C_3 axis such that the single methyl group at one end of the axis is remote from the viewer. The parameters relating to this unique ring are asterisked [1].

The three isomers of $[Co(meen)_2(en)]^{3+}$ detected in an equilibrium solution (charcoal) are designated **F**, **G** and **H** according to their chromatographic elution order on Sephadex with the eluent Na_3PO_4. These were single geometric isomers–diastereoisomers by ^{13}C NMR, and their independence in the basic eluent indicated them to be of the three different geometries *cis*-CH_3, *cis*-NH_2, *cis*-CH_3, *trans*-NH_2 and *trans*-CH_3, *cis*-NH_2. **G** was assigned as the most stable diastereoisomer (unknown) in the *cis*-CH_3, *cis*-NH_2 geometry from its C_1 symmetry by ^{13}C NMR, but the particular geometries of **F** and **H**, which were each of C_2 symmetry, could not be assigned. **F** is now shown to be

F = Λ-*trans*-CH_3, *cis*-NH_2-[Co(meen)$_2$(en)]$Br_3 \cdot$
H_2O-*RR*-δδδ

It now follows that the most predominant isomer **H** has the geometry *cis*-CH_3, *trans*-NH_2, and that it must be one of the C_2-symmetry diastereoisomers Λ-*RR* or Λ-*SS*.

Figure 4 highlights the structural relationships between the three complexes, for the same configuration Λ. The rings 3 are the same in the broad stereochemical sense with parameters *R**, δ*, *eq**, *lel** (although these rings show actual small differences due to crystallographic effects). The rings 1 have corresponding stereochemistries in complexes **C** and **F**, and differing from that in ring 1 in **A**. Further, ring 2 has the same conformation δ in **A** and **F** (although ring 2 in **F** lacks the methyl substituent), but is different to ring 2 in **C** which is λ.

It is notable that over these three structures there are two stereochemical features which predominate: the ring conformation arrangements are *lel* (δ for Λ, λ for Δ), and the methyl dispositions are *equatorial* (*R*δ or *S*λ) [1]. This is not surprising from the completely stereospecific coordination of propane-1,2-diamine (pn) to Co(III) [17]. However, there are deviations from these features with **A** and **C**, so that *axial* methyl occurs with one ring in **A**, and the *ob* arrangement occurs with one ring in each of **A** and **C**; the deviant ring in **A** is both *axial* and *ob*. The experimental energy differences between the three $[Co(meen)_3]^{3+}$ isomers is small (equilibrium ratio **A**:**B**:**C** in solution *ca.* 3:1:2), emphasizing that the effects of *lel*/*ob* and *equatorial*/*axial* characters in determining the stabilities of molecular structures are considerably smaller than in the analogous pn systems [17]. Each diastereoisomer **A**, **B** or **C** should therefore exist in solution as a mixture of conformers.

Supplementary Material

Tables of thermal parameters, hydrogen-atom parameters, and structure factor amplitudes are available from the authors on request.

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