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[*N,N*-Bis(2-aminoethyl)-*N'*-(2-aminoethylidene)ethane-1,2-diamine]chlorocobalt(III) Perchlorate

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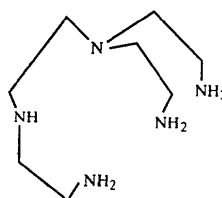
Abstract

The structure of the title compound, [CoCl(C₈H₂₁N₅)₂][ClO₄], consists of octahedral [Co(trenenim)Cl]²⁺ cations [where trenenim = *N,N*-bis(2-aminoethyl)-*N'*-(2-aminoethylidene)ethane-1,2-diamine] with two perchlorate anions acting as counterions. The bond lengths and angles about N(2) and C(3) provide clear evidence for the presence of an imine bond. A short Co—N(2) distance of 1.863 (2) Å reflects the fact that this N atom is an imine N atom. The corresponding Co—N distance in the related saturated system [Co(trenen)Cl]²⁺ [where trenen = *N,N,N'*-tris-

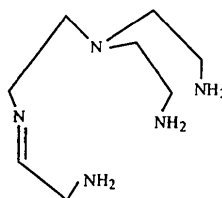
(2-aminoethyl)ethane-1,2-diamine] is also substantially shorter than the others. In both cases, the secondary N atom on the appended arm has a stronger affinity for Co^{III} than the primary and tertiary N atoms within the ligand framework.

Comment

The coordination chemistry of pentadentate ligands has attracted our attention because these ligands can be applied in the synthesis of binuclear complexes linked by a single bridging group. We have recently reported the synthesis and X-ray structure of [Co(trenen)Cl]Cl(ClO₄)₂·H₂O (Gatehouse, Martin, McLachlan, Platts & Spiccia, 1992) and the peroxo-bridged complex [(trenen)CoO₂Co(trenen)](ClO₄)₄ (Gatehouse, McLachlan, Martin, Martin & Spiccia, 1991), where trenen is the pentadentate ligand, *N,N,N'*-tris(2-aminoethyl)ethane-1,2-diamine (1). In these complexes, the disposition of the ligand is such that the Cl and O atoms from the peroxide bridge are *trans* to the secondary N atom. A further feature of these complexes is the short Co—N(secondary) distance compared with the other Co—N distances. We report here the X-ray structure of [Co(trenenim)Cl](ClO₄)₂, where trenenim is *N,N*-bis(2-aminoethyl)-*N'*-(2-aminoethylidene)ethane-1,2-diamine (2). This structure is of interest because the complex is the precursor to [Co(trenen)Cl]²⁺ (Gatehouse *et al.*, 1992) and [(trenen)CoO₂Co(trenen)]⁴⁺ (Gatehouse *et al.*, 1991).



(1) trenen



(2) trenenim

Fig. 1 shows the structure of the complex cation [Co(trenenim)Cl]²⁺ and the perchlorate counter ions. The primary coordination sphere of the Co^{III} atom comprises five N atoms from the trenenim ligand and one Cl atom. As in the previously reported peroxo and chloro complexes of trenen (Gatehouse *et al.*, 1991; Gatehouse *et al.*, 1992), the chloro ligand is *trans* to the secondary N atom because the ligand

is generated by template synthesis around the inert Co^{III} . The presence of the imine moiety is clear from the short $\text{N}(2)\text{—C}(3)$ distance of 1.268 (5) Å, which is much shorter than any other C—N distance (> 1.45 Å). The $\text{Co—N}(2)$ distance of 1.863 (2) Å is also much shorter than the other Co—N distances [average 1.964 (8) Å]. In addition, the three bond angles about the imine N atom, $\text{Co—N}(2)\text{—C}(2)$, $\text{Co—N}(2)\text{—C}(3)$ and $\text{C}(2)\text{—N}(2)\text{—C}(3)$, are all close to 120° (and total 360°) as is the $\text{N}(2)\text{—C}(3)\text{—C}(4)$ angle. This confirms the planarity of the imine moiety. The bite angle of $83.1(1)^\circ$ in the five-membered chelate ring containing the imine is smaller than those of all the other chelate rings [average $86.4(5)^\circ$]; this is a reflection of the rigidity introduced by the imine bond. It is interesting to note that the bite angles for complexes of the fully saturated derivative trenen are remarkably constant: $86.0(9)^\circ$ for $[(\text{trenen})\text{CoO}_2\text{Co}(\text{trenen})]^{4+}$ (Gatehouse *et al.*, 1991), $86.2(8)^\circ$ for $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$ (Gatehouse *et al.*, 1992) and $86(1)^\circ$ for $[\text{Co}(\text{trenen})\text{N}_3]^{2+}$ (Maxwell, 1971).

The $\text{Co—N}(2)$ distance is substantially shorter than the mean Co—imine bond distance of 1.916 (9) Å in reported cobalt(III) complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). For example, the Co—imine bond distance in the (α -amino- γ -amino- α -methylvaleric acid)triamminecobalt(III) ion is 1.943 Å (Tucker, 1979). Thus, the imine N atom is more strongly attached to the Co^{III} centre than might have been expected on the basis of previously reported Co—imine distances. In fact, for $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$ (Gatehouse *et al.*, 1992) and $[(\text{trenen})\text{CoO}_2\text{Co}(\text{trenen})]^{4+}$ (Gatehouse *et al.*, 1991), the $\text{Co—N}(\text{secondary})$ bond distances are significantly shorter than other Co—N distances. Thus, the short $\text{Co—N}(\text{secondary})$ bond is either a feature of this pentadentate ligand system or, alternatively, is related to the fact that weak-field ligands occupy the positions *trans* to this N atom.

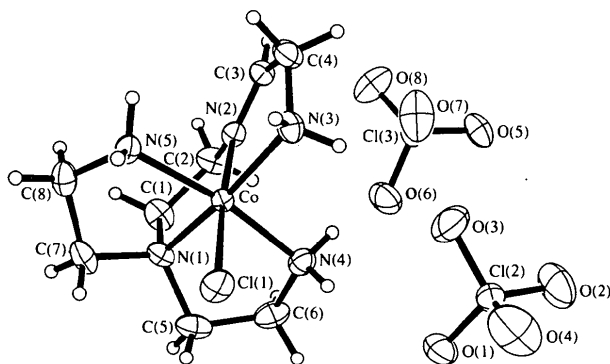


Fig. 1. Structure of $[\text{Co}(\text{trenenim})\text{Cl}](\text{ClO}_4)_2$, showing the stereochemistry of the $[\text{Co}(\text{trenenim})\text{Cl}]^{2+}$ cation. Displacement ellipsoids are shown at the 40% probability level.

Experimental

$[\text{Co}(\text{tren})\text{Cl}_2]\text{Cl}$ and $[\text{Co}(\text{tren})(\text{NH}_2\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_3)\text{Cl})\text{Cl}(\text{ClO}_4)]$ and aqueous solutions containing a mixture of $[\text{Co}(\text{trenenim})\text{OH}_2]^{3+}$ and $[\text{Co}(\text{trenenim})\text{Cl}]^{2+}$ were all prepared by literature methods (Golding, Harrowfield & Sargeson, 1974; Buckingham, Cresswell & Sargeson, 1975; Engelhardt *et al.*, 1988). Cation-exchange chromatography of the mixture of trenenim complexes gave two major fractions on elution with dilute HCl. Evaporation of these fractions gave a red complex which was analysed as $[\text{Co}(\text{trenenim})\text{Cl}]\text{Cl}_2$ (yield 10%) and an orange complex which was analysed as $[\text{Co}(\text{trenenim})\text{OH}_2]\text{Cl}(\text{ClO}_4)_2$ (yield 50%). The elemental analyses, molar conductivity and visible spectra were in agreement with literature reports (Gatehouse *et al.*, 1991).

In order to obtain crystalline salts of $[\text{Co}(\text{trenenim})\text{Cl}](\text{ClO}_4)_2$, the aquo complex $[\text{Co}(\text{trenenim})\text{OH}_2]\text{Cl}(\text{ClO}_4)_2$ was dissolved in 2M HCl and the solution evaporated to dryness under vacuum leaving a residue which was recrystallized from a minimum amount of hot water. Small red-orange crystals suitable for X-ray diffraction studies were grown by slow evaporation of an aqueous solution of the complex. Density D_m was measured by flotation in $\text{CCl}_4/\text{C}_2\text{H}_2\text{Br}_4$.

Crystal data

$[\text{CoCl}(\text{C}_8\text{H}_{21}\text{N}_5)]_2\text{ClO}_4$
 $M_r = 480.6$
 Monoclinic
 $P2_1/c$
 $a = 12.615(3)$ Å
 $b = 11.408(2)$ Å
 $c = 11.990(3)$ Å
 $\beta = 98.78(1)^\circ$
 $V = 1705.2(7)$ Å³
 $Z = 4$
 $D_x = 1.87$ Mg m⁻³
 $D_m = 1.88(1)$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 24 reflections
 $\theta = 10\text{--}18^\circ$
 $\mu = 1.53$ mm⁻¹
 $T = 293$ K
 Prismatic
 $0.40 \times 0.26 \times 0.22$ mm
 Red-orange

Data collection

Philips PW1100 diffractometer
 ω scans
 Absorption correction: analytical (SHELX; Sheldrick, 1976)
 $T_{\text{min}} = 0.694$, $T_{\text{max}} = 0.767$
 5408 measured reflections
 4965 independent reflections

3104 observed reflections
 $[|F_o| \geq 6\sigma(|F_o|)]$
 $R_{\text{int}} = 0.0281$
 $\theta_{\text{max}} = 30^\circ$
 $h = -17 \rightarrow 17$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 16$
 3 standard reflections
 frequency: 240 min
 intensity variation: none

Refinement

Refinement on F
 $R = 0.038$
 $wR = 0.038$
 $S = 1.652$
 3104 reflections
 227 parameters
 Only H-atom U 's refined
 $w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.88$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U _{eq}
Co	0.28216 (3)	0.03943 (3)	0.31612 (3)	0.0212 (1)
Cl(1)	0.43823 (7)	0.12910 (8)	0.38924 (7)	0.0386 (3)
Cl(2)	0.26654 (6)	0.47159 (7)	0.22988 (7)	0.0334 (2)
Cl(3)	-0.02847 (7)	0.20454 (8)	0.10086 (7)	0.0369 (2)
C(1)	0.2486 (3)	-0.1447 (3)	0.1530 (3)	0.0385 (11)
C(2)	0.1396 (3)	-0.0915 (3)	0.1589 (3)	0.0405 (12)
C(3)	0.0691 (3)	0.0035 (3)	0.3113 (3)	0.0323 (10)
C(4)	0.0931 (3)	0.0835 (3)	0.4097 (3)	0.0395 (12)
C(5)	0.3956 (3)	-0.0031 (4)	0.1401 (3)	0.0452 (14)
C(6)	0.3216 (3)	0.0956 (4)	0.0939 (3)	0.0476 (15)
C(7)	0.4122 (3)	-0.1529 (3)	0.2943 (3)	0.0388 (11)
C(8)	0.3545 (5)	-0.1875 (3)	0.3902 (3)	0.0376 (12)
N(1)	0.3390 (2)	-0.0734 (2)	0.2179 (2)	0.0290 (8)
N(2)	0.1475 (2)	-0.0223 (2)	0.2613 (2)	0.0246 (7)
N(3)	0.1995 (2)	0.1382 (2)	0.4063 (2)	0.0331 (9)
N(4)	0.2734 (2)	0.1480 (2)	0.1882 (2)	0.0324 (9)
N(5)	0.3108 (2)	-0.0793 (2)	0.4364 (2)	0.0294 (8)
O(1)	0.3235 (2)	0.4060 (2)	0.1538 (2)	0.0497 (10)
O(2)	0.1896 (3)	0.5447 (3)	0.1646 (3)	0.0720 (13)
O(3)	0.2140 (3)	0.3923 (3)	0.2948 (3)	0.0723 (14)
O(4)	0.3387 (3)	0.5424 (3)	0.3033 (3)	0.0897 (14)
O(5)	-0.0937 (2)	0.2930 (2)	0.0432 (2)	0.0485 (9)
O(6)	0.0597 (2)	0.1806 (3)	0.0407 (3)	0.0584 (11)
O(7)	0.0141 (3)	0.2425 (3)	0.2125 (2)	0.0701 (12)
O(8)	-0.0894 (3)	0.1004 (3)	0.1045 (3)	0.0675 (12)

Table 2. Selected geometric parameters (Å, °)

Co—Cl(1)	2.2725 (9)	N(3)—C(4)	1.486 (5)
Co—N(1)	1.954 (3)	C(5)—C(6)	1.512 (6)
Co—N(2)	1.863 (2)	N(4)—C(6)	1.488 (5)
Co—N(3)	1.968 (3)	C(7)—C(8)	1.505 (6)
Co—N(4)	1.962 (3)	N(5)—C(8)	1.493 (4)
Co—N(5)	1.971 (3)	Cl(2)—O(1)	1.452 (3)
N(1)—C(1)	1.516 (4)	Cl(2)—O(2)	1.421 (3)
N(1)—C(5)	1.492 (5)	Cl(2)—O(3)	1.422 (4)
N(1)—C(7)	1.502 (4)	Cl(2)—O(4)	1.418 (4)
C(1)—C(2)	1.515 (5)	Cl(3)—O(5)	1.414 (3)
N(2)—C(2)	1.450 (5)	Cl(3)—O(6)	1.441 (3)
N(2)—C(3)	1.268 (5)	Cl(3)—O(7)	1.431 (3)
C(3)—C(4)	1.486 (5)	Cl(3)—O(8)	1.419 (3)
Cl(1)—Co—N(1)	98.8 (1)	Co—N(2)—C(3)	118.7 (2)
Cl(1)—Co—N(2)	174.6 (1)	C(2)—N(2)—C(3)	124.7 (3)
Cl(1)—Co—N(3)	91.8 (1)	N(2)—C(3)—C(4)	116.0 (3)
Cl(1)—Co—N(4)	87.7 (1)	C(3)—C(4)—N(3)	108.2 (3)
Cl(1)—Co—N(5)	88.6 (1)	Co—N(3)—C(4)	109.3 (2)
N(1)—Co—N(2)	86.4 (1)	N(1)—C(5)—C(6)	107.6 (3)
N(1)—Co—N(3)	169.4 (1)	C(5)—C(6)—N(4)	108.8 (3)
N(1)—Co—N(4)	85.8 (1)	Co—N(4)—C(6)	111.1 (2)
N(1)—Co—N(5)	86.9 (1)	N(1)—C(7)—C(8)	107.5 (3)
N(2)—Co—N(3)	83.1 (1)	C(7)—C(8)—N(5)	108.4 (3)
N(2)—Co—N(4)	91.3 (1)	Co—N(5)—C(8)	109.5 (2)
N(2)—Co—N(5)	93.1 (1)	O(1)—Cl(2)—O(2)	108.5 (2)
N(3)—Co—N(4)	95.6 (1)	O(1)—Cl(2)—O(3)	109.5 (2)
N(3)—Co—N(5)	92.6 (1)	O(1)—Cl(2)—O(4)	110.5 (2)
N(4)—Co—N(5)	171.1 (1)	O(2)—Cl(2)—O(3)	109.8 (2)
Co—N(1)—C(1)	110.2 (2)	O(2)—Cl(2)—O(4)	109.1 (2)
Co—N(1)—C(5)	106.1 (2)	O(3)—Cl(2)—O(4)	109.4 (2)
Co—N(1)—C(7)	106.2 (2)	O(5)—Cl(3)—O(6)	109.1 (2)
C(1)—N(1)—C(5)	111.2 (3)	O(5)—Cl(3)—O(7)	110.4 (2)
C(1)—N(1)—C(7)	109.4 (3)	O(5)—Cl(3)—O(8)	109.6 (2)
C(5)—N(1)—C(7)	113.5 (3)	O(6)—Cl(3)—O(7)	108.5 (2)
N(1)—C(1)—C(2)	112.2 (3)	O(6)—Cl(3)—O(8)	108.6 (2)
C(1)—C(2)—N(2)	108.2 (3)	O(7)—Cl(3)—O(8)	110.6 (2)
Co—N(2)—C(2)	116.5 (2)		

Intensity data were processed as described previously (Fallon & Gatehouse, 1980). The atomic scattering factors for neutral atoms were corrected for anomalous dispersion by using values from Ibers & Hamilton (1984). All calculations were performed on a VAX 11/780 computer. The program used for

least-squares refinement was *SHELX76* (Sheldrick, 1976). The structure was solved by direct methods. Refinement was by full-matrix least-squares employing anisotropic displacement parameters for all non-H atoms and a single isotropic displacement parameter for H atoms positioned in geometrically idealized positions, which refined to 0.043 (2) Å² (C—H 0.96, N—H 0.90 Å).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: OH1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro[(1-methyl-2-imidazolyl-κN³-methyl)-bis(2-pyridyl-κN-methyl)amine-κN]copper(II) Hexafluorophosphate, [CuCl(C₁₇H₁₉N₅)]PF₆

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Abstract

The coordination polyhedron of the Cu^{II} ion in the title compound is best described as a distorted trigo-