

with hard acids (class *a* metals) (Pearson, 1963; Ahrland, Chatt & Davies, 1958). Cu^{II} is on the borderline between hard and soft (Yingst & McDaniel, 1967), thus, the nature of the other ligands attached to it has a very great effect on the coordination behaviour of the thiocyanato group (Wu & Chung, 1986; Bennett, Clark & Goodwin, 1967). It is interesting that a thiocyanato group is bonded to a Cu^{II} ion through the S atom in four Cu^{II} complexes of open-chain tetraamines (Wu & Chung, 1986; Marongiu, Lingafelter & Paoletti, 1969); however, in this complex, the two isothiocyanato groups are bonded in Cu^{II} through the N atoms.

The basicity of the polydentate ligand has a very important effect on the coordination behaviour of the thiocyanato group. It has been suggested (Burmeister & Basolo, 1964) that the bonding $M\text{—SCN}$ is stabilized by π bonding which is formed between the *d* electrons of the metal and an empty antibonding π orbital located on the S atom of the thiocyanato group. The availability of the metal *d* electrons for $M\text{—SCN}$ π bonding will, however, be increased by the basicity of the other ligands (Bertini & Sabatini, 1966). A structural change from N-bonded to S-bonded thiocyanates may therefore be expected if the basicity of the polydentate organic ligand is increased.

The authors thank the National Science Council for support in the form of both a research grant NSC80-0208-M007-99 and the use of the Nonius CAD-4 diffractometer. They are also indebted to Miss Shu-Fang Tung for collecting the diffraction data.

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Acta Cryst. (1992). **C48**, 271–274

Structure of *N,N*-Bis(2-aminoethyl)diethylenetriamine(chloro)cobalt(III) Chloride Perchlorate Hydrate

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(Received 20 May 1991; accepted 2 August 1991)

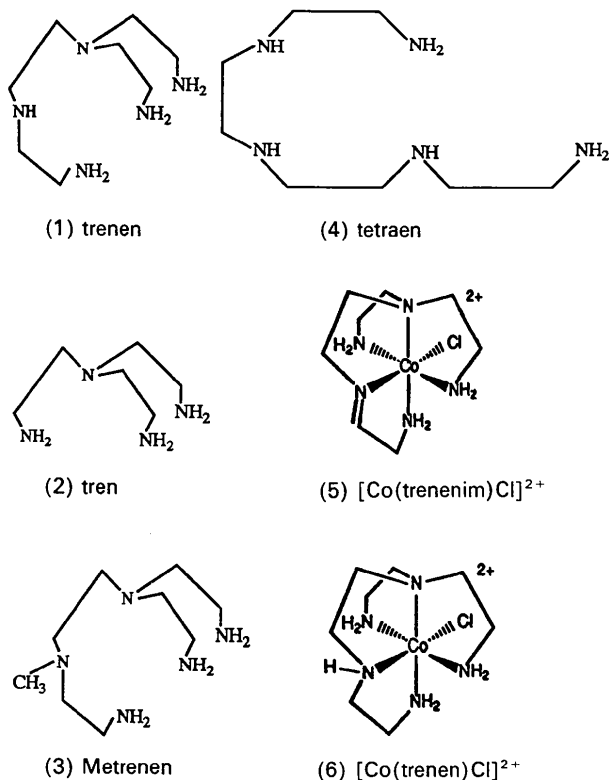
Abstract. $[\text{Co}(\text{C}_8\text{H}_{23}\text{N}_5)\text{Cl}]\text{Cl}(\text{ClO}_4)\cdot\text{H}_2\text{O}$, $M_r = 436.6$, monoclinic, $P2_1/n$, $a = 14.769$ (3), $b = 13.558$ (1), $c = 9.056$ (2) Å, $\beta = 105.281$ (3)°, $V = 1749$ (1) Å³, $Z = 4$, $D_m = 1.66$ (1), $D_x = 1.658$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 14.67$ cm⁻¹, $F(000) = 904$, $T = 293$ K, final $R = 0.046$ for 5092 counter-measured reflections. The structure consists of octahedral cations $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$ with one chloride and one perchlorate ion together with one water molecule involved in hydrogen bonding in the gross structure. The mean Co—N distance is 1.960 (18) and Co—Cl is 2.267 (1) Å. The Co—

N(sec) distance [1.932 (3) Å] is significantly shorter than the other Co—N distances and indicates stronger binding to the secondary N atom.

Introduction. Recently Gatehouse, McLachlan, Martin, Martin & Spiccia (1991) reported the synthesis, properties and X-ray structure of the peroxo-bridged Co^{III} complex, $[(\text{trenen})\text{CoO}_2\text{Co}(\text{trenen})](\text{ClO}_4)_4$, where $\text{trenen} = N,N,N'$ -tris(2-aminoethyl)ethane-1,2-diamine (1). An interesting structural feature of this complex is the short Co—N distance *trans* to the bridging peroxo group, *viz.* 1.928 (6) Å compared with the average Co—N distance of 1.952 (21) Å. This is unusual for peroxo-bridged

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complexes where, in general, it is found that Co—N(*trans*) is longer than Co—N(*av*) because of the large *trans* influence of the bridging peroxy group. To understand further the origin of the short Co—N(*trans*) distance, the structure of [Co(trenen)Cl]²⁺ has been determined and is reported here.



Experimental. The following precursors were used in the preparation of [Co(trenen)Cl]Cl(ClO₄).H₂O: [Co(tren)Cl₂]Cl, *p*-[Co(tren){NH₂CH₂CH(OCH₂-CH₃)₂}Cl]Cl(ClO₄) and [Co(trenenim)Cl]Cl₂ (5), where tren = tris(2-aminoethyl)amine and trenenim = *N,N*-bis(2-aminoethyl)-*N'*-(2-aminoethylidene)ethane-1,2-diamine. All these complexes were prepared by literature methods (Golding, Harrowfield & Sargeson, 1974; Buckingham, Cresswell & Sargeson, 1975; Engelhardt, Gainsford, Gainsford, Golding, Harrowfield, Herlt, Sargeson & White, 1988) with the exception that the imine complex was purified using ion-exchange chromatography. The product was eluted with hydrochloric acid and on work-up was obtained as the chloride salt rather than the perchlorate reported in the literature. Elemental and spectroscopic analyses were consistent with the given formulae.

The [Co(trenen)Cl]Cl(ClO₄).H₂O (6) complex was prepared by the method of Golding, Harrowfield & Sargeson (1974) using [Co(trenenim)Cl]Cl₂ as the

starting material rather than the perchlorate salt. As a consequence the product that was isolated was analysed as a chloro-perchlorate salt. [Calculated for CoC₈H₂₃Cl₃N₅O₄: C 23.0, H 5.5, N 16.7, Cl 25.4%; found: C 23.0, H 5.7, N 16.7, Cl 25.5%]

A suitable orange-red tabular crystal 0.28 × 0.37 × 0.18 mm was selected from the recrystallized product. Density measured by flotation in hexane/carbon tetrachloride.

Space group *P*2₁/*n* from systematic absences 0*k*0 *k* odd and *h*0*l* *h* + *l* odd; cell parameters determined from 24 reflections (17 < θ < 18°) with a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator as described previously (Canty, Chaichit & Gatehouse, 1980). Three standard reflections measured at 4 h intervals indicated that up to 3.1% decomposition had occurred for which a correction was applied. Data collected using ω-scan technique with a symmetric scan width of ± 0.65° in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0.05° s⁻¹. No reflection was sufficiently intense to require the insertion of an attenuation filter. Data processed using a program written specifically for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). Values of *I* and σ(*I*) corrected for Lorentz and polarization effects. Absorption correction applied on the basis of indexed crystal faces, maximum and minimum transmission factors 0.8219 and 0.7252 respectively. 5480 (5092 unique, *R*_{int} = 0.032) reflections measured to sin θ/λ = 0.704 Å⁻¹, 3140 with [*I* > 3σ(*I*)] used in analysis; index ranges *h* -20/20, *k* 0/19, *l* 0/12. Co parameters found from Patterson synthesis and all non-H atoms located in subsequent difference Fourier syntheses. Function minimized in full-matrix least-squares refinement Σ*w*(|*F*_o - |*F*_c||)², where *w* is the weight [σ²(*F*_o)]⁻¹. All non-H atoms refined anisotropically; H atoms in their calculated positions (the water H atoms were located in a difference Fourier synthesis), refined using a riding model with a single isotropic thermal parameter for all H atoms. 202 variable parameters, final *R* = 0.046 and *wR* = 0.062 (for observed reflections); maximum Δσ in final cycle 0.090 for *U*₃₃ of Co. Goodness of fit 1.55. Final difference Fourier synthesis had Δρ within 0.9 and -0.6 e Å⁻³, both in the vicinity of the perchlorate group indicating minor rotational disorder. Scattering factors for neutral atoms and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations performed on the Monash University VAX 11/780 computer system. Major programs used: *SHELX76* (Sheldrick, 1976) and *ORFFE* (Busing, Martin & Levy, 1964).

Discussion. Atomic positions, equivalent isotropic thermal parameters, bond distances and angles and

also in the trigonal bipyramidal Cu^{II} complex, [Cu(trenen)]²⁺ (Cannas, Cristini & Marongiu, 1976). Thus, the stronger affinity of the secondary N atom of trenen for metal centres is not restricted to the peroxo dimer nor is it restricted to octahedral Co^{III} complexes, with the exception of the azido complex, [Co(trenen)N₃]²⁺, where Co—N(sec) is indistinguishable from four of the other Co—N distances (Maxwell, 1971); the effect appears to be independent of the ligand *trans* to the secondary N and is therefore ligand derived. The azido complex is unusual in the sense that the azido group introduces steric effects which lengthen one of the *cis*-Co—N(prim) distances. The azido group may also influence the Co—N(sec) distance. It is interesting to note in the case of [Co(tetraen)Cl]²⁺, where the ligand tetraen is the long chain analogue of trenen, the Co—N distance to all secondary N atoms, including that *trans* to the chloride, is indistinguishable from that to the primary N atoms (Snow, 1970). The structure of the complex, [Co(Metrenen)Cl]²⁺, is somewhat different (Buckingham, Dwyer, Sargeson & Watson, 1972). The chloride is now *trans* to the tertiary N which exhibits the shortest Co—N distance [1.923 (3) Å], shorter than that to the secondary N atom. Steric hindrance introduced by the methyl group may be responsible for the longer Co—N(sec) bond when compared with that found in the unmethylated complex, [Co(trenen)Cl]²⁺, reported here.

The rate of base-catalyzed hydrolysis of [Co(trenen)Cl]²⁺ is much faster than for [Co(NH₃)₅Cl]²⁺ (Buckingham, Marzilli & Sargeson, 1969). This has been attributed to the greater acidity of the proton on the secondary N which is *trans* to the leaving group, Cl⁻. Deprotonation results in the donation of electron density onto Co^{III} which weakens the bond to the leaving group and facilitates the

formation of the five-coordinate intermediate through which substitution reactions on Co^{III} are widely believed to occur (Buckingham, Dwyer, Sargeson & Watson, 1972; Buckingham, Marzilli & Sargeson, 1969). The structure of [Co(trenen)Cl]²⁺ indicates that the greater acidity of the secondary amine can be attributed to its shorter Co—N distance when compared with that of the primary amine.

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Acta Cryst. (1992). **C48**, 274–279

Structures of Dichlorobis(trimethylamine oxide)cobalt(II), Diiodobis(trimethylamine oxide)cobalt(II), Dichlorobis(trimethylamine oxide)zinc and Dibromobis(trimethylamine oxide)zinc

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(Received 2 July 1991; accepted 21 August 1991)

Abstract. [CoCl₂(C₃H₉NO)₂] (1), *M*_r = 280.1, orthorhombic, *Pna*2₁, *a* = 40.800 (10), *b* = 10.882 (5), *c* = 10.966 (5) Å, *V* = 4868.7 (33) Å³, *Z* = 16, *D*_m = 1.47

(room temperature), *D*_x = 1.53 (150 K) g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 18.26 cm⁻¹, *F*(000) = 2320, *T* = 150 K, *R* = 0.0564 for 2605 observed