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—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—SCN π bonding will, however, be increased by the basicity of the other ligands (Bertini & Sabatini, 1966). A structural change from Nbonded 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.

References

- AHRLAND, S., CHATT, J. & DAVIES, N. R. (1958). Q. Rev. Chem. Soc. pp. 265–276.
- BENNETT, M. A., CLARK, R. J. H. & GOODWIN, A. D. J. (1967). Inorg. Chem. 6, 1625–1631.
- BERTINI, I. & SABATINI, A. (1966). Inorg. Chem. 5, 1025-1028.
- BURMEISTER, J. L. (1990). Coord. Chem. Rev. 105, 77-133.
- BURMEISTER, J. L. & BASOLO, F. (1964). Inorg. Chem. 3, 1587-1593.
- GABE, E. J., LE PAGE, Y., WHITE, P. S. & LEE, F. L. (1987). Acta Cryst. A43, C294.
- MARONGIU, G., LINGAFELTER, E. C. & PAOLETTI, P. (1969). *Inorg. Chem.* 8, 2763–2767.
- MITCHELL, P. C. H. & WILLIAMS, R. J. P. (1960). J. Chem. Soc. pp. 1912–1918.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351-359.
- PEARSON, R. G. (1963). J. Am. Chem. Soc. 85, 3533-3539.
- WEI, L. W., CHAO, M. S. & CHUNG, C. S. (1979). J. Chin. Chem. Soc. (Taipei), 26, 145–151.
- WU, D. T. & CHUNG, C. S. (1986). Inorg. Chem. 25, 3584-3587.
- YINGST, A. & MCDANIEL, D. H. (1967). Inorg. Chem. 6, 1067–1068.

Acta Cryst. (1992). C48, 271-274

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

BY B. M. GATEHOUSE,* R. L. MARTIN, G. MCLACHLAN, S. N. PLATTS AND L. SPICCIA

Chemistry Department, Monash University, Clayton, Victoria, 3168, Australia

(Received 20 May 1991; accepted 2 August 1991)

 $[Co(C_8H_{23}N_5)Cl]Cl(ClO_4).H_2O,$ $M_{-} =$ Abstract. 436.6, monoclinic, $P2_1/n$, a = 14.769 (3), *b* = 13.558 (1), c = 9.056 (2) Å, $\beta = 105.281$ (3)°, V =Z = 4, $D_m = 1.66 (1),$ 1749 (1) Å³, $D_r =$ 1.658 g cm^{-3} $\mu =$ λ (Mo $K\alpha$) = 0.7107 Å, 14.67 cm⁻¹, F(000) = 904, T = 293 K, final R = 0.046for 5092 counter-measured reflections. The structure consists of octahedral cations $[Co(trenen)Cl]^{2+}$ 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-

0108-2701/92/020271-04\$03.00

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 peroxobridged Co^{III} complex, [(trenen)CoO₂Co(trenen)]-(ClO₄)₄, where 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

© 1992 International Union of Crystallography

^{*} Author to whom correspondence should be addressed.

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 peroxo 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 $[Co(trenen)Cl]Cl(ClO_4).H_2O$: $[Co(tren)Cl_2]Cl_2$ $p-[Co(tren){NH_2CH_2CH(OCH_2 CH_{3}_{2}Cl]Cl(ClO_{4})$ 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 $[Co(trenen)Cl]Cl(ClO_4).H_2O(6)$ complex was prepared by the method of Golding, Harrowfield & Sargeson (1974) using $[Co(trenenim)Cl]Cl_2$ 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 $CoC_8H_{23}Cl_3N_5O_4$: 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 $0.28 \times 0.37 \times 0.18$ mm was selected from the recrystallized product. Density measured by flotation in hexane/carbon tetrachloride.

Space group $P2_1/n$ from systematic absences 0k0 kodd and h0l h + l odd; cell parameters determined from 24 reflections $(17 < \theta < 18^\circ)$ 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 $\pm 0.65^{\circ}$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0.05^{\circ} \text{ s}^{-1}$. 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 $\sigma(I)$ 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 $\sin \theta / \lambda = 0.704 \text{ Å}^{-1}$, 3140 with $[I > 3\sigma(I)]$ 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 $\sum w(|F_o| - |F_c|)^2$, where w is the weight $[\sigma^2(F_o)]^{-1}$. 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 Δ/σ in final cycle 0.090 for U_{33} of Co. Goodness of fit 1.55. Final difference Fourier synthesis had $\Delta \rho$ within 0.9 and $-0.6 \text{ e} \text{ Å}^{-3}$, 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

Table 1. Atomic parameters for [Co(trenen)Cl]-Cl(ClO₄).H₂O (e.s.d.'s in parentheses)

$U_{eq} = \frac{1}{2}$	$\frac{1}{3}\sum_i \sum_j$	U _{ij} a,*	$a_j * \mathbf{a}_i \cdot \mathbf{a}_j$	
------------------------	----------------------------	---------------------	---	--

	x	у	Z	$U_{eq}(\text{\AA}^2)$
Co	0.09366 (3)	0.20843 (3)	0.13480 (5)	0.0222 (1)
Cl(1)	-0.04241 (6)	0.15024 (7)	- 0.01987 (12)	0.0397 (3)
Cl(2)	0.35600 (6)	0.06109 (7)	0.33774 (12)	0.0403 (3)
Cl(3)	0.25022 (9)	0.00258 (9)	0.79406 (14)	0.0540 (4)
O(1)	0.2530 (4)	0.0946 (4)	0.7194 (5)	0.107 (2)
O(2)	0.1941 (4)	0.0077 (3)	0.8982 (6)	0.098 (2)
O(3)	0.2255 (5)	- 0.0757 (5)	0.6990 (9)	0.176 (4)
O(4)	0.3461 (4)	- 0.0103 (4)	0.8883 (6)	0.114 (2)
O(5)	0.0307 (3)	0.3560 (3)	0.7289 (4)	0.067 (2)
N(1)	0.0381 (2)	0.3422 (2)	0.1044 (3)	0.030 (1)
N(2)	0.1301 (2)	0.0696 (2)	0.1802 (3)	0.028 (1)
N(3)	0.0554 (2)	0.2091 (2)	0.3260 (3)	0.030 (1)
N(4)	0.2150 (2)	0.2536 (2)	0.2538 (3)	0.029 (1)
N(5)	0.1465 (2)	0.2173 (2)	-0.0421 (3)	0.033 (1)
C(1)	-0.0100 (3)	0.3679 (3)	0.2250 (5)	0.039 (1)
C(2)	- 0.0294 (3)	0.2730 (3)	0.3012 (5)	0.039 (1)
C(3)	0.1108 (3)	0.0394 (3)	0.3269 (5)	0.040 (1)
C(4)	0.0337 (3)	0.1040 (3)	0.3575 (5)	0.040 (1)
C(5)	0.1357 (3)	0.2483 (3)	0.4523 (4)	0.038 (1)
C(6)	0.2039 (3)	0.3073 (3)	0.3878 (4)	0.040 (1)
C(7)	0.2638 (3)	0.3033 (3)	0.1507 (5)	0.037 (1)
C(8)	0.2490 (3)	0.2410 (3)	0.0094 (5)	0.041 (2)

torsion angles are given in Tables 1 and 2.* Fig. 1 shows the structure of the complex cation, [Co(trenen)Cl]²⁺. The primary coordination sphere is comprised of five N atoms from the trenen ligand and one chloride. The disposition of the chloride trans to the secondary N atom [N(4)] is a result of the template synthesis of the complex. The imine complex is formed by attack of the carbinolamine at the N trans to the Cl atom since the protons on this N are more acidic than those on N trans to N (Golding, Harrowfield & Sargeson, 1974; Buckingham, Cresswell & Sargeson, 1975; Engelhardt, Gainsford, Gainsford, Golding, Harrowfield, Herlt, Sargeson & White, 1988). Selective reduction of the imine complex preserves the stereochemistry around Co because of the kinetic inertness of Co^{III}.

The Co—N distances [1.932 (3)–1.979 (3) Å] are typical of many Co^{III} amine complexes including those containing polyamine ligands such as tren (2), metrenen (3) and tetraen (4), (Gatehouse, McLachlan, Martin, Martin & Spiccia, 1991; Engelhardt, Gainsford, Gainsford, Golding, Harrowfield, Herlt, Sargeson & White, 1988; Buckingham, Dwyer, Sargeson & Watson, 1972; Snow, 1970). A recent compilation by Orpen, Brammer, Allen, Kennard, Watson & Taylor (1989) gives the following average Co^{III}—N distances for octahedral complexes: primary N atoms 1.965 (21), secondary N atoms

Table 2. Interatomic distances (Å) and selected bond angles (°) and torsion angles (°) for [Co(trenen)Cl]Cl-(ClO₄).H₂O (e.s.d.'s in parentheses)

Co-N(1)	1.979 (3)	C(6)—N(4)	1.461 (5)
Co-N(2)	1.971 (3)	N(3)-C(4)	1.505 (5)
Co-N(3)	1.958 (3)	C(4) - C(3)	1.518 (6)
Co-N(4)	1.932 (3)	C(3)-N(2)	1.487 (6)
Co-N(5)	1.962 (3)	N(4)—C(7)	1.484 (5)
$C_0 - Cl(1)$	2.2670 (9)	C(7)—C(8)	1.500 (6)
N(1) - C(1)	1.492 (6)	C(8)-N(5)	1.496 (5)
C(1) - C(2)	1.522 (6)	Cl(3)*-O(1)	1.425 (5)
C(2) - N(3)	1.491 (5)	Cl(3)—O(2)	1.412 (6)
N(3) - C(5)	1.510 (4)	Cl(3)—O(3)	1.355 (7)
C(5) - C(6)	1.519 (6)	Cl(3)—O(4)	1.458 (5)
., .,			
N(1) - Co - N(2)	169.8 (1)	$C_0 - N(1) - C(1)$	111.9 (2)
N(1) - Co - N(3)	85.0 (1)	N(1) - C(1) - C(2)	108.5 (3)
N(1)—Co— $N(4)$	94.4 (1)	C(1)-C(2)-N(3)	108.0 (3)
N(1)—Co— $N(5)$	94.0 (1)	C(2)—N(3)—Co	107.2 (2)
N(2) - Co - N(3)	86.9 (1)	C(2) - N(3) - C(5)	111.7 (3)
N(2) - Co - N(4)	91.4 (1)	C(2) - N(3) - C(4)	111.5 (3)
N(2) - Co - N(5)	94.8 (1)	N(3) - C(5) - C(6)	111.2 (3)
N(3) - Co - N(4)	86.9 (1)	C(5) - C(6) - N(4)	106.7 (3)
N(3) - Co - N(5)	172.5 (1)	C(6)—N(4)—Co	109.3 (2)
N(4) - Co - N(5)	85.8 (1)	C(6) - N(4) - C(7)	118.4 (3)
N(1)—Co—Cl (1)	88.00 (8)	N(4) - C(7) - C(8)	107.2 (3)
N(2)—Co—Cl(1)	86.86 (8)	C(7) - C(8) - N(5)	107.2 (3)
N(3)—Co—Cl(1)	97.63 (9)	C(8)-N(5)-Co	110.3 (2)
N(4)—Co—Cl(1)	175.1 (1)	N(3) - C(4) - C(3)	107.7 (3)
N(5)—Co—Cl(1)	89.74 (9)	C(4) - C(3) - N(2)	109.5 (3)
		C(3) - N(2) - Co	110.1 (2)
	$\begin{array}{l} C(2) = N(3) \\ N(3) = C(5) \\ C(5) = C(6) \\ N(1) = Co = N(2) \\ N(1) = Co = N(3) \\ N(1) = Co = N(3) \\ N(1) = Co = N(3) \\ N(2) = Co = N(3) \\ N(2) = Co = N(3) \\ N(2) = Co = N(3) \\ N(3) = Co = N(5) \\ N(3) = Co = N(5) \\ N(4) = Co = N(5) \\ N(4) = Co = N(5) \\ N(1) = Co = C(1) \\ N(3) = Co = C(1) \\ N(3) = Co = C(1) \\ N(3) = Co = C(1) \\ N(4) = Co = C(1) \\ N(4) = Co = C(1) \\ N(5) = Co = C(1) \\ \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$

Looking from 2 to 3 the sign is positive if a clockwise rotation of 1 would superimpose it on 4.

* Cl(3) perchlorate ion.



Fig. 1. Structure of the cation, $[Co(trenen)Cl]^{2^+}$, of $[Co(trenen)-Cl]Cl(ClO_4).H_2O$.

1.968 (30) and tertiary N atoms 1.961 (27) Å. However, the Co—N distance to the secondary N [N(4) 1.932 (3) Å] is significantly shorter than all the others, as was found in the recently reported peroxo dimer, $[(trenen)CoO_2Co(trenen)]^{4+}$ (Gatehouse, McLachlan, Martin, Martin & Spiccia, 1991), and

^{*} Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54571 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0478]

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, $[Co(trenen)N_3]^{2+}$, 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 $[Co(NH_3)_5Cl]^{2+}$ (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.

References

- BUCKINGHAM, D. A., CRESSWELL, P. J. & SARGESON, A. M. (1975). Inorg. Chem. 14, 1485–1490.
- BUCKINGHAM, D. A., DWYER, M., SARGESON, A. M. & WATSON, K. J. (1972). Acta Chem. Scand. 26, 2813–2816.
- BUCKINGHAM, D. A., MARZILLI, P. A. & SARGESON, A. M. (1969). Inorg. Chem. 8, 1595–1604.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORFFE. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
- CANNAS, M., CRISTINI, A. & MARONGIU, G. (1976). Inorg. Chim. Acta, 19, 241–244.
- CANTY, A. J., CHAICHIT, N. & GATEHOUSE, B. M. (1980). Acta Cryst. B36, 786–789.
- ENGELHARDT, L. M., GAINSFORD, A. R., GAINSFORD, G. J., GOLDING, B. T., HARROWFIELD, J. MACB., HERLT, A. J., SAR-GESON, A. M. & WHITE, A. H. (1988). *Inorg. Chem.* 27, 4551– 4563.
- GATEHOUSE, B. M., MCLACHLAN, G., MARTIN, L. L., MARTIN, R. L. & SPICCIA, L. (1991). Aust. J. Chem. 44, 351–359.
- GOLDING, B. T., HARROWFIELD, J. MACB. & SARGESON, A. M. (1974). J. Am. Chem. Soc. 96, 3003–3004.
- HORNSTRA, J. & STUBBE, B. (1972). PW1100. Data-processing program. Philips Research Laboratories, Eindhoven, The Netherlands.
- MAXWELL, I. E. (1971). Inorg. Chem. 10, 1782-1788.
- ORPEN, A. G., BRAMMER, L., ALLEN, F. H., KENNARD, O., WATSON, D. G. & TAYLOR, R. (1989). J. Chem. Soc. Dalton Trans. S1.
- SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- SNOW, M. R. (1970). J. Am. Chem. Soc. 92, 3610-3617.

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

BY SONGCHUN JIN, MARK NIEUWENHUYZEN, WARD T. ROBINSON AND C. J. WILKINS

Chemistry Department, University of Canterbury, Christchurch, New Zealand

(Received 2 July 1991; accepted 21 August 1991)

Abstract. $[CoCl_2(C_3H_9NO)_2]$ (1), $M_r = 280.1$, orthorhombic, $Pna2_1$, a = 40.800 (10), b = 10.882 (5), $c = \lambda(Mo \ K\alpha) = 0.71069$ Å, $\mu = 18.26 \text{ cm}^{-1}$, F(000) = 10.966 (5) Å, V = 4868.7 (33) Å³, Z = 16, $D_m = 1.47$ 2320, T = 150 K, R = 0.0564 for 2605 observed

0108-2701/92/020274-06\$03.00 © 1992 International Union of Crystallography