with hard acids (class a metals) (Pearson, 1963; Ahrland, Chatt \& Davies, 1958). $\mathrm{Cu}^{\text {II }}$ 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 $\mathrm{Cu}^{\mathrm{II}}$ ion through the S atom in four $\mathrm{Cu}^{\mathrm{II}}$ complexes of open-chain tetraamines (Wu \& Chung, 1986; Marongiu, Lingafelter \& Paoletti, 1969); however, in this complex, the two isothiocyanato groups are bonded in $\mathrm{Cu}^{\mathrm{II}}$ 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 $M-\mathrm{SCN}$ is stabilized by $\pi$ bonding which is formed between the $d$ electrons of the metal and an empty antibonding $\pi$ orbital located on the S atom of the thiocyanato group. The availability of the metal $d$ electrons for $M-\operatorname{SCN} \pi$ 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.

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# 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<br>Chemistry Department, Monash University, Clayton, Victoria, 3168, Australia

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#### Abstract

Co}\left(\mathrm{C}_{8} \mathrm{H}_{23} \mathrm{~N}_{5}\right) \mathrm{Cl}\right] \mathrm{Cl}\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}, \quad M_{r}=\) 436.6, monoclinic, $\quad P 2_{1} / n, \quad a=14.769$ (3), $\quad b=$ 13.558 (1),$\quad c=9.056$ (2) $\AA, \quad \beta=105.281$ (3) ${ }^{\circ}, \quad V=$ 1749 (1) $\AA^{3}, \quad Z=4, \quad D_{m}=1.66$ (1), $\quad D_{x}=$ $1.658 \mathrm{~g} \mathrm{~cm}^{-3}, \quad \lambda($ Mo $K \alpha)=0.7107 \AA, \quad \mu=$ $14.67 \mathrm{~cm}^{-1}, F(000)=904, T=293 \mathrm{~K}$, final $R=0.046$ for 5092 counter-measured reflections. The structure consists of octahedral cations $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$ with one chloride and one perchlorate ion together with one water molecule involved in hydrogen bonding in the gross structure. The mean $\mathrm{Co}-\mathrm{N}$ distance is 1.960 (18) and $\mathrm{Co}-\mathrm{Cl}$ is 2.267 (1) $\AA$. The $\mathrm{Co}-$


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$\mathrm{N}(\mathrm{sec})$ distance $[1.932(3) \AA$ ] is significantly shorter than the other $\mathrm{Co}-\mathrm{N}$ 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 $\mathrm{Co}^{\text {III }}$ complex, [(trenen) $\mathrm{CoO}_{2} \mathrm{Co}$ (trenen)]$\left(\mathrm{ClO}_{4}\right)_{4}$, where trenen $=N, N, N^{\prime}$-tris $(2$-aminoethyl)-ethane-1,2-diamine (1). An interesting structural feature of this complex is the short $\mathrm{Co}-\mathrm{N}$ distance trans to the bridging peroxo group, viz. 1.928 (6) $\AA$ compared with the average $\mathrm{Co}-\mathrm{N}$ distance of 1.952 (21) $\AA$. This is unusual for peroxo-bridged
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complexes where, in general, it is found that Co $\mathrm{N}($ trans $)$ is longer than $\mathrm{Co}-\mathrm{N}(\mathrm{av})$ 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 $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$ has been determined and is reported here.

(1) trenen

(2) tren

(3) Metrenen

(5) $[\mathrm{Co}(\text { trenenim }) \mathrm{Cl}]^{2+}$

(6) $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$

Experimental. The following precursors were used in the preparation of $[\mathrm{Co}($ trenen $) \mathrm{Cl}] \mathrm{Cl}\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}$ : $\left[\mathrm{Co}(\right.$ tren $\left.) \mathrm{Cl}_{2}\right] \mathrm{Cl}, \quad p-\left[\mathrm{Co}(\right.$ tren $)\left\{\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}\left(\mathrm{OCH}_{2}-\right.\right.$ $\left.\left.\left.\mathrm{CH}_{3}\right)_{2}\right\} \mathrm{Cl}\right] \mathrm{Cl}\left(\mathrm{ClO}_{4}\right)$ and $[\mathrm{Co}($ trenenim $) \mathrm{Cl}] \mathrm{Cl}_{2}(5)$, where $\operatorname{tren}=\operatorname{tris}(2$-aminoethyl)amine and trenenim $=N, N$-bis(2-aminoethyl)- $N^{\prime}$-(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 $[\mathrm{Co}($ trenen $) \mathrm{Cl}] \mathrm{Cl}\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}(6)$ complex was prepared by the method of Golding, Harrowfield \& Sargeson (1974) using $\left[\mathrm{Co}(\right.$ trenenim $) \mathrm{Cl}^{2} \mathrm{Cl}_{2}$ 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 $\mathrm{CoC}_{8} \mathrm{H}_{23} \mathrm{Cl}_{3} \mathrm{~N}_{5} \mathrm{O}_{4}$ : C 23.0 , H 5.5, N 16.7, Cl 25.4\%; found: $\mathrm{C} 23.0, \mathrm{H} 5.7, \mathrm{~N} 16.7, \mathrm{Cl} 25.5 \%$ ]

A suitable orange-red tabular crystal $0.28 \times 0.37$ $\times 0.18 \mathrm{~mm}$ was selected from the recrystallized product. Density measured by flotation in hexane/carbon tetrachloride.
Space group $P 2_{1} / n$ from systematic absences $0 k 0 k$ odd and $h 0 l h+l$ 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 $\omega$-scan technique with a symmetric scan width of $\pm 0.65^{\circ}$ in $\omega$ from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0.05^{\circ} \mathrm{s}^{-1}$. 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, $R_{\text {int }}=$ 0.032 ) reflections measured to $\sin \theta / \lambda=0.704 \AA^{-1}$, 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 $\sum w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2}$, where $w$ is the weight $\left[\sigma^{2}\left(F_{o}\right)\right]^{-1}$. 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 $w R=0.062$ (for observed reflections); maximum $\Delta / \sigma$ 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 $-0.6 \mathrm{e} \AA^{-3}$, 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 $[\mathrm{Co}($ trenen $) \mathrm{Cl}]-$ $\mathrm{Cl}\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}$ (e.s.d.'s in parentheses)

| $U_{\text {eq }}=\frac{1}{3} \sum_{i} \sum_{j} U_{i j} a_{i}{ }^{*} a_{j}{ }^{*} \mathbf{a}_{i} \cdot \mathbf{a}_{j}$. |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $x$ | $y$ | $z$ | $U_{\text {eq }}\left(\AA^{2}\right)$ |
| Co | 0.09366 (3) | 0.20843 (3) | 0.13480 (5) | 0.0222 (1) |
| $\mathrm{Cl}(1)$ | -0.04241 (6) | 0.15024 (7) | -0.01987 (12) | 0.0397 (3) |
| $\mathrm{Cl}(2)$ | 0.35600 (6) | 0.06109 (7) | 0.33774 (12) | 0.0403 (3) |
| $\mathrm{Cl}(3)$ | 0.25022 (9) | 0.00258 (9) | 0.79406 (14) | 0.0540 (4) |
| $\mathrm{O}(1)$ | 0.2530 (4) | 0.0946 (4) | 0.7194 (5) | 0.107 (2) |
| $\mathrm{O}(2)$ | 0.1941 (4) | 0.0077 (3) | 0.8982 (6) | 0.098 (2) |
| $\mathrm{O}(3)$ | 0.2255 (5) | -0.0757 (5) | 0.6990 (9) | 0.176 (4) |
| $\mathrm{O}(4)$ | 0.3461 (4) | -0.0103 (4) | 0.8883 (6) | 0.114 (2) |
| $\mathrm{O}(5)$ | 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) |
| $\mathrm{N}(2)$ | 0.1301 (2) | 0.0696 (2) | 0.1802 (3) | 0.028 (1) |
| $\mathrm{N}(3)$ | 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) |
| $\mathrm{N}(5)$ | 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) |
| $\mathrm{C}(2)$ | -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, $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$. 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 $[\mathrm{N}(4)$ ] 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 $\mathrm{Co}^{11 \mathrm{I}}$.

The $\mathrm{Co}-\mathrm{N}$ distances $[1.932$ (3)-1.979 (3) $\AA$ ] are typical of many $\mathrm{Co}^{\mathrm{III}}$ 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 $\mathrm{Co}^{\mathrm{III}}-\mathrm{N}$ distances for octahedral complexes: primary N atoms $1.965(21)$, secondary N atoms

[^1]Table 2. Interatomic distances ( $\AA$ ) and selected bond angles $\left({ }^{\circ}\right)$ and torsion angles $\left({ }^{\circ}\right)$ for $[\mathrm{Co}($ trenen $) \mathrm{Cl}] \mathrm{Cl}-$ $\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}$ (e.s.d.'s in parentheses)

| $\mathrm{Co}-\mathrm{N}(1)$ | 1.979 (3) | $\mathrm{C}(6)-\mathrm{N}(4)$ | 1.461 (5) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Co}-\mathrm{N}(2)$ | 1.971 (3) | $\mathrm{N}(3)-\mathrm{C}(4)$ | 1.505 (5) |
| $\mathrm{Co}-\mathrm{N}(3)$ | 1.958 (3) | $\mathrm{C}(4)-\mathrm{C}(3)$ | 1.518 (6) |
| $\mathrm{Co}-\mathrm{N}(4)$ | 1.932 (3) | $\mathrm{C}(3)-\mathrm{N}(2)$ | 1.487 (6) |
| $\mathrm{Co}-\mathrm{N}(5)$ | 1.962 (3) | $\mathrm{N}(4)-\mathrm{C}(7)$ | 1.484 (5) |
| $\mathrm{Co}-\mathrm{Cl}(1)$ | 2.2670 (9) | $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.500 (6) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.492 (6) | $\mathrm{C}(8)-\mathrm{N}(5)$ | 1.496 (5) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.522 (6) | $\mathrm{Cl}(3) *-\mathrm{O}(1)$ | 1.425 (5) |
| $\mathrm{C}(2)-\mathrm{N}(3)$ | 1.491 (5) | $\mathrm{Cl}(3)-\mathrm{O}(2)$ | 1.412 (6) |
| $\mathrm{N}(3)-\mathrm{C}(5)$ | 1.510 (4) | $\mathrm{Cl}(3)-\mathrm{O}(3)$ | 1.355 (7) |
| C(5)-C(6) | 1.519 (6) | $\mathrm{Cl}(3)-\mathrm{O}(4)$ | 1.458 (5) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{N}(2)$ | 169.8 (1) | $\mathrm{Co}-\mathrm{N}(1)-\mathrm{C}(1)$ | 111.9 (2) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{N}(3)$ | 85.0 (1) | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 108.5 (3) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{N}(4)$ | 94.4 (1) | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{N}(3)$ | 108.0 (3) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{N}(5)$ | 94.0 (1) | $\mathrm{C}(2)-\mathrm{N}(3)-\mathrm{Co}$ | 107.2 (2) |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{N}(3)$ | 86.9 (1) | $\mathrm{C}(2)-\mathrm{N}(3)-\mathrm{C}(5)$ | 111.7 (3) |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{N}(4)$ | 91.4 (1) | $\mathrm{C}(2)-\mathrm{N}(3)-\mathrm{C}(4)$ | 111.5 (3) |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{N}(5)$ | 94.8 (1) | $\mathrm{N}(3)-\mathrm{C}(5)-\mathrm{C}(6)$ | 111.2 (3) |
| $\mathrm{N}(3)-\mathrm{Co}-\mathrm{N}(4)$ | 86.9 (1) | $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{N}(4)$ | 106.7 (3) |
| $\mathrm{N}(3)-\mathrm{Co}-\mathrm{N}(5)$ | 172.5 (1) | $\mathrm{C}(6)-\mathrm{N}(4)-\mathrm{Co}$ | 109.3 (2) |
| $\mathrm{N}(4)-\mathrm{Co}-\mathrm{N}(5)$ | 85.8 (1) | $\mathrm{C}(6)-\mathrm{N}(4)-\mathrm{C}(7)$ | 118.4 (3) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{Cl}(1)$ | 88.00 (8) | $\mathrm{N}(4)-\mathrm{C}(7)-\mathrm{C}(8)$ | 107.2 (3) |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{Cl}(1)$ | 86.86 (8) | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{N}(5)$ | 107.2 (3) |
| $\mathrm{N}(3)-\mathrm{Co}-\mathrm{Cl}(1)$ | 97.63 (9) | $\mathrm{C}(8)-\mathrm{N}(5)-\mathrm{Co}$ | 110.3 (2) |
| $\mathrm{N}(4)-\mathrm{Co}-\mathrm{Cl}(1)$ | 175.1 (1) | $\mathrm{N}(3)-\mathrm{C}(4)-\mathrm{C}(3)$ | 107.7 (3) |
| $\mathrm{N}(5)-\mathrm{Co}-\mathrm{Cl}(1)$ | 89.74 (9) | $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{N}(2)$ | 109.5 (3) |
|  |  | $\mathrm{C}(3)-\mathrm{N}(2)-\mathrm{Co}$ | 110.1 (2) |
|  | 123 | 4 |  |
|  | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{N}(3) \quad 42.4$ (4) |  |  |
|  | $\mathrm{N}(3)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{N}(4)$ | N(4) -41.3 (4) |  |
|  | $\mathrm{N}(3)-\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{N}(2)$ | N(2) -45.3 (4) |  |
|  | $\mathrm{N}(4)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{N}(5)$ | $\mathrm{N}(5) \quad 48.2$ (4) |  |

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

* $\mathrm{Cl}(3)$ perchlorate ion.


Fig. 1. Structure of the cation, $\left[\mathrm{Co}(\right.$ trenen $) \mathrm{Cl}^{2+}$, of $[\mathrm{Co}$ (trenen)$\mathrm{Cl}] \mathrm{Cl}\left(\mathrm{ClO}_{4}\right) \cdot \mathrm{H}_{2} \mathrm{O}$.
1.968 (30) and tertiary N atoms 1.961 (27) $\AA$. However, the Co-N distance to the secondary $\mathrm{N}[\mathrm{N}(4)$ $1.932(3) \AA$ ] is significantly shorter than all the others, as was found in the recently reported peroxo dimer, $\quad\left[(\text { trenen }) \mathrm{CoO}_{2} \mathrm{Co}(\text { trenen })\right]^{4+} \quad($ Gatehouse, McLachlan, Martin, Martin \& Spiccia, 1991), and
also in the trigonal bipyramidal $\mathrm{Cu}^{\mathrm{II}}$ complex, $[\mathrm{Cu}(\text { trenen })]^{2+}$ (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 $\mathrm{Co}^{\mathrm{III}}$ complexes, with the exception of the azido complex, $\left[\mathrm{Co}(\text { trenen }) \mathrm{N}_{3}\right]^{2+}$, where $\mathrm{Co}-\mathrm{N}(\mathrm{sec})$ is indistinguishable from four of the other $\mathrm{Co}-\mathrm{N}$ 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-CoN (prim) distances. The azido group may also influence the $\mathrm{Co}-\mathrm{N}(\mathrm{sec})$ distance. It is interesting to note in the case of $[\mathrm{Co}(\text { tetraen }) \mathrm{Cl}]^{2+}$, where the ligand tetraen is the long chain analogue of trenen, the $\mathrm{Co}-\mathrm{N}$ 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, $[\mathrm{Co}(\text { Metrenen }) \mathrm{Cl}]^{2+}$, is somewhat different (Buckingham, Dwyer, Sargeson \& Watson, 1972). The chloride is now trans to the tertiary N which exhibits the shortest $\mathrm{Co}-\mathrm{N}$ distance $[1.923$ (3) $\AA$ ], shorter than that to the secondary N atom. Steric hindrance introduced by the methyl group may be responsible for the longer $\mathrm{Co}-\mathrm{N}(\mathrm{sec})$ bond when compared with that found in the unmethylated complex, $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$, reported here.

The rate of base-catalyzed hydrolysis of $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$ is much faster than for $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]^{2+}$ (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, $\mathrm{Cl}^{-}$. Deprotonation results in the donation of electron density onto $\mathrm{Co}^{\text {III }}$ which weakens the bond to the leaving group and facilitates the
formation of the five-coordinate intermediate through which substitution reactions on $\mathrm{Co}^{\mathrm{III}}$ are widely believed to occur (Buckingham, Dwyer, Sargeson \& Watson, 1972; Buckingham, Marzilli \& Sargeson, 1969). The structure of $[\mathrm{Co}(\text { trenen }) \mathrm{Cl}]^{2+}$ indicates that the greater acidity of the secondary amine can be attributed to its shorter $\mathrm{Co}-\mathrm{N}$ distance when compared with that of the primary amine.

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# 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<br>Chemistry Department, University of Canterbury, Christchurch, New Zealand

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[^2](room temperature), $\quad D_{x}=1.53(150 \mathrm{~K}) \mathrm{g} \mathrm{cm}^{-3}$,
$\lambda(\mathrm{Mo} \mathrm{K} \mathrm{\alpha})=0.71069 \AA, \quad \mu=18.26 \mathrm{~cm}^{-1}, \quad F(000)=$
$2320, \quad T=150 \mathrm{~K}, \quad R=0.0564$ for 2605 observed
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[^0]:    * Author to whom correspondence should be addressed.

[^1]:    * 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 CHI 2HU, England. [CIF reference: AL0478]

[^2]:    Abstract. $\left[\mathrm{CoCl}_{2}\left(\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{NO}\right)_{2}\right]$ (1), $M_{r}=280.1$, orthorhombic, Pna $_{1}, a=40.800$ (10), $b=10.882$ (5), $c=$ 10.966 (5) $\AA, V=4868.7$ (33) $\AA^{3}, Z=16, D_{m}=1.47$

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