The Structure of a Novel Complex of Cobalt(III) with a Tridentate Macrocyclic Ligand with Tertiary Amine Donors, $[CoL(NCCH_3)_2Cl]CoCl_4$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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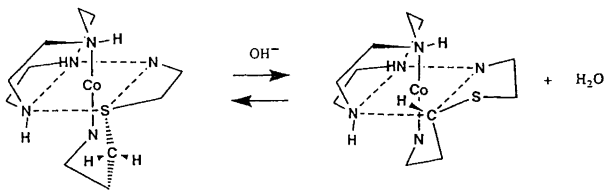
The structure of bis(acetonitrile)chloro(1,4,7-trimethyl-1,4,7-triazacyclononane)-cobalt(III) tetrachlorocobaltate(II), $[Co(Me_3tacn)(NCCH_3)_2Cl]CoCl_4$ has been solved by X-ray diffraction: $M_r = 548.52$, monoclinic, $P2_1/c$, $a = 12.172(3)$ Å, $b = 14.331(4)$ Å, $c = 26.032(5)$ Å, $\beta = 98.37(2)°$, $V = 4492(3)$ Å^3, $D_x = 1.63$ g cm^{-3}, Mo$K\alpha = 0.710\,73$ Å, $\mu = 20.838$ cm^{-1}, $F(000) = 2232$, $Z = 8$, $R = 0.058$ for 3476 unique reflections. There are two independent formula units which are structurally similar but not identical. The cobalt(III) ions are surrounded by six atoms: three N atoms from ligand Me_3tacn, two N atoms from acetonitrile molecules and one chloride ion. The three Co–N bond lengths to the chelate are quite constant, lying in the range 1.967(8)–1.989(9) Å. The chloride ion does not introduce a structural *trans*-effect in the cation. The tetrachlorocobaltate(II) anions are closely tetrahedral as usual. The crowded structures in these cations indicate that coordination of a second chelate ligand, as in $[Co(Me_3tacn)(aeaps)]^{3+}$, would be unlikely on account of steric hindrance by the methyl groups.

Macrocyclic ligands play an important role in coordination chemistry. Complexes of several metal ions, other than cobalt(III), with the macrocyclic triamine ligand 1,4,7-triazacyclononane (tacn) and its derivatives and analogues have been studied in recent years.[1-4] The tacn ligand must always coordinate facially.

Recently we reported the preparation and characterization of a new type of cobalt(III) complex in which a tridentate ligand is coordinated through a carbanion group as well as through two amine groups.[5] This novel complex was isolated from the various unsymmetrical-facial geometric isomers of the bis(2-aminoethyl-3-aminopropyl sulfide)cobalt(III) cation, $[Co(aeaps)_2]^{3+}$, when these were separately treated with base. In each instance one thioether becomes decoordinated and an adjacent methylene carbon deprotonates and becomes the donor. The product is denoted $[Co(aeaps)(C\text{-}aeaps)]^{2+}$ and is the same particular *u-fac* isomer from the different *u-fac* substrates. A further instance of this phenomenon was demonstrated with the mixed complex (1,4,7-triazacyclononane) (2-aminoethyl-3-aminopropyl sulfide)cobalt(III) cation, from which the carbanion complex *fac*-$[Co(tacn)(C\text{-}aeaps)]^{2+}$ was obtained with base (Scheme 1). It therefore seems that this kind of carbanion coordination may be characteristic of a six-membered chelate ring involving a thioether donor.

To study the reaction further and investigate the role of various types of acidic protons possibly involved in a conjugate base mechanism for the alkyl coordination, we wished to prepare the cobalt(III) complexes of the ligand aeaps with the other coordination positions occupied by the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane, Me_3tacn. It was considered that these latter positions, lacking acidic protons, might thereby be eliminated from any involvement in the reaction process.

We accordingly prepared $[Co(Me_3tacn)(NO_2)_3]$, which on treatment with hydrochloric acid gave $[Co(Me_3tacn)Cl_3]$ to be used as an intermediate for preparing $[Co(Me_3tacn)(aeaps)]^{3+}$. Pure $[Co(Me_3tacn)Cl_3]$ could not be obtained on recrystallization, but instead a previously unknown compound was obtained. As the chemical analysis did not give any conclusive results as to the identity of the reaction product, a structure determination was undertaken. It was



Scheme 1.

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shown that the compound isolated was [Co(Me$_3$tacn)-(NCCH$_3$)$_2$Cl]CoCl$_4$. The crystal structure of this complex is of interest in order to ascertain the degree of crowding conferred by the *N*-trimethylated triamine ligand, and perhaps to indicate if the complex [Co(Me$_3$tacn)(aeaps)]$^{3+}$ would be impossible to prepare, as indeed indicated earlier.[2]

Experimental

Preparation of Me$_3$tacn · 3HCl. The hydrochloride of the free ligand was obtained by methylation of tacn · 3HCl[6] using the formic acid/formaldehyde procedure.[7]

Preparation of [Co(Me$_3$tacn)(NO$_2$)$_3$]. This was prepared by adaptions of methods used previously for *mer*-[Co(dien)-(NO$_2$)$_3$] and [Co(tacn)(NO$_2$)$_3$].[8-10] Co(NO$_3$)$_2$ · 6H$_2$O (2.76 g, excess) and NaNO$_2$ (2.9 g, excess) were dissolved in an acetate buffer (19 ml of a mixture of 1 M HOAc and 1 M NaOAc). Aeration was commenced, and a solution of Me$_3$tacn · 3HCl (2.0 g, 7.1 mmol) and NaOH (0.86 g) in water (16 ml) was added dropwise over 10 min. After aeration for 2 h the solution was allowed to stand, and the precipitated product was filtered off after 1 day. The brown–orange powder was washed with water, ethanol and acetone, and air-dried. Yield: 2.1 g, 81 %.

Preparation of [Co(Me$_3$tacn)Cl$_3$] and [Co(Me$_3$tacn)-(NCCH$_3$)$_2$Cl]CoCl$_4$. [Co(Me$_3$tacn)(NO$_2$)$_3$] (2.1 g) was added to 50 ml 1 M HCl, and the solution was gradually heated to 80° and held at this temperature for 1 h.[10,11] The dark blue–green solution was rotary-evaporated essentially to dryness. The crude [Co(Me$_3$tacn)Cl$_3$] material contained no detectable Co(II). The complex was moderately soluble in acetonitrile, and dissolution in this solvent followed by rotary evaporation gave a dark emerald-green powder. This was washed with ethanol and dried at 50 °C. Yield: 1.8 g. The product hydrolyses rapidly with water, and has low solubility in ethanol, acetone and chloroform. Crystals for X-ray analysis were obtained by slow recrystallization from acetonitrile aided by vapour diffusion with *n*-heptane.

Preparation of [Co(Me$_3$tacn)(aeaps)]Cl$_3$ was attempted by treating the crude [Co(Me$_3$tacn)Cl$_3$] with aeaps (slight excess) in dimethyl sulfoxide at 80 °C.[11] No product precipitated, as did [Co(tacn)(aeaps)]Cl$_3$ from [Co(tacn)Cl$_3$].[11] Passage of this solution (with added water) through cation-exchange resins showed no yellow–orange bands corresponding to (3+)-charged complexes.

X-Ray crystallography. [Co(Me$_3$tacn)(NCCH$_3$)$_2$Cl]CoCl$_4$ crystallizes as dark emerald-green plates. Preliminary photographs showed that they belong to the monoclinic system, and the systematically absent reflections $h0l(l = 2n+1)$ and $0k0(k = 2n+1)$ uniquely determine the space group to be $P2_1/c$. The low resolution of the diffraction pattern indicated a poor crystal quality, and is in accordance with the disorder of the structure (*vide infra*).

Table 1. Crystal data and a summary of data collection and refinement results.

Formula	$Co_2N_5Cl_5C_{13}H_{27}$
Formula weight / g mol^{-1}	548.52
Wavelength (Mo$K\alpha$) / Å	0.710 73
Space group	$P2_1/c$
Cell parameters at 110 K:	
a / Å	12.172(3)
b / Å	14.331(4)
c / Å	26.032(5)
β / °	98.37(2)
V / Å^3	4492(3)
Z	8
D_c / g cm^{-3} (110 K)	1.622
D_x / g cm^{-3} (273 K)	1.63
μ(Mo$K\alpha$) / cm^{-1}	20.838
Crystal size / mm	0.20×0.20×0.09
Scan mode	ω–2θ
Scan range, $\Delta\omega$	0.80 + 0.35 tan θ
θ range / °	1-25
No. of independent reflections	7888
No. of observed reflections, n [$\|F\|^2 \geq \sigma(\|F\|^2)$]	3476
w^{-1}	$\sigma^2_{cs}(F)+0.0012\|F\|^2$
No. of variables, m	363
$S = \Sigma w(\Delta F)^2/(n-m)$	1.1
$R = (\Sigma \|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.058
$R_w = \{[\Sigma w(\|F_o\| - \|F_c\|)^2]/\Sigma w\|F_o\|^2\}^{1/2}$	0.062
Max. shift / error	0.06

Diffraction data were collected with a CAD-4 diffractometer using graphite monochromated Mo$K\alpha$ radiation. The crystal was cooled to ca. 110 K using an Enraf–Nonius gas-flow low temperature device. The temperature was monitored with a thermocouple placed a few centimetres above the crystal in the exhaust pipe, and it remained constant (± 1 K) throughout data collection. The unit-cell dimensions were determined from the 2θ values of 22 reflections ($15 < \theta < 19°$). The selection of scan mode and scan range was based on an analysis of the reflection profiles. The crystal data and summary of the data collection and refinement results are listed in Table 1.

The intensities of the standard reflections were recorded every 10000 s, and the orientation of the crystal was checked every 300 reflections. These measurements showed that no mis-setting or deterioration of the crystal had occurred during the data collection. The data reduction included corrections for Lorentz-polarization and absorption effects. The latter correction was performed by the Gaussian integration procedure; transmission factors were in the range 0.645–0.835. Symmetry-related reflections were averaged: $R_{int} = 0.048$.

The structure was solved by Patterson and heavy-atom Fourier methods. It was refined by a full matrix least-squares analysis minimizing $\Sigma w(\Delta F)^2$. The low resolution of the diffraction pattern gave a limited number of observed reflections. In order not to increase the number of variables unnecessarily, anisotropic thermal parameters were only introduced if the difference Fourier indicated that this would improve the model. The positions of the

Table 2. Fractional coordinates and equivalent isotropic parameters (in Å) for $[Co(Me_3tacn)(NCCH_3)_2Cl]CoCl_4$.

Atom	*x/a*	*y/b*	*z/c*	B_{iso}[a]/Å^2
Co1	0.2861(1)	0.2493(1)	−0.06966(5)	1.35(3)
N11	0.3534(6)	0.3102(6)	−0.1257(3)	1.5(2)*
C11	0.4475(9)	0.2505(8)	−0.1382(4)	2.2(2)*
C12	0.4364(9)	0.1517(8)	−0.1200(4)	2.5(2)*
N12	0.4046(7)	0.1553(6)	−0.0665(3)	1.8(2)*
C15	0.503(1)	0.1846(8)	−0.0278(5)	2.8(2)*
C16	0.464(1)	0.2530(9)	0.0097(5)	2.8(2)*
N13	0.3886(7)	0.3229(6)	−0.0192(3)	2.1(2)*
C13	0.3960(9)	0.4011(8)	−0.1036(4)	2.5(2)*
C14	0.4567(9)	0.3849(8)	−0.0482(4)	2.5(2)*
C1M1	0.2772(9)	0.3300(9)	−0.1748(4)	2.6(3)
C1M2	0.3711(9)	0.0587(8)	−0.0532(5)	2.5(3)
C1M3	0.334(1)	0.3805(9)	0.0185(5)	3.3(3)
N1A1	0.1729(7)	0.3430(6)	−0.0736(3)	1.8(2)
C1A11	0.0971(9)	0.3899(8)	−0.0779(4)	1.8(2)
C1A12	−0.0012(9)	0.4531(7)	−0.0846(4)	2.2(2)
N1A2	0.2225(7)	0.1910(6)	−0.0154(3)	1.6(2)
C1A21	0.1731(9)	0.1517(8)	0.0123(4)	2.2(2)
C1A22	0.109(1)	0.0981(9)	0.0453(5)	3.7(3)
Cl1	0.1694(2)	0.1643(2)	−0.1252(1)	2.06(6)
Co2	0.8450(1)	0.2079(1)	0.25389(5)	1.46(3)
N21	0.8129(8)	0.1435(6)	0.1862(4)	2.5(2)*
C21	0.899(1)	0.172(1)	0.1563(5)	4.2(3)*
C22	0.937(1)	0.261(1)	0.1649(6)	4.8(3)*
N22	0.9306(7)	0.2992(6)	0.2179(3)	1.6(2)*
C25	0.865(1)	0.384(1)	0.2136(5)	4.1(3)*
C26	0.7466(9)	0.3746(8)	0.2094(5)	2.7(2)*
N23	0.7115(7)	0.2850(6)	0.2308(3)	1.8(2)*
C23	0.700(1)	0.175(1)	0.1609(5)	3.8(3)*
C24	0.641(1)	0.229(1)	0.1930(6)	4.8(3)*
C2M1	0.807(2)	0.037(1)	0.1913(8)	7.5(5)*
C2M2	1.041(1)	0.319(1)	0.2444(5)	7.2(4)
C2M3	0.645(1)	0.308(1)	0.2737(5)	5.6(3)
N2A1	0.7613(7)	0.1194(6)	0.2886(3)	1.8(2)
C2A11	0.729(1)	0.0640(8)	0.3129(4)	2.8(3)
C2A12	0.683(1)	−0.0095(8)	0.3447(4)	3.4(3)
N2A2	0.8767(8)	0.2748(6)	0.3179(3)	2.1(2)
C2A21	0.8932(9)	0.3091(7)	0.3575(4)	2.0(2)
C2A22	0.9125(9)	0.3579(8)	0.4075(4)	2.1(2)
Cl2	0.9937(3)	0.1187(2)	0.2808(1)	3.10(6)
Co3	0.8062(1)	0.2910(1)	0.01120(5)	1.68(3)
Cl31	0.7776(2)	0.1368(2)	0.0250(1)	2.05(6)
Cl32	0.9913(2)	0.3182(2)	0.0287(1)	2.32(6)
Cl33	0.7372(2)	0.3235(2)	−0.0732(1)	2.25(6)
Cl34	0.7155(2)	0.3882(2)	0.0614(1)	2.12(6)
Co4	0.3476(1)	0.3972(1)	0.67933(7)	2.61(3)
Cl41(0.60)[b]	0.3355(5)	0.2387(4)	0.7015(3)	4.8(1)
Cl42	0.4704(3)	0.4583(2)	0.7453(1)	3.74(8)
Cl43	0.1771(2)	0.4573(2)	0.6808(1)	2.61(6)
Cl44(0.70)[b]	0.4131(4)	0.4130(3)	0.6058(2)	2.80(8)*
Cl41A(0.30)[b]	0.340(1)	0.2436(9)	0.6583(4)	4.1(2)*
Cl41C(0.10)[b]	0.245(3)	0.278(2)	0.164(1)	4.1(7)*
Cl44A(0.30)[b]	0.3812(8)	0.4604(7)	0.5936(4)	2.7(2)*

[a]Atoms marked with an asterisk were refined isotropically. For atoms refined with anisotropic temperature factors:

$$B_{iso} = \frac{8\pi^2}{3} \sum_i \sum_j u_{ij} \bar{a}_i \bar{a}_j a_i^* a_j^*$$

[b]Population parameters are given in parentheses.

hydrogen atoms were located in a difference Fourier map. The geometries of these atoms were then idealized and the atoms given a fixed isotropic thermal parameter of $B = 3.5$ Å^2. During the refinement it became evident from an analysis of the displacement parameters that one of the tetrachlorocobaltate(II) ions (Co4) is heavily disordered in the crystal. Several models were employed to describe this disorder. The 'best' (on the basis of giving reasonable physical parameters and a small residual electron density) was one with two fully populated chlorine positions refined with anisotropic thermal parameters and five partially occupied chlorine positions refined with isotropic thermal parameters. The population parameters were constrained to sum to unity for the partially occupied positions. The maximum shift in the final cycle of least-squares was 0.06σ. The final difference electron density had values between 1.87 and −0.82 e Å^{-3} with the largest peaks close to the disordered tetrachlorocobaltate(II) ion. The crystallographic computations were performed with the SDP system.[12] The atomic scattering factors, including corrections for anomalous dispersion, were taken from Ref. 13 and used as contained in the program. The final positional parameters are listed in Table 2. Anisotropic displacement parameters, positional parameters for the hydrogen atoms and lists of observed and calculated structure amplitudes are available from the authors.

Results and discussion

The presumed $[Co(Me_3tacn)Cl_3]$ material could not be analysed satisfactorily and did not react with aeaps to give an anticipated $[Co(Me_3tacn)(aeaps)]^{3+}$ complex. It was recrystallized with difficulty from acetonitrile to give emerald-green crystals. These were subjected to X-ray crystal structure analysis which showed the compound to be $[Co(Me_3tacn)(NCCH_3)_2Cl]CoCl_4$. Thus, attempted recrystallization of the crude trichloro-complex leads to substitution by the solvent, and this is apparently accompanied by reduction of some of the cobalt to form a counter-anion with charge matching that of the cation.

Selected bond lengths, bond and torsion angles are listed in Table 3. The cations observed in the crystal structure are shown in Fig. 1. There are two crystallographically independent but chemically equivalent complex cations in the unit cell, labelled 1 and 2 in Fig. 1. The derived geometries are similar, but not identical. The two independent cations shown in Fig. 1 have ring conformations of opposite chiralities, as indicated by the sign of the dihedral angles for N–C–C–N in the chelate rings (cation 1, λλλ and cation 2, δδδ), but the centrosymmetric unit cell also contains their enantiomers (cation 1, λλλ and cation 2, δδδ). A slight disorder of cation 2 is apparent from the large values of the thermal ellipsoids in Fig. 1 and the short C–C distances. This could indicate the presence of different conformations of cation 2.

Table 3. Selected bond lengths (in Å), bond and torsion angles (in °).

Atoms				*i* = 1	*i* = 2
Co*i*			N*i*1	1.978(9)	1.978(9)
Co*i*			N*i*2	1.967(8)	1.989(9)
Co*i*			N*i*3	1.981(8)	1.984(8)
Co*i*			N*i*A1	1.916(8)	1.932(9)
Co*i*			N*i*A2	1.900(9)	1.911(8)
Co*i*			Cl*i*	2.235(3)	2.243(3)
N*i*1			C*i*1	1.503(14)	1.45(2)
N*i*1			C*i*3	1.486(14)	1.51(2)
N*i*2			C*i*2	1.499(15)	1.50(2)
N*i*2			C*i*5	1.506(13)	1.45(2)
N*i*3			C*i*4	1.49(2)	1.45(2)
N*i*3			C*i*6	1.484(14)	1.486(15)
C*i*1			C*i*2	1.51(2)	1.37(2)
C*i*3			C*i*4	1.54(2)	1.41(2)
C*i*5			C*i*6	1.51(2)	1.43(2)
N*i*1			C*i*M1	1.493(13)	1.54(2)
N*i*2			C*i*M2	1.497(14)	1.45(2)
N*i*3			C*i*M3	1.51(2)	1.51(2)
N*i*A1			C*i*A11	1.133(13)	1.122(15)
C*i*A11			C*i*A12	1.49(2)	1.49(2)
N*i*A2			C*i*A21	1.151(14)	1.135(13)
C*i*A21			C*i*A22	1.46(2)	1.465(14)
N*i*1	Co*i*		N*i*2	87.3(3)	86.4(4)
N*i*2	Co*i*		N*i*3	87.1(3)	87.3(3)
N*i*3	Co*i*		N*i*1	88.0(4)	86.7(4)
N*i*1	Co*i*		N*i*A1	91.3(4)	93.5(4)
N*i*1	Co*i*		N*i*A2	179.5(3)	177.7(4)
N*i*2	Co*i*		N*i*A1	178.5(4)	180.0(9)
N*i*2	Co*i*		N*i*A2	92.5(4)	91.6(4)
N*i*3	Co*i*		N*i*A1	92.3(4)	92.5(4)
N*i*3	Co*i*		N*i*A2	91.5(4)	92.1(4)
N*i*A1	Co*i*		N*i*A2	88.9(4)	88.5(4)
N*i*1	Co*i*		Cl*i*	93.2(2)	93.3(3)
N*i*2	Co*i*		Cl*i*	92.7(3)	93.9(3)
N*i*3	Co*i*		Cl*i*	178.7(3)	178.8(3)
N*i*A1	Co*i*		Cl*i*	87.9(3)	86.4(3)
N*i*A2	Co*i*		Cl*i*	87.3(2)	87.9(3)
Co*i*	N*i*1		C*i*1	108.6(6)	106.4(7)
Co*i*	N*i*1		C*i*3	105.0(6)	107.4(7)
Co*i*	N*i*1		C*i*M1	116.3(6)	113.1(9)
C*i*1	N*i*1		C*i*3	110.4(8)	111.6(9)
C*i*1	N*i*1		C*i*M1	108.7(8)	111.9(11)
C*i*3	N*i*1		C*i*M1	107.7(8)	106.4(10)
Co*i*	N*i*2		C*i*2	105.7(6)	107.3(7)
Co*i*	N*i*2		C*i*5	110.0(7)	105.4(7)
Co*i*	N*i*2		C*i*M2	114.8(6)	115.0(8)
C*i*2	N*i*2		C*i*5	110.2(8)	109.5(9)
C*i*2	N*i*2		C*i*M2	107.4(8)	110.1(10)
C*i*5	N*i*2		C*i*M2	108.6(8)	109.4(10)
Co*i*	N*i*3		C*i*4	108.9(6)	106.2(8)
Co*i*	N*i*3		C*i*6	105.0(7)	109.2(6)
Co*i*	N*i*3		C*i*M3	115.2(7)	113.5(7)
C*i*4	N*i*3		C*i*6	108.1(8)	113.4(9)
C*i*4	N*i*3		C*i*M3	109.6(9)	107.0(10)
C*i*6	N*i*3		C*i*M3	109.8(8)	107.8(9)
N*i*1	C*i*1		C*i*2	111.2(9)	115.1(12)
N*i*2	C*i*2		C*i*1	107.9(9)	115.4(13)
N*i*1	C*i*3		C*i*4	108.9(9)	114.7(11)
N*i*3	C*i*4		C*i*3	109.7(9)	113.7(12)
N*i*2	C*i*5		C*i*6	108.7(9)	117.6(11)
N*i*3	C*i*6		C*i*5	109.9(9)	113.1(10)
Co*i*	N*i*A1		C*i*A11	171.6(8)	168.9(9)
Co*i*	N*i*A2		C*i*A21	170.9(8)	175.2(9)
N*i*1	C*i*1	C*i*2	N*i*2	− 43.9(11)	29(2)
N*i*1	C*i*3	C*i*3	N*i*3	− 45.6(11)	31(2)
N*i*2	C*i*5	C*i*6	N*i*3	− 45.0(12)	23(2)

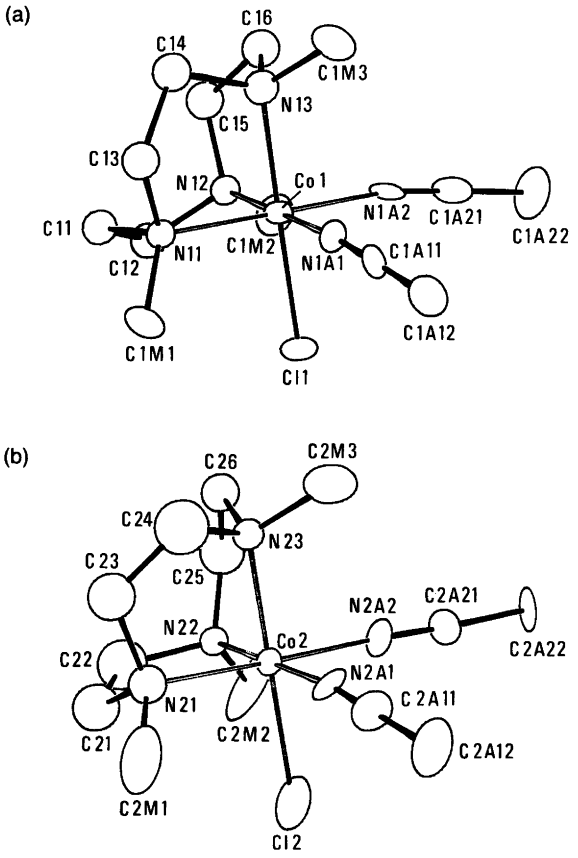

Fig. 1. ORTEP[15] drawings of the two [Co(Me$_3$tacn)(NCCH$_3$)$_2$Cl]$^{2+}$ cations showing the atomic numbering. The thermal ellipsoids are scaled to include 50 % probability. (a) Cation 1 (λλλ); (b) cation 2 (δδδ).

The three Co–N bond lengths of the Me$_3$tacn ligand for cation 1 and cation 2 average to 1.975(7) and 1.984(6) Å, respectively; values that are very close to those obtained for [Co((R)-2-Me-tacn)$_2$]$^{3+}$, where the average Co–N bond distance found is 1.974 Å.[4] These distances are also in good agreement with the Co–N distances of tacn in [Co(tacn)-(gly)(NH$_3$)]$^{2+}$ 1.946 Å,[3] and [Co(tacn)(aeaps)]$^{3+}$ 1.968 Å.[11] This demonstrates clearly that acetonitrile and chloride ion ligands have a similar structural influence as a *trans* ligand.

The average Co–N (NCCH$_3$) bond length is 1.905(5) Å for cation 1 and 1.922(5) Å for cation 2. This may be compared with the corresponding Co–N bonds 1.89 Å in a macrocyclic cobalt(III) complex with two acetonitrile ligands *trans*.[14]

The three methyl groups on Me$_3$tacn seem to hinder efficiently the binding of another chelate ligand as noted earlier.[2] The apparent flatness of Me$_3$tacn in cation 2 is not reflected in larger distances between the methyl carbon atoms and the coordination sites of chloride and aceto-nitrile. Thus the Me$_3$tacn is supposed to be relatively rigid, for all its bulkiness. We therefore conclude that the ligand Me$_3$tacn does prevent the metal ion from taking up another chelate ligand.

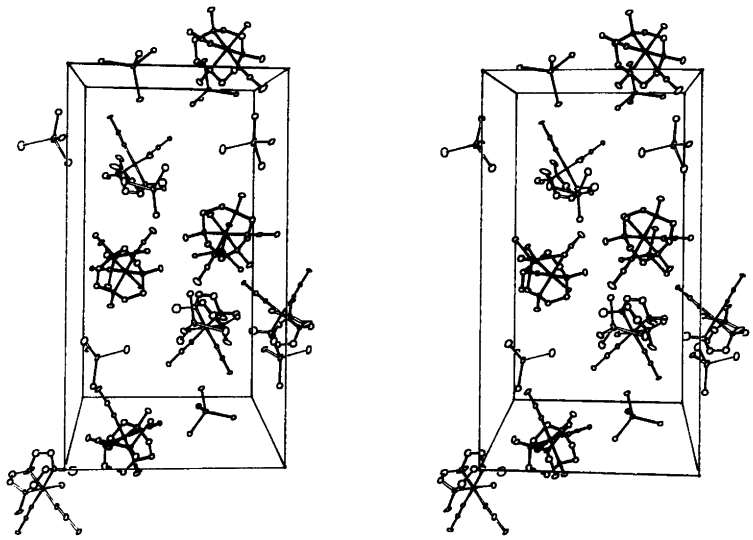

Fig. 2. ORTEP stereoscopic drawing of the unit cell seen along the crystallographic *a*-axis. The solid bond indicates cation 1. Only Cl_{41}–Cl_{44} are drawn for the anion Co(4).

The geometry of the ordered $CoCl_4^{2-}$ ion does not deviate from the usual values. Bond lengths and angles in the two anions are part of the supplementary material.

The crystal packing appears to be determined by electrostatic and non-bonded interactions since no hydrogen bonding is present (Fig. 2).

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