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The Crystal and Molecular Structure of an Isomer of Chloropyridine-tris-(2-aminoethyl)amine Cobalt(III)tetrachlorozincate(II), Hemihydrate: [Co(*tren*)pyCl] $ZnCl_4 \cdot \frac{1}{2}H_2O$

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The structure of the title compound has been determined by counter data. The crystals are orthorhombic, space group $P2_12_12_1$, with a = *18.177(8),* b = *12.564(6),* c = *8.932(4)* Å, *Z = 4. The structure has been refined by full-matrix least-squares to a final conventional* R *value of 0.044. The coordination geometry of the complex cation is near regular octahedral, with the* tren *ligand coordinating to the cobalt ion with the nitrogen atoms occupying one apical (Nte·rt) and three equatorial positions. The pyridine is bound through its nitrogen atom* trans *to the tertiary amine of the* tren *ligand. The $ZnCl_4$ anion assumes a distorted tetrahedral configuration.*

Introduction

In our attempts to prepare the various stereoisomeric forms of $[Co(\textit{trien})pyCl]^{2+}$ (*trien* = 1,8-diamino-3,6-diazaoctane) in order to examine the extent to which the sensitivity towards base hydrolysis depended upon the arrangement of the quadridentate ligand, we obtained a purple-red crystalline material whose analysis was in very good agreement with that calculated and whose visible absorption spectrum bore the same relationship to that of the reported β_2-*cis* isomer [(Cl *trans* to NH_2, ligand RR(SS)], [1], as did the α-*cis*-$[Co(\textit{trien})CH_3NH_2Cl]^{2+}$ species to its β-*cis* isomer. A comparison of the reactivities of α- and β-*cis* isomers was considered to be of special importance in this case as we wanted to see whether the presence of a coordinated pyridine in any way altered the very big difference in the base hydrolysis rate constants of the α- and β-*cis* isomers of complexes of the type $[Co(L_4)ACl]^{n+}$ where L_4 is a linear quadridentate ligand containing secondary amine nitrogens in the non-terminal positions [2]. The X-ray structure determination shows that these crystals contain the $[Co(\textit{tren})pyCl]^{2+}$ cation [*tren* = tris(2-aminoethyl)amine], the quadridentate *tren* being a known isomeric impurity in certain batches of commercial trien. Starting with an authentic sample of $[Co(\textit{tren})Cl_2]Cl$, the same compound is readily obtained by reaction with a slight excess of pyridine.

Experimental

X-ray Structure Analysis

Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from least-squares refinement of the $2\theta, \omega, \chi$ and ϕ values of 20 carefully centered high angle reflexions. Intensity data were collected from a crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm, on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.03° s^{-1}) by using a graphite monochromatized Mo$K\bar{\alpha}$ radiation. 2811 independent reflexions up to $\theta = 25°$ were measured, of which 1817 had $I \geqslant 3\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. During the data collection

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TABLE I. Atomic Coordinates (×10^4) with e.s.d.s in Parentheses.

	x	y	z		x	y	z
Co	2513(1)	1878(1)	4731(1)				
Zn	4215(1)	5247(1)	3297(1)				
Cl(1)	2500(2)	113(2)	4160(3)				
Cl(2)	4195(1)	4203(3)	5357(4)				
Cl(3)	3273(2)	6438(2)	3639(3)				
Cl(4)	5300(2)	6059(3)	3041(4)				
Cl(5)	3911(2)	4329(3)	1216(4)				
N(1)	1678(4)	2188(6)	3411(10)				
N(2)	3127(4)	2109(7)	2946(9)	H(22)	3454	1525	2834
				H(23)	3402	2745	3075
N(3)	2500(4)	3393(5)	5165(9)	H(32)	2988	3634	5337
				H(33)	2210	3516	6032
N(4)	1778(4)	1544(7)	6271(10)	H(42)	1855	1994	7111
				H(43)	1831	822	6567
N(5)	3368(4)	1641(6)	6075(10)				
C(1)	1893(5)	1808(9)	1871(12)	H(10)	1882	1053	1836
				H(11)	1562	2088	1149
C(2)	2662(5)	2210(8)	1563(12)	H(20)	2643	2935	1264
				H(21)	2875	1796	784
C(3)	1513(6)	3360(8)	3425(13)	H(30)	1372	3575	2446
				H(31)	1122	3496	4103
C(4)	2181(5)	3981(8)	3888(12)	H(40)	2043	4679	4186
				H(41)	2525	4022	3090
C(5)	1023(6)	1589(9)	4010(12)	H(50)	1066	857	3762
				H(51)	583	1867	3590
C(6)	1010(6)	1719(9)	5689(12)	H(60)	685	1212	6118
				H(61)	848	2417	5935
C(7)	3427(5)	2168(8)	7397(11)	H(71)	3046	2647	7673
C(8)	4009(5)	2037(8)	8348(13)	H(81)	4026	2416	9268
C(9)	4573(6)	1355(9)	7962(13)	H(91)	4982	1254	8608
C(10)	4523(6)	820(9)	6589(14)	H(101)	4899	343	6280
C(11)	3922(5)	997(9)	5709(13)	H(111)	3897	639	4773
O	4483(11)	−1561(17)	4447(24)	H(1)[a]	4786	−1599	5261
				H(2)[a]	4209	−1231	4075

Anisotropic thermal parameters (×10^3) with e.s.d.s in parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	21.0(5)	23.4(5)	24.6(5)	−0.1(5)	0.5(6)	−2.8(6)
Zn	26.0(5)	33.1(5)	39.8(7)	4.0(6)	0.2(5)	−3.7(5)
Cl(1)	49(1)	26(1)	41(1)	−2(1)	−1(1)	−5(1)
Cl(2)	28(1)	67(2)	83(2)	45(2)	−9(2)	−9(1)
Cl(3)	47(2)	44(1)	42(2)	−1(1)	2(1)	15(1)
Cl(4)	48(2)	91(3)	52(2)	−4(2)	14(2)	−37(2)
Cl(5)	51(2)	56(2)	61(2)	−18(2)	−2(2)	−7(1)
N(1)	22(4)	31(4)	35(5)	3(4)	−1(4)	−7(3)
N(2)	21(4)	35(4)	29(5)	−8(4)	4(3)	−2(3)
N(3)	23(3)	27(3)	38(4)	1(3)	−4(4)	−1(4)
N(4)	29(4)	38(5)	30(5)	7(4)	0(4)	−4(4)
N(5)	26(4)	31(4)	33(5)	−2(4)	−6(4)	3(4)
C(1)	37(2)					
C(2)	38(3)					
C(3)	38(2)					
C(4)	31(2)					
C(5)	41(3)					

(continued on facing page)

TABLE I. *(continued)*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(6)	38(2)					
C(7)	30(2)					
C(8)	38(2)					
C(9)	44(3)					
C(10)	44(3)					
C(11)	36(2)					
O	78(6)					

[a] Values not refined found in the last difference map.

TABLE II. Distances (Å) and Angles (°) with e.s.d.s. in Parentheses.

Co–Cl(1)	2.276(3)	C(3)–C(4)	1.50(1)
Co–N(1)	1.960(8)	C(5)–C(6)	1.51(2)
Co–N(2)	1.969(8)	N(5)–C(7)	1.36(1)
Co–N(3)	1.942(7)	N(5)–C(11)	1.33(1)
Co–N(4)	1.962(8)	C(7)–C(8)	1.37(1)
Co–N(5)	1.987(8)	C(8)–C(9)	1.38(1)
N(1)–C(1)	1.51(1)	C(9)–C(10)	1.40(2)
N(1)–C(3)	1.50(1)	C(10)–C(11)	1.36(1)
N(1)–C(5)	1.51(1)	Zn–Cl(2)	2.259(3)
N(2)–C(2)	1.50(1)	Zn–Cl(3)	2.295(3)
N(3)–C(4)	1.48(1)	Zn–Cl(4)	2.232(3)
N(4)–C(6)	1.51(1)	Zn–Cl(5)	2.257(3)
C(1)–C(2)	1.51(1)	O–H(1)	0.91
		O–H(2)	0.73
N(4)–Co–N(1)	86.4(3)	N(1)–C(3)–C(4)	110.5(8)
N(1)–Co–N(2)	85.6(3)	C(3)–C(4)–N(3)	105.7(8)
N(2)–Co–N(5)	93.9(3)	C(4)–N(3)–Co	109.9(6)
N(4)–Co–N(5)	94.4(3)	Co–N(2)–C(2)	111.1(5)
N(2)–Co–N(3)	91.4(3)	N(2)–C(2)–C(1)	110.0(8)
N(2)–Co–Cl(1)	88.2(3)	C(2)–C(1)–N(1)	107.5(8)
N(1)–Co–N(3)	85.2(3)	Co–N(5)–C(7)	120.9(7)
N(1)–Co–Cl(1)	92.9(2)	Co–N(5)–C(11)	122.3(7)
N(4)–Co–N(3)	93.6(4)	N(5)–C(7)–C(8)	123(1)
N(4)–Co–Cl(1)	86.7(3)	C(10)–C(11)–N(5)	124(1)
N(3)–Co–N(5)	92.0(3)	C(11)–N(5)–C(7)	117(1)
N(5)–Co–Cl(1)	89.8(3)	C(7)–C(8)–C(9)	120(1)
Co–N(4)–C(6)	111.0(6)	C(8)–C(9)–C(10)	118(1)
N(4)–C(6)–C(5)	108.2(9)	C(9)–C(10)–C(11)	119(1)
C(6)–C(5)–N(1)	108.1(9)	Cl(2)–Zn–Cl(3)	105.0(1)
C(3)–N(1)–C(1)	111.7(8)	Cl(2)–Zn–Cl(4)	111.3(1)
C(5)–N(1)–C(1)	111.7(8)	Cl(2)–Zn–Cl(5)	111.7(1)
C(5)–N(1)–C(3)	109.2(8)	Cl(3)–Zn–Cl(4)	112.0(1)
C(5)–N(1)–Co	107.4(6)	Cl(3)–Zn–Cl(5)	105.1(1)
C(1)–N(1)–Co	106.6(6)	Cl(4)–Zn–Cl(5)	111.5(1)
C(3)–N(1)–Co	110.2(6)		

two standard reflexions were measured every 150 min to check the stabilities of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects and put in an absolute scale by Wilson's method. An experimental absorption correction was applied [3].

Crystal Data

$C_{11}H_{24}N_{5\;0.5}Cl_5CoZn$. M = 534.9. Orthorhombic, space group $P2_12_12_1$, a = 18.177(8), b = 12.564(6), c = 8.932(4), U = 2039.8 Å^3, $F(000)$ = 1080 e, D_o = 1.75, D_c = 1.74 g cm^{-3} for Z = 4, MoK$\bar{\alpha}$ radiation, λ = 0.71069 Å, μ(MoK$\bar{\alpha}$) = 25.9 cm^{-1}.

TABLE III. Least-Squares Planes with Deviations (Å) of the Relevant Atoms in Square Brackets. The Equation of a Plane in the Direct Space is given by PX + QY + RZ = S.[a]

	P	Q	R	S
Plane 1	0.3712	12.1671	2.2199	3.4106
Co, N(1), N(2), N(4), N(5) [Co 0.018, N(4) –0.079, N(1) 0.071 N(2) –0.074, N(5) 0.060, N(3) 1.957, Cl(1) – 2.257]				
Plane 2	8.6299	9.4828	–4.0435	2.0158
N(5), C(7), C(8), C(9), C(10), C(11) [N(5) –0.010, C(7) 0.007, C(8) 0.000, C(9) –0.004, C(10) 0.001, C(11) 0.006]				
Plane 3	14.1720	–1.6750	5.4650	5.7607
Co, Cl(1), N(4), N(2), N(3) [Co 0.072, Cl(1) 0.037, N(4) –0.072, N(2) –0.072, N(3) 0.037]				
Plane 4	11.3932	2.0826	–6.8004	0.0436
Co, Cl(1), N(1), N(3), N(5) [Co –0.007, Cl(1) –0.001, N(1) 0.004, N(3) –0.001, N(5) 0.004]				
Plane 5	0.1939	11.9796	2.6907	3.5715
Co, N(4), N(1) [C(6) 0.038, C(5) –0.569]				
Plane 6	1.3173	12.2006	2.0320	3.5837
Co, N(1), N(2) [C(2) –0.219, C(1) –0.748]				
Plane 7	11.4692	2.0395	–6.7761	0.0595
Co, N(1), N(3) [C(3) 0.040, C(4) 0.619]				
Line 8				
Co–Cl(1)				

Angles

1–2	51.1	1–3	87.8	2–3	89.6	1–4	89.1	2–4	39.9
3–4	90.0	5–6	5.6	5–7	86.2	6–7	88.2	1–5	3.2
1–6	3.2	1–7	88.9	1–8	1.6				

[a] For a plane and line, the angle is to the normal of the plane.

TABLE IV. Torsion Angles (°).[a]

Co–N(4)–C(6)–C(5)	26
N(1)–C(5)–C(6)–N(4)	–45
Co–N(1)–C(5)–C(6)	44
Co–N(1)–C(1)–C(2)	–47
N(1)–C(1)–C(2)–N(2)	41
Co–N(2)–C(2)–C(1)	–16
Co–N(1)–C(3)–C(4)	23
N(1)–C(3)–C(4)–N(3)	–43
Co–N(3)–C(4)–C(3)	44

[a] The torsion angles w(IJKL) is defined as the angle between the vector KL when viewed down JK. It is positive if clockwise and negative if counter-clockwise.

TABLE V. Possible Hydrogen-Bonding Interactions.

C(5)···Cl(2)$^{\mathrm{I}}$	3.51	H(51)···Cl(2)$^{\mathrm{I}}$	3.01
C(6)···Cl(2)$^{\mathrm{I}}$	3.62	H(60)···Cl(2)$^{\mathrm{I}}$	3.06
		H(60)···Cl(4)$^{\mathrm{I}}$	3.03
N(3)···Cl(3)$^{\mathrm{II}}$	3.41	H(33)···Cl(3)$^{\mathrm{II}}$	2.49
C(4)···Cl(5)$^{\mathrm{II}}$	3.57	H(40)···Cl(5)$^{\mathrm{II}}$	2.80
Cl(3)···C(2)	3.55	Cl(3)···H(20)$^{\mathrm{II}}$	2.98
N(4)···Cl(1)$^{\mathrm{III}}$	3.57	H(43)···Cl(1)$^{\mathrm{III}}$	2.87
O···C(1)$^{\mathrm{III}}$	3.32	O···H(11)$^{\mathrm{III}}$	2.52
Cl(4)···N(2)$^{\mathrm{IV}}$	3.27	Cl(4)···H(22)$^{\mathrm{IV}}$	2.47
Cl(5)···O$^{\mathrm{IV}}$	3.18	Cl(5)···H(1)$^{\mathrm{IV}}$	2.95

(continued on facing page)

TABLE V. *(continued)*

	Key for symmetry
I	–½ + x, ½ – y, 1 – z
II	½ – x, 1 – y, ½ + z
III	½ – x, –y, ½ + z
IV	1 – x, ½ + y, ½ – z

Structure Solution and Refinement

The molecular structure of the complex was solved by Patterson-Fourier methods. The refinement of the structural model, which was by the method of full-matrix least-squares was carried out allowing all non-hydrogen atoms to vibrate anisotropically. Hydrogen atoms could not be located from electron density difference maps and therefore were included in the scattering model in calculated idealized positions (C–H = 0.95 Å), but not varied.

The function minimized was $\Sigma w[|F_o|-|F_c|]^2$ and unit weights were applied. Weighting-scheme analyses showed no serious dependence of the mean $w\Delta^2$ on either $|F_o|$ and $\lambda^{-1}\sin\theta$. The final electron density difference map showed no unusual features. Atomic scattering factors were taken from reference 4. Allowance was made for the anomalous scattering of zinc, cobalt and chlorine atoms, using values of $\Delta f'$ and $\Delta f''$ from reference 4.

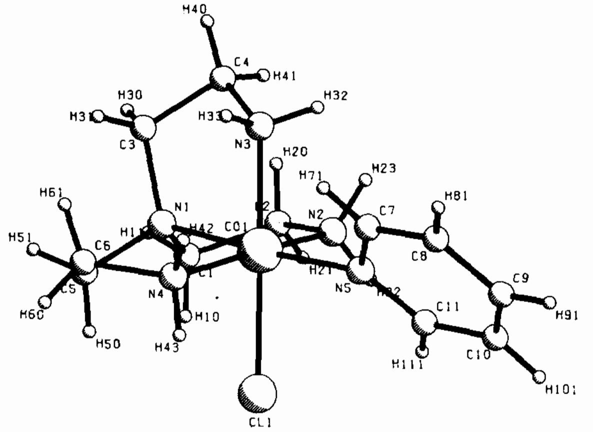

Fig. 1. View of the cation down *c*.

The final conventional *R* value for the 1817 observed reflexions with $I \geqslant 3\sigma(I)$ was 0.044.

As pointed out by Ibers and Hamilton [5], the absolute configuration of the present complex cation may be determined from the anomalous scattering effects even though no Bijvoet pairs of reflexions (hkl and $\overline{hkl}$) have been measured. Consequently the refinement was repeated with the direction of the *a*, *b* and *c* axes reversed. The resulting value of the reliability factor *R* then was 0.053. The significantly higher discrepancy index confirmed that the original model indeed was of correct handedness. In addition the application of Hamilton's *R*-factor ratio test [6] gives $R = R_2/R_1 = 1.204$. Comparison with the theoretical value of acceptance of the second configuration with a 99.5% probability (R_1, 1540, 0.005 = 1.02) indicates the configuration presented in this study to the correct one. Final atomic parameters and a selection of functions derived from them are presented in Tables I–V.

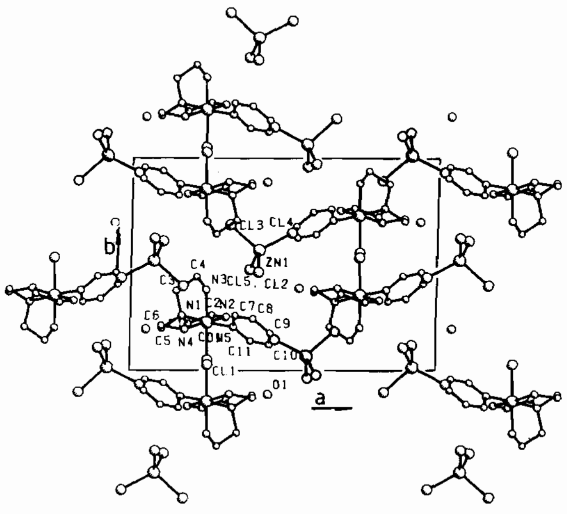

Fig. 2. Packing of the molecules viewed down *c*.

All calculations were carried out on the CYBER 76 computer of the 'C.I.N.E.C.A.' with the SHELX-76 program for crystal structure determination [7].

Results and Discussion

The stereochemical arrangement of the complex cation is shown in Fig. 1, along with atom nomenclature, and the crystal packing arrangement is illustrated in Fig. 2. The ligands are arranged in a near octahedral geometry.

The *tren* ligand is linked to cobalt by all four of its nitrogens [N(1), N(2), N(3), N(4)] and the pyridine, which is planar within the experimental error, is bound, through its nitrogen [N(5)] *trans* to the tertiary nitrogen [N(1)] of tren. The chlorine occupies the remaining coordination site. The plane of the pyridine makes an angle of about 40° with the plane defined by Co, Cl N(1), N(3) and N(5). Within experimental error the N(5)–Co bond lies in the plane of the pyridine. This structure corresponds to that of the red, p- of $[Co(tren)NH_3Cl]^{2+}$, assigned by Buckingham *et al.* on the basis of chemical evidence [8]. The requirements of the octahedral coordination cause the *tren* ligand to deviate from the threefold symmetry which is favoured by its tripod-like structure and found in trigonal bipyramidal five-coordinated complexes such as Zn(*tren*)(NCS)(SCN), [9] and Cu(*tren*)(NCS)(SCN), [10]. The mean of the Co–N(*tren*) bond distances is 1.958(7) Å and is comparable with corresponding values in some *tren* analogues [11]. However, the Co–N(3) bond *trans* to chlorine 1.942(7) Å is the shortest among the three Co–N (primary) distances, indicating that the *trans* influence of the chlorine is smaller than that of a primary amine group. The Co–N(py) distance, 1.987(8) Å is significantly longer than the other Co–N bonds of this cation and is also longer than that predicted from radii-sum rules, 1.92 Å, [12], but, nevertheless falls within the range found for this distance in several crystal structures of cobalt complexes containing the pyridine ligand [13]. The Co–Cl(1) bond distance, 2.276(3) Å, which is significantly longer than the sum of appropriate covalent radii; 2.21 Å [12], agrees with the Co–Cl bond in several cobalt(III)-complexes [1].

There are no significant intra-ligand distortions in the polyamine skeleton. In fact within the *tren* ligand all internal angles at C and N are close to the regular tetrahedral value and all C–C and C–N distances are reasonably close to their usual values [12]. Since the angles subtended at the cobalt atom by the *tren* chelate rings are all close to 86° [mean: 85.7(3)°] the coordination plane deviates significantly from coplanarity as already found in analogous compounds [11].

The three five-membered ring moieties have unsymmetrical envelope conformations, whose helicity [13] is λ for all chelate rings.

In the tetrachlorozincate(II) anion a distorted tetrahedral arrangement of chlorine atoms about the central zinc atom is observed, with mean Zn–Cl bond distances of 2.260(3) Å. A comparable values in related compounds are: 2.263 Å in [Co(*picdien*)Cl]$ZnCl_4$, [14], 2.26(3) and 2.27(1) in π and χ isomers of [Co(*en*)(*dien*)Cl]$ZnCl_4$, [15] and 2.264(17) Å in [β-Co(*en*)(*dtp*)Cl]$ZnCl_4$ [16].

The crystal packing arrangement which is shown in Fig. 2 is mainly determined by coulombic forces, N–H···Cl, C–H···Cl, C–H···O and O–H···Cl hydrogen bonds.

In particular the cations and anions are linked by a hydrogen bonding system between C(4), C(5), C(6), N(2), N(3), N(4) of the cation and Cl(2), Cl(3), Cl(4), Cl(5) of the anion. The water molecule holds together cations and anions through bonding interactions involving both cations (of the type O···H–C) and anions (of the type O–H···Cl).

The main features of these interactions are reported in Table V.

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