Crystal structure of carbonato[tris(2-aminoethyl)amine]cobalt(III) chloride dihydrate, $[\text{Co}(\text{tren})\text{CO}_3]\text{Cl} \cdot 2 \text{H}_2\text{O}$

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Abstract

$\text{C}_7\text{H}_{22}\text{ClCoN}_4\text{O}_5$, orthorhombic, *Pbca* (No. 61), $a = 11.225(2) \text{ \AA}$, $b = 14.354(3) \text{ \AA}$, $c = 16.926(3) \text{ \AA}$, $V = 2727.2 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.038$, $R_w(F^2) = 0.099$, $T = 293 \text{ K}$.

Source of material

$[\text{Co}(\text{tren})\text{CO}_3]\text{Cl}$ was prepared by the reaction of $\text{tren} \cdot 3\text{HCl}$, NaHCO_3 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with PbO_2 according to [1]. Red crystals were grown from a $\text{H}_2\text{O}/\text{EtOH}$ mixture. The C,H,N-analysis was in agreement with the composition $\text{C}_7\text{H}_{22}\text{ClCoN}_4\text{O}_5$ and the ^{13}C -NMR spectrum (D_2O) showed the expected total of four signals for the tren-ligand, indicating an averaged C_s point group symmetry for the cation in solution on the NMR time scale.

Discussion

$[\text{Co}(\text{tren})\text{CO}_3]\text{Cl}$ ($\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$) has previously been reported to crystallise from a saturated aqueous NaCl solution as a trihydrate in the monoclinic space group $P2_1/c$ [2]. Crystallisation from an $\text{EtOH}/\text{H}_2\text{O}$ mixture yielded, however, the dihydrate $[\text{Co}(\text{tren})\text{CO}_3]\text{Cl} \cdot 2\text{H}_2\text{O}$, which crystallises in the orthorhombic space group *Pbca*. The geometry of the $[\text{Co}(\text{tren})\text{CO}_3]^+$ cation in these two structures is almost identical, showing a slightly asymmetric coordination of the bidentate carbonate ligand. In both structures, the oxygen atom in *trans* position to the tertiary amino group forms a slightly shorter Co–O bond than the corresponding oxygen atom which is *trans* oriented to the primary amino group. In contrast to the findings in previous

reports [3], the bond lengths from cobalt to the tertiary nitrogen atom (N1) and the primary nitrogen atom (N2) do not differ within significance. The two amino groups which are oriented *trans* to each other exhibit, however, considerably longer Co–N bonds than the amino groups which are oriented *trans* to an oxygen donor of the carbonate. The three five-membered chelate rings of the $\text{Co}(\text{tren})$ moiety adopt a $\delta \lambda$ conformation. The structure is stabilised by a network of hydrogen bonds, and by analogy with the previously reported trihydrate, the shortest intermolecular distances are observed for the hydrogen bonds to the non coordinated oxygen atom O(3) of the carbonate ligand ($\text{O}(3) \cdots \text{O}(4)$: $2.820(4) \text{ \AA}$ and $\text{O}(3) \cdots \text{N}(2)$: $2.875(4) \text{ \AA}$).

Table 1. Data collection and handling.

Crystal:	red prism, size $0.1 \times 0.1 \times 0.2 \text{ mm}$
Wavelength:	Mo K_{α} radiation ($0.71073 \text{ \AA}$)
μ :	14.74 cm^{-1}
Diffractometer, scan mode:	Stoe AED2, ω/θ
$2\theta_{\text{max}}$:	48°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4058, 2141
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1845
$N(\text{param})_{\text{refined}}$:	251
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8c	0.069(9)	0.152(6)	0.677(5)	0.15(3)
H(2)	8c	0.103(3)	0.075(2)	0.482(2)	0.014(8)
H(3)	8c	−0.077(3)	0.119(2)	0.377(2)	0.024(9)
H(4)	8c	0.061(3)	0.012(2)	0.204(2)	0.026(9)
H(5)	8c	0.040(4)	0.005(3)	0.424(3)	0.05(1)
H(6)	8c	−0.016(3)	0.029(3)	0.280(2)	0.029(9)
H(7)	8c	−0.072(3)	0.148(3)	0.463(2)	0.03(1)
H(8)	8c	0.243(3)	0.015(2)	0.271(2)	0.017(8)
H(9)	8c	−0.018(4)	0.259(3)	0.367(2)	0.03(1)
H(10)	8c	0.394(3)	0.160(2)	0.477(2)	0.024(8)
H(11)	8c	0.264(4)	0.159(3)	0.503(2)	0.03(1)
H(12)	8c	0.355(3)	0.069(2)	0.373(2)	0.026(9)
H(13)	8c	0.290(4)	0.020(3)	0.447(2)	0.04(1)
H(14)	8c	0.149(4)	−0.046(3)	0.325(2)	0.04(1)
H(15)	8c	0.105(4)	0.154(3)	0.199(2)	0.03(1)
H(16)	8c	0.251(4)	0.287(3)	0.436(2)	0.03(1)
H(17)	8c	0.251(4)	0.437(3)	0.137(3)	0.04(1)
H(18)	8c	−0.003(4)	0.168(3)	0.239(2)	0.04(1)
H(19)	8c	0.338(4)	0.263(3)	0.387(2)	0.03(1)
H(20)	8c	0.050(4)	0.260(3)	0.433(2)	0.04(1)
H(21)	8c	0.252(4)	0.511(4)	0.102(3)	0.05(2)
H(22)	8c	0.045(5)	0.207(4)	0.610(3)	0.05(2)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	8c	0.16843(3)	0.20173(3)	0.32550(2)	0.0117(3)	0.0144(3)	0.0187(3)	0.0004(2)	0.0012(1)	0.0006(1)
Cl	8c	0.13831(8)	0.14786(6)	0.04798(5)	0.0346(5)	0.0421(5)	0.0317(5)	0.0049(4)	0.0029(3)	0.0100(4)
O(1)	8c	0.3031(2)	0.1966(1)	0.2543(1)	0.016(1)	0.018(1)	0.026(1)	0.0029(9)	0.0048(9)	0.0027(9)
O(2)	8c	0.1856(2)	0.3159(2)	0.2678(1)	0.021(1)	0.017(1)	0.032(1)	0.0030(9)	0.0071(9)	0.0039(9)
O(3)	8c	0.3407(2)	0.3270(2)	0.1833(1)	0.027(1)	0.024(1)	0.040(2)	0.001(1)	0.014(1)	0.009(1)
N(1)	8c	0.1723(2)	0.0790(2)	0.3725(1)	0.018(1)	0.019(1)	0.021(1)	0.002(1)	0.002(1)	0.002(1)
N(2)	8c	0.0328(2)	0.2291(2)	0.3923(2)	0.015(1)	0.021(1)	0.025(1)	0.003(1)	−0.000(1)	−0.002(1)
N(3)	8c	0.0672(3)	0.1453(2)	0.2434(2)	0.017(2)	0.023(1)	0.023(1)	0.004(1)	−0.001(1)	0.001(1)
C(1)	8c	0.2796(3)	0.2826(2)	0.2318(2)	0.017(2)	0.020(2)	0.022(2)	−0.003(1)	0.000(1)	0.001(1)
C(3)	8c	0.0717(3)	0.0681(2)	0.4309(2)	0.023(2)	0.024(2)	0.023(2)	−0.002(1)	0.007(1)	0.002(1)
N(4)	8c	0.2793(2)	0.2403(2)	0.4084(2)	0.013(1)	0.027(2)	0.027(2)	−0.004(1)	0.001(1)	−0.003(1)
C(4)	8c	0.0570(3)	0.0421(2)	0.2554(2)	0.029(2)	0.023(2)	0.030(2)	−0.007(2)	0.002(2)	−0.006(1)
C(5)	8c	0.1615(3)	0.0127(2)	0.3051(2)	0.035(2)	0.016(2)	0.030(2)	−0.000(1)	0.002(1)	−0.003(2)
C(2)	8c	−0.0248(3)	0.1400(2)	0.4162(2)	0.017(2)	0.029(2)	0.028(2)	−0.004(1)	0.005(1)	−0.000(1)
C(6)	8c	0.2916(3)	0.0719(2)	0.4124(2)	0.020(2)	0.030(2)	0.030(2)	0.005(2)	−0.001(1)	0.008(2)
C(7)	8c	0.3103(3)	0.1599(3)	0.4596(2)	0.022(2)	0.043(2)	0.028(2)	−0.001(2)	−0.009(2)	0.003(2)
O(4)	8c	0.2069(3)	0.4752(2)	0.1195(2)	0.033(2)	0.036(2)	0.058(2)	0.001(2)	−0.007(1)	0.008(1)
O(5)	8c	0.0117(3)	0.1752(2)	0.6274(2)	0.028(2)	0.037(2)	0.086(3)	−0.003(1)	−0.015(2)	0.003(2)

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