Crystal structure of bis[tris(ethylenediamine)cobalt(III)] pentaoxalatocobaltate(II) tetrahydrate, $[Co(C_2H_8N_2)_3]_2[Co_2(C_2O_4)_5] \cdot 4H_2O$

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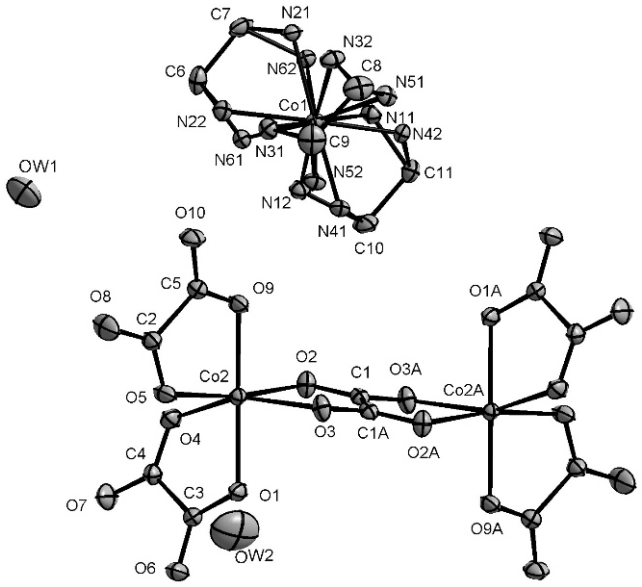

Abstract

$C_{22}H_{56}Co_4N_{12}O_{24}$, triclinic, $P\bar{1}$ (no. 2), a = 7.988(2) Å, b = 10.218(2) Å, c = 12.873(3) Å, α = 100.85(3)°, β = 92.14(3)°, γ = 93.57(3)°, V = 1028.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.119, T = 293 K.

Source of material

A mixture of CoO · $6H_2O$ (0.0582 g, 0.2 mmol), oxalic acid (0.018 g, 0.2 mmol), ethylenediamine (0.013 ml, 0.2 mmol), and water (0.6 ml) was sealed under vacuum in a Pyrex tube and heated to 150 °C for 2 days under autogenous pressure, followed by cooling to 30 °C with 10 °C/h. The solid products were recovered by vacuum filtration and washed with water. Red polyhedral crystals suitable for analysis with unidentified white powder were obtained.

Experimental details

The hydrogen atoms of lattice water molecules were not located (large thermal parameters of oxygen atoms). Also, all hydrogen atoms on ethylenediamine cannot be found due to the disorder of all nitrogen atoms.

Discussion

The crystal structure of the title compound comprises discrete centrosymmetric dinuclear $[Co_2(C_2O_4)_5]^{6-}$ anions, mononuclear $[Co(C_2H_8N_2)_3]^{3+}$ cations, and water molecules. The anionic dimer contains four terminal chelating and one bridging bis-bidentate oxalate ligands. Each Co2 atom is coordinated in a slightly distorted octahedral manner by six oxygen atoms of three oxalate ligands in the range of 77.83(9)° - 114.98(10)° and 156.40(9)° - 170.74(9)°. The cobalt-to-bridging oxalate bond lengths are slightly longer than those involving the terminal oxalate ligands. A similar trend can be observed in several other $[M_2(C_2O_4)_5]^{n-}$ anionic complexes (M = Fe, Cr, Ni, Zn; n = 4 or 6) [1-7]. The BVS calculation for Co in $[Co_2(C_2O_4)_5]^{6-}$ anions gives a value of 2.02, indicating an oxidation state of +2 [8]. Co1 in $[Co(en)_3]^{3+}$ is coordinated to three ethylenediamine molecules in a slightly distorted octahedral manner. Two nitrogen atoms in each ethylenediamine molecule are disordered almost equally over two positions, giving two possible conformations, *gauche*- and and *syn*- conformation. The *gauche*-conformation is considered more likely since it minimizes nitrogen-nitrogen repulsions and is usually observed for $M(en)_3$ cations [9-12]. Therefore, two sets of *gauche*-conformational $[Co(en)_3]^{3+}$ cations are almost equally distributed in the structure, i.e., one set of N1–C6–C7–N4, N5–C8–C9–N8, N9–C10–C11–N12, and the other set of N2–C6–C7–N3, N6–C8–C9–N7, N10–C10–C11–N11, with torsional angles in the range of 56.51(3)° - 61.76(3)°. The other possible arrangement is *synperiplanar*. However, the *syn*-conformation of ethylenediamine in octahedral $M(en)_3$ geometry is energetically unfavorable and is not reported yet. The crystal packing of the title complex is stabilized by hydrogen bonds between the $[Co(C_2H_8N_2)_3]^{3+}$ cations and $[Co_2(C_2O_4)_5]^{6-}$ anions. Besides, two inequivalent lattice water molecules are further hydrogen bonded among to the monomeric cations, dimeric anions, or to each other in a complex arrangement.

Table 1. Data collection and handling.

Crystal:	red polyhedral, size 0.16 × 0.23 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.86 cm^{-1}
Diffractometer, scan mode:	Regaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10220, 4659
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4070
$N(param)_{refined}$:	340
Programs:	SHELXS-97, SHELXL-97 [13], DIAMOND [14]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	2*i*		0.07526(4)	0.27340(3)	0.25000(3)	0.0186(2)	0.0232(2)	0.0223(2)	0.0020(1)	0.0006(1)	0.0052(1)
Co(2)	2*i*		–0.40012(5)	0.70669(4)	0.16424(3)	0.0313(2)	0.0232(2)	0.0213(2)	0.0060(2)	–0.0025(2)	0.0012(1)
O(1)	2*i*		–0.6136(3)	0.7944(2)	0.1282(2)	0.028(1)	0.026(1)	0.049(1)	–0.0011(8)	–0.0102(9)	0.0076(9)
O(2)	2*i*		–0.3360(3)	0.6228(2)	0.0116(2)	0.039(1)	0.032(1)	0.027(1)	–0.0077(9)	0.0064(9)	0.0019(8)
O(3)	2*i*		–0.5692(3)	0.5295(2)	0.1280(2)	0.048(1)	0.029(1)	0.0215(9)	–0.0023(9)	0.0097(9)	0.0030(8)
O(4)	2*i*		–0.2985(3)	0.8965(2)	0.1490(2)	0.025(1)	0.035(1)	0.052(1)	0.0000(8)	–0.001(1)	0.007(1)
O(5)	2*i*		–0.4245(3)	0.7865(3)	0.3250(2)	0.057(2)	0.048(1)	0.025(1)	0.031(1)	–0.003(1)	0.0004(9)
O(6)	2*i*		–0.7081(3)	0.9945(2)	0.1360(2)	0.034(1)	0.035(1)	0.070(2)	0.012(1)	–0.006(1)	0.005(1)
O(7)	2*i*		–0.3846(3)	1.1015(3)	0.1618(3)	0.050(2)	0.027(1)	0.090(2)	–0.009(1)	–0.014(2)	0.008(1)
O(8)	2*i*		–0.3044(5)	0.7885(3)	0.4829(2)	0.114(3)	0.077(2)	0.024(1)	0.054(2)	–0.011(1)	–0.008(1)
O(9)	2*i*		–0.2392(3)	0.5958(2)	0.2383(2)	0.052(1)	0.038(1)	0.029(1)	0.024(1)	–0.004(1)	–0.0020(9)
O(10)	2*i*		–0.1476(3)	0.5670(3)	0.3967(2)	0.056(2)	0.044(1)	0.039(1)	0.022(1)	–0.008(1)	0.012(1)
OW(1)	2*i*		0.3275(6)	0.9464(5)	0.4064(4)	0.097(3)	0.096(3)	0.128(4)	0.043(3)	0.006(3)	–0.020(3)
OW(2)	2*i*		–0.8754(6)	0.7436(6)	0.2686(5)	0.078(3)	0.151(5)	0.196(6)	–0.012(3)	0.034(3)	0.064(5)
N(11)	2*i*	0.542(8)	0.1450(5)	0.2200(5)	0.1030(3)	0.026(2)	0.029(2)	0.024(2)	0.005(2)	0.006(2)	0.005(2)
N(12)	2*i*	0.458	0.0237(7)	0.4115(5)	0.1639(4)	0.035(3)	0.028(3)	0.026(3)	0.008(2)	0.000(2)	0.006(2)
N(21)	2*i*	0.544(8)	0.2994(5)	0.2357(5)	0.3035(4)	0.023(2)	0.029(2)	0.034(2)	0.004(2)	–0.004(2)	0.009(2)
N(22)	2*i*	0.456	0.1586(7)	0.4200(6)	0.3724(4)	0.031(3)	0.032(3)	0.028(3)	0.003(2)	–0.001(2)	0.002(2)
N(31)	2*i*	0.545(8)	–0.0114(6)	0.3067(5)	0.3916(3)	0.030(2)	0.033(3)	0.025(2)	0.003(2)	0.005(2)	0.005(2)
N(32)	2*i*	0.455	0.1079(7)	0.1371(6)	0.3323(5)	0.030(3)	0.036(3)	0.040(3)	0.002(2)	–0.002(2)	0.019(2)
N(41)	2*i*	0.571(7)	–0.1367(5)	0.3124(4)	0.1845(3)	0.023(2)	0.030(2)	0.033(2)	0.008(2)	–0.001(2)	0.002(2)
N(42)	2*i*	0.429	–0.0004(7)	0.1423(5)	0.1264(4)	0.025(3)	0.023(3)	0.028(3)	0.000(2)	–0.007(2)	0.001(2)
N(51)	2*i*	0.565(8)	–0.0061(5)	0.0819(4)	0.2463(4)	0.028(2)	0.025(2)	0.037(2)	–0.001(2)	0.004(2)	0.010(2)
N(52)	2*i*	0.435	–0.1527(7)	0.2824(6)	0.3058(5)	0.023(3)	0.032(3)	0.035(3)	0.006(2)	0.005(2)	0.009(2)
N(61)	2*i*	0.545(7)	0.1658(5)	0.4566(4)	0.2658(4)	0.027(2)	0.022(2)	0.031(2)	0.003(2)	–0.003(2)	0.002(2)
N(62)	2*i*	0.455	0.3089(6)	0.2766(5)	0.2096(4)	0.022(3)	0.027(3)	0.031(3)	0.002(2)	–0.001(2)	0.003(2)
C(1)	2*i*		–0.4322(3)	0.5268(3)	–0.0334(2)	0.032(1)	0.022(1)	0.020(1)	0.005(1)	0.003(1)	0.0065(9)
C(2)	2*i*		–0.3263(4)	0.7438(3)	0.3876(2)	0.042(2)	0.033(2)	0.027(1)	0.013(1)	–0.002(1)	0.003(1)
C(3)	2*i*		–0.5942(4)	0.9187(3)	0.1366(2)	0.028(1)	0.026(1)	0.031(1)	0.004(1)	–0.005(1)	0.003(1)
C(4)	2*i*		–0.4088(4)	0.9794(3)	0.1499(2)	0.032(1)	0.026(1)	0.036(2)	–0.002(1)	–0.004(1)	0.005(1)
C(5)	2*i*		–0.2270(4)	0.6264(3)	0.3374(2)	0.031(1)	0.027(1)	0.031(1)	0.004(1)	–0.001(1)	0.005(1)
C(6)	2*i*		0.3204(4)	0.4732(3)	0.3496(3)	0.040(2)	0.038(2)	0.037(2)	–0.013(1)	0.003(1)	–0.004(1)
C(7)	2*i*		0.4168(4)	0.3542(4)	0.3098(3)	0.023(1)	0.044(2)	0.056(2)	–0.004(1)	–0.011(1)	0.015(2)
C(8)	2*i*		–0.0587(5)	0.0761(4)	0.3594(3)	0.042(2)	0.052(2)	0.053(2)	–0.002(2)	0.006(2)	0.031(2)
C(9)	2*i*		–0.1444(5)	0.2010(4)	0.4003(3)	0.049(2)	0.058(2)	0.044(2)	–0.006(2)	0.021(2)	0.014(2)
C(10)	2*i*		–0.0978(5)	0.3296(4)	0.0695(3)	0.060(2)	0.058(2)	0.030(2)	0.027(2)	–0.014(2)	0.004(2)
C(11)	2*i*		–0.0079(4)	0.2066(3)	0.0300(2)	0.040(2)	0.039(2)	0.027(1)	0.003(1)	–0.005(1)	–0.001(1)

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