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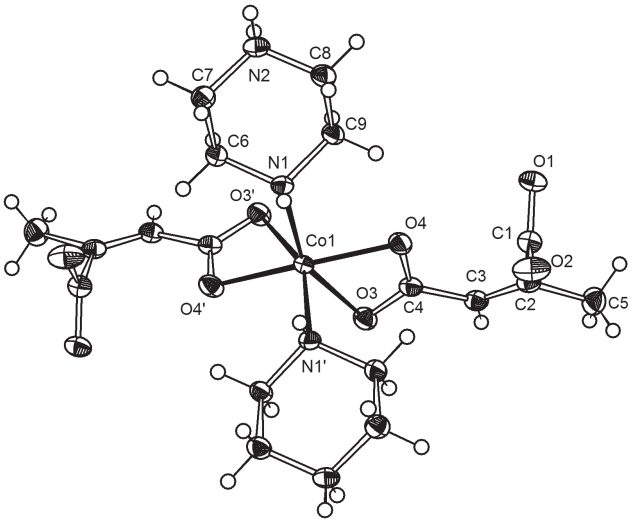
Jaeun Kang, Kang Min Ok and Junghwan Do*

Crystal structure of *trans*-bis(2-methylmaleato-κ^2O,O′) bis(piperazinium-κN) cobalt(II) trihydrate, $C_{18}H_{36}CoN_4O_{11}$



DOI 10.1515/ncrs-2015-0186
Received August 19, 2015; accepted January 25, 2016; available online February 17, 2016

Abstract

$C_{18}H_{36}CoN_4O_{11}$, monoclinic, *C2/c* (no. 15), $a = 19.3607(4)$ Å, $b = 13.4260(3)$ Å, $c = 11.2917(2)$ Å, $\beta = 125.299(1)$, $V = 2395.50(8)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0251$, $wR_{ref}(F^2) = 0.0719$, $T = 123$ K.

CCDC no.: 1449645

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Purple, polyhedra, size 0.18×0.19×0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.81 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω scans
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10812, 2938
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2724
$N(param)_{refined}$:	168
Programs:	SHELX [10], Diamond [11]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3A)	8*f*	0.0330	0.4344	−0.0457	0.025
H(5A)	8*f*	0.1038	0.3235	−0.2080	0.047
H(5B)	8*f*	0.1887	0.3751	−0.0768	0.047
H(5C)	8*f*	0.1010	0.4345	−0.1593	0.047
H(1)	8*f*	−0.0645	0.0743	0.1270	0.022
H(2A)	8*f*	−0.2436	0.1352	−0.2487	0.025
H(2B)	8*f*	−0.2590	0.0258	−0.2652	0.025
H(6A)	8*f*	−0.0187	0.1206	−0.0103	0.027
H(6B)	8*f*	−0.0927	0.2018	−0.0892	0.027
H(7A)	8*f*	−0.1343	0.0631	−0.2412	0.029
H(7B)	8*f*	−0.1176	−0.0095	−0.1144	0.029
H(8A)	8*f*	−0.2150	0.0082	−0.0298	0.028
H(8B)	8*f*	−0.2885	0.0904	−0.1085	0.028
H(9A)	8*f*	−0.1887	0.2192	−0.0077	0.025
H(9B)	8*f*	−0.1721	0.1488	0.1206	0.025
H(2)	8*f*	−0.215(1)	0.364(2)	−0.191(2)	0.042(5)
H(3)	8*f*	−0.149(1)	0.404(1)	−0.083(2)	0.036(5)
H(4)	8*f*	0.034(1)	0.098(1)	−0.183(2)	0.044(5)

Source of material

The mixture of $CoCl_2 \cdot 6H_2O$ (0.071 g, 0.3 mmol), piperazine (0.078 g, 0.9 mmol), citraconic acid (2-methylmaleic acid) (0.039 g, 0.3 mmol) and ethanol (1.0 mL) was sealed under vacuum in a Pyrex tube and heated to 70°C for 68 h, then cooled to room temperature at 20 °C/h. The solid products were recovered by vacuum filtration and washed with

***Corresponding author: Junghwan Do,** Department of Chemistry, Konkuk University, Seoul 147–701, Republic of Korea, e-mail: junghwan@konkuk.ac.kr
Jaeun Kang: Department of Chemistry, Konkuk University, Seoul 147–701, Republic of Korea
Kang Min Ok: Department of Chemistry, Chung-Ang University, Seoul 156–756, Republic of Korea

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	4*e*	0	0.24394(2)	0.25	0.0144(1)	0.0205(1)	0.0166(1)	0.0	0.00775(9)	0.0
O(1)	8*f*	0.23208(6)	0.24502(6)	0.1719(1)	0.0184(4)	0.0210(4)	0.0246(4)	0.0025(3)	0.0073(4)	0.0000(3)
O(2)	8*f*	0.12826(6)	0.15262(7)	−0.0065(1)	0.0343(5)	0.0198(4)	0.0313(5)	−0.0018(4)	0.0071(4)	−0.0034(3)
O(3)	8*f*	−0.03052(5)	0.36226(6)	0.08547(9)	0.0213(4)	0.0260(4)	0.0267(4)	0.0028(3)	0.0134(4)	0.0028(3)
O(4)	8*f*	0.08162(6)	0.26687(7)	0.1915(1)	0.0190(4)	0.0340(5)	0.0256(4)	0.0053(3)	0.0117(4)	0.0135(3)
C(1)	8*f*	0.15934(8)	0.23364(8)	0.0548(1)	0.0210(5)	0.0185(5)	0.0227(5)	0.0003(4)	0.0111(4)	0.0004(4)
C(2)	8*f*	0.11081(7)	0.32841(8)	−0.0202(1)	0.0186(5)	0.0185(5)	0.0186(5)	−0.0028(4)	0.0076(4)	0.0011(4)
C(3)	8*f*	0.05786(7)	0.37315(8)	0.0026(1)	0.0194(5)	0.0180(5)	0.0207(5)	0.0006(4)	0.0088(4)	0.0046(4)
C(4)	8*f*	0.03557(7)	0.33299(8)	0.0984(1)	0.0171(5)	0.0201(5)	0.0186(5)	−0.0018(4)	0.0071(4)	0.0004(4)
C(5)	8*f*	0.12753(9)	0.3689(1)	−0.1252(2)	0.0337(7)	0.0338(7)	0.0322(6)	0.0032(5)	0.0223(6)	0.0086(5)
N(1)	8*f*	−0.08105(6)	0.13693(7)	0.0843(1)	0.0154(4)	0.0202(4)	0.0160(4)	0.0010(3)	0.0069(3)	0.0014(3)
N(2)	8*f*	−0.22447(6)	0.07503(7)	−0.2013(1)	0.0191(4)	0.0179(4)	0.0187(4)	−0.0018(3)	0.0065(4)	−0.0017(3)
C(6)	8*f*	−0.07748(7)	0.13506(9)	−0.0434(1)	0.0188(5)	0.0271(6)	0.0207(5)	−0.0027(4)	0.0114(4)	−0.0039(4)
C(7)	8*f*	−0.13631(7)	0.05819(9)	−0.1558(1)	0.0223(5)	0.0248(5)	0.0232(5)	−0.0012(4)	0.0123(5)	−0.0048(4)
C(8)	8*f*	−0.22982(7)	0.07505(9)	−0.0752(1)	0.0196(5)	0.0241(5)	0.0234(5)	−0.0045(4)	0.0109(4)	−0.0034(4)
C(9)	8*f*	−0.16977(7)	0.15199(9)	0.0354(1)	0.0164(5)	0.0235(5)	0.0218(5)	−0.0023(4)	0.0101(4)	−0.0034(4)
OW(1)	8*f*	−0.19663(6)	0.41019(7)	−0.1372(1)	0.0225(5)	0.0219(4)	0.0255(4)	0.0037(3)	0.0066(4)	0.0009(3)
OW(2)	4*e*	0	0.0609(1)	−0.25	0.0289(7)	0.0204(6)	0.0258(6)	0	0.0104(5)	0

distilled water. Violet polyhedral crystals were obtained together with unidentified brown powder. The product is stable in air. The yield of the compound was about 25% based on cobalt.

Experimental details

All hydrogen atoms were placed in calculated positions and refined as riding model. The U_{iso} value of the methyl group was set to $1.5U_{eq}$(C) and the U_{iso} values of the other hydrogen atoms were set to $1.2U_{eq}$(C, N). The hydrogen atoms in water molecules were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined.

Discussion

Aliphatic, unsaturated dicarboxylate are of special interest because they may give new structures with intriguing physical properties [1–3]. Particularly, coordination compounds containing citraconate (2-methylmaleate) or its isomer, mesaconate are known to exhibit interesting electrical and optical properties [4–8]. The crystal structure of the title compound comprises discrete cobalt(II) complex moieties and lattice water molecules. The crystallographically unique Co atom is coordinated by four oxygen atoms from two symmetry related citraconate ligands (d(Co–O) = 2.0579(9) and 2.2484(8) Å) in a κ^2O,O' mode (see the figure). The nitrogen atoms of two monoprotonated piperazine ligands (d(Co–N) = 2.1529(9) Å) in *trans*-configuration complete the distorted octahedral environment of Co1. The bond valence sum (BVS) calculation for Co gives a value of +2.04 indicating an oxidation state of +2 [9]. Not a classical case of zwitterion as there are several cationic and anionic regions. The crystal packing of the title complex is stabilized by extensive hydrogen bonds with water molecules in the range of d(OH···O) = 2.712(1)–2.781(1) Å and d(NH···O) = 2.709(1) Å. In addition, each citraconate ligands forms a NH···O (d = 2.684(1) Å) hydrogen bond to the NH_2^+ group of an adjacent complex.

Acknowledgements: This paper was supported by Konkuk University in 2013.

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