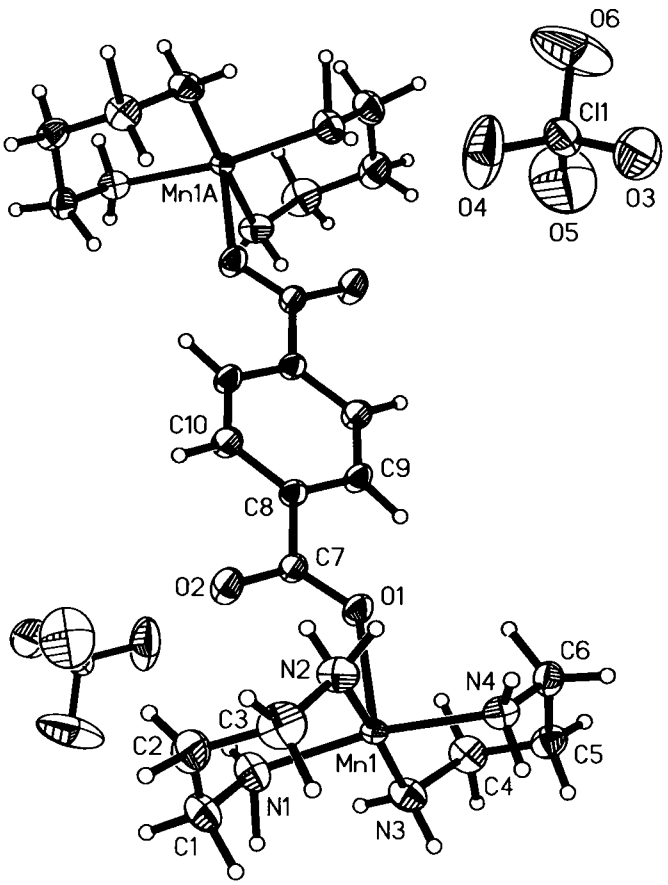
Z. Kristallogr. NCS 221 (2006) 407-408 / DOI 10.1524/ncrs.2006.0130

Crystal structure of μ-terephthalatobis[bis(1,3-diaminopropane)-manganese(II)] diperchlorate, $[Mn_2\{C_3H_6(NH_2)_2\}_4\{C_6H_4(COO)_2\}][ClO_4]_2$

S.-P. Xu*,[I], C.-H. Liu[II] and C.-H. Zhu[II]

[I] Xuzhou Normal University, Chemistry Department, Xuzhou 221116, P. R. China
[II] Nanjing University, School of Life Sciences, Nanjing 210093, P. R. China

Received July 25, 2006, accepted and available on-line September 12, 2006; CCDC no. 1267/1853



Abstract

$C_{20}H_{44}Cl_2Mn_2N_8O_{12}$, monoclinic, $P12_1/n1$ (no. 14), a = 10.160(3) Å, b = 10.139(4) Å, c = 16.008(3) Å, β = 93.06(1)°, V = 1646.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.211, T = 293 K.

Source of material

$Mn(ClO_4)_2 \cdot 6H_2O$, equimolar terephthalic acid and two equivalent molar 1,3-diaminopropane were dissolved in 30 % aqueous ammonium solution, with stirring, giving a clear pale pink solution, which was stood in air for three days, and pink prism crystals were precipitated. These were filtered and washed with water for three times and dried in vacuo using $CaCl_2$ (yield 58 %).

Discussion

Transition metal terephthalate complexes with various organic amine ligands are a hot topics in the field coordination chemistry. Recently, some of these kinds of complexes were prepared and structurally determinated by single X-ray structure analysis [1-4]. Due to their biologically relevant important behaviors, many manganese complexes with polyamine ligands have been reported [5-7], however, to our knowledge, there are no structure reports about manganese(II, III) terephthalate complexes with organic amine molecules.

The title crystal structure consists of one dinuclear manganese(II) complex cation and two perchlorate anions. In the cation, there are two equivalent manganese(II) atoms, bridged by a μ_2-terephthalate dianion at the distance of 11.810 Å. Each manganese atom is coordinated by four nitrogen atoms from two 1,3-diaminopropane molecules and one oxygen atom from a benzoate group of the terephthalate, the latter behaved as a μ_2 bridge. The metal atom is in a square-pyramidal environment, with the four N atoms being the basal plane of the polyhedron. The mean deviation of the basal plane is 0.055 Å, and the metal atom is 0.140 Å above the plane towards the apical oxygen atom. This plane is nearly perpendicular to the intra-molecular benzene ring with a dihedral angle of 89.2°. In order to minimize the steric strain of the neighboring atoms, the carboxylate group is deviated from the aromatic ring to which it is attached at the angle of 6.5°. As expected, the six-membered cycle consists of one manganese atom and one 1,3-diaminopropane molecule in a typical chain conformation, with the Mn atom and a C atom occupying the apical positions of the chair. All the nitrogen atoms, three of the four oxygen atoms of each perchlorate anion and the uncoordinated oxygen atoms in the carboxylate groups participate to form intra- and intermolecular hydrogen bonds, which first join the molecules into one-dimensional chains along the b axis and then into two-dimensional layers parallel to the a,b plane.

Table 1. Data collection and handling.

Crystal:	pink prism, size 0.30 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.96 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	51.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3335, 3152
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2217
$N(param)_{refined}$:	199
Program:	SHELXTL [8]

* Correspondence author (e-mail: suoping_xu863@yahoo.com.cn)

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

Atom	Site	x	y	z	U_{iso}
H(1NA)	4e	0.9402	−0.1324	0.7247	0.1
H(1NB)	4e	1.0920	−0.1232	0.7506	0.1
H(2NA)	4e	0.7679	0.1172	0.7988	0.1
H(2NB)	4e	0.7937	0.2274	0.8066	0.1
H(1A)	4e	1.0803	−0.0661	0.8835	0.1
H(1B)	4e	1.0023	−0.2176	0.8466	0.1
H(2A)	4e	0.8825	−0.0879	0.9598	0.1
H(2B)	4e	0.8161	−0.1224	0.8708	0.1
H(3A)	4e	0.9720	0.1286	0.9231	0.1
H(3B)	4e	0.8156	0.0865	0.9317	0.1
H(3NA)	4e	1.1103	−0.0175	0.6334	0.1
	4e	1.1918	0.1019	0.6643	0.1
H(4NA)	4e	1.0826	0.3205	0.7203	0.1
H(4NB)	4e	0.9425	0.3527	0.7219	0.1
H(4A)	4e	1.0050	0.1057	0.5234	0.1
H(4B)	4e	1.1920	0.0990	0.5142	0.1
H(5A)	4e	1.1011	0.3206	0.5074	0.1
H(5B)	4e	1.1819	0.3007	0.5891	0.1
H(6A)	4e	0.9010	0.2926	0.5808	0.1
H(6B)	4e	1.0035	0.4398	0.6128	0.1
H(9)	4e	0.6945	0.1208	0.4872	0.1
H(10)	4e	0.4773	−0.1161	0.6284	0.1

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4e	0.97063(6)	0.11021(7)	0.72145(4)	0.0363(3)	0.0408(4)	0.0267(3)	0.0024(3)	0.0000(2)	−0.0016(3)
N(1)	4e	0.9753(6)	−0.0792(5)	0.7619(4)	0.093(4)	0.070(4)	0.075(4)	0.008(3)	0.009(3)	0.010(3)
N(2)	4e	0.8453(5)	0.1495(6)	0.8130(3)	0.066(3)	0.098(4)	0.048(3)	0.009(3)	0.009(2)	0.001(3)
C(1)	4e	0.9909(8)	−0.1104(8)	0.8518(5)	0.098(5)	0.088(5)	0.091(5)	0.002(4)	−0.017(4)	0.038(4)
C(2)	4e	0.8812(8)	−0.0557(9)	0.8985(5)	0.098(5)	0.118(6)	0.064(4)	−0.019(5)	0.001(4)	0.032(4)
C(3)	4e	0.8763(9)	0.0983(9)	0.8980(4)	0.111(6)	0.146(8)	0.042(3)	−0.006(6)	0.012(4)	0.004(4)
N(3)	4e	1.1096(5)	0.0695(6)	0.6368(3)	0.075(3)	0.077(3)	0.062(3)	0.018(3)	0.007(3)	−0.001(3)
N(4)	4e	0.9956(5)	0.3046(5)	0.6973(3)	0.062(3)	0.065(3)	0.050(2)	0.000(2)	0.002(2)	−0.010(2)
C(4)	4e	1.0946(7)	0.1386(7)	0.5546(4)	0.087(4)	0.084(5)	0.047(3)	0.006(4)	0.014(3)	−0.007(3)
C(5)	4e	1.1019(6)	0.2841(7)	0.5637(4)	0.062(3)	0.089(5)	0.061(4)	−0.007(3)	0.007(3)	0.003(3)
C(6)	4e	0.9877(6)	0.3435(6)	0.6079(4)	0.070(4)	0.054(3)	0.066(4)	−0.009(3)	0.001(3)	0.001(3)
O(1)	4e	0.7985(4)	0.0879(4)	0.6267(3)	0.059(2)	0.076(3)	0.063(2)	−0.024(2)	−0.017(2)	0.016(2)
O(2)	4e	0.6926(4)	−0.0629(5)	0.6964(3)	0.078(3)	0.103(3)	0.052(2)	−0.033(2)	−0.018(2)	0.032(2)
C(7)	4e	0.7037(5)	0.0115(6)	0.6348(3)	0.050(3)	0.060(3)	0.044(3)	−0.010(2)	−0.004(2)	0.009(2)
C(8)	4e	0.5968(5)	0.0069(5)	0.5654(3)	0.045(2)	0.053(3)	0.045(3)	−0.006(2)	−0.003(2)	0.004(2)
C(9)	4e	0.6116(5)	0.0757(6)	0.4924(3)	0.050(3)	0.069(4)	0.049(3)	−0.018(3)	−0.008(2)	0.012(3)
C(10)	4e	0.4843(6)	−0.0688(6)	0.5733(4)	0.057(3)	0.079(4)	0.048(3)	−0.011(3)	−0.006(2)	0.016(3)
Cl(1)	4e	0.1805(2)	0.6697(2)	0.6598(1)	0.084(1)	0.0620(9)	0.077(1)	0.0041(8)	−0.0097(9)	0.0046(8)
O(3)	4e	0.2371(7)	0.7841(6)	0.6966(5)	0.129(5)	0.097(4)	0.190(7)	−0.028(4)	−0.041(5)	−0.026(4)
O(4)	4e	0.167(1)	0.5766(8)	0.7175(5)	0.237(8)	0.163(6)	0.124(5)	−0.103(6)	−0.043(5)	0.069(5)
O(5)	4e	0.240(1)	0.618(1)	0.5916(7)	0.27(1)	0.200(9)	0.205(9)	0.053(7)	0.121(8)	−0.042(7)
O(6)	4e	0.0627(9)	0.709(1)	0.6265(6)	0.199(7)	0.213(8)	0.223(8)	0.103(6)	−0.136(6)	−0.080(7)

References

1. Zhu, H.-L.; Tong, Y.-X.; Chen, X.-M.; Ren, C.-X.: Synthesis, crystal structure and physical properties of two terephthalate-bridged copper(II) and nickel(II) complexes. Transition Met. Chem. **26** (2001) 528-531.
2. Zhu, H.-L.; Liu, X.-Y.; Wang, X.-J.; Yang, F.; Usman, A.; Fun, H.-K.: Syntheses and Crystal Structures of Three Polymeric Silver(I) Terephthalate Complexes with Organic N-Donor Ligands: $[Ag(pren)]_2(tp)\cdot 2H_2O$, $[Ag(en)][Ag(\mu_2\text{-tp})]\cdot H_2O$, and $[Ag_2(\mu_4\text{-tp})(apy)_2]$. Z. Anorg. Allg. Chem. **629** (2003) 1986-1990.
3. Zhu, H.-L.; Wang, Z.-G.; Lin, Y.-S.; Zou, Y.; Tang, L.-L.; Shao, S.-C.: Tris(l-1,6-diaminohexane)diterephthalatotetrasilver(I) dihydrate. Acta Crystallogr. **E59** (2003) m942-m943.
4. Li, Y.-G.; Zhu, H.-L.; Song, Y.; Ng, S. W.: Bis[bis(4-aminopyridine-κN)-silver(I)] terephthalate decahydrate. Acta Crystallogr. **E61** (2005) m2564-m2565.
5. Li, S.-Y.; Li, Y.-H.; Zhu, H.-L.; Wang, D.-Q.: Crystal structure of bis(diaquamanganese(II))hexaacetatomanganese(II) octahydrate, $((H_2O)_2Mn)_2(C_2H_3O_2)_6Mn\cdot 8H_2O$. Z. Kristallogr. NCS **218** (2003) 319-320.
6. You, Z.-L.; Zhu, H.-L.; Liu, W.-S.: Tris[2-(cyclopropyliminomethyl)-phenolato]manganese(III). Acta Crystallogr. **E60** (2004) m603-m605.
7. Ma, J.-L.; You, Z.-L.; Zhu, H.-L.: Di-μ_2-acetato-bis[μ_2-*N*,*N*′- bis(salicylidene)-butane-1,4-diaminato]trimanganese(II). Acta Crystallogr. **E61** (2005) m1286-m1288.
8. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.10. Bruker AXS, Madison, Wisconsin, USA 1998.