The title complex was isolated in a similar manner to the yttrium analog (Grillone *et al.*, 1991) by reacting $YbCl_3.6H_2O$ with a MeOH solution of (1,10-phenanthroline).H_2O in a molar ratio of about 1:6. IR spectra reveal two reaction products, depending on the experimental conditions. Good prismatic crystals of the title compound have only been obtained in about 50% yield from a MeOH/Me_2CO mixture.

The clathrated methanol molecule (one per dimer) with the O atom at the inversion center $(0,\frac{1}{2},\frac{1}{2})$ is statistically disordered about this position.

Calculations were carried out using *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71042 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1028]

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Structure of Bis(hydronium) Bis(pyrazine-2,3-dicarboxylato)manganate, a Polymeric Mn^{II} Complex

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(*Received* 27 *April* 1992; *accepted* 31 *March* 1993)

Abstract

The structure of the title compound consists of centrosymmetric anionic units, $[Mn(C_6H_2N_2O_4)_2]^{2-}$, which are linked by hydrogen bonds to the hydronium cations. The Mn atom is in a six-coordinate N_2O_4 octahedral environment. One carboxylato group acts as a bridge between the molecular units and gives the polymeric structure.

Comment

Manganese(II) forms a variety of compounds with dicarboxylates (Chiswell, McKenzie & Lindoy, 1987), or carboxylates having other functional groups. Pyrazinedicarboxylate is a potential tetradentate ligand with different donor sites comprised of the O atoms of the dicarboxylic acid and the N atoms of the aromatic ring. Complexes with some metallic cations have been prepared. Their insolubility in both polar and non-polar solvents was indicative of polymeric structure, however, single-crystal X-ray structure analysis was not possible (Allan, Paton, Turvey, Bowley & Gerrard, 1988). In this work the structure of a polymeric Mn^{II} complex of pyrazinedicarboxylate is reported which is the first example involving this type of ligand.

The Mn atom sits on a crystallographic centre of symmetry in a distorted octahedral arrangement with each of the pyrazinedicarboxylate ligands acting as a dianionic tridentate NO_2 donor. Mn^{II} is bound to two bidentate chelating groups [O(1) and N(2)] of two pyrazinedicarboxylate ligands and to two monodentate carboxylato groups [O(3)] from two different molecular units, resulting in the polymeric structure. The hydronium counterion acts as a bridge between

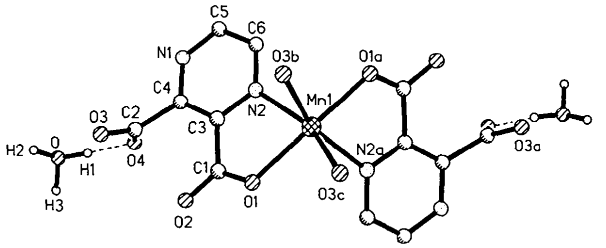

Fig. 1. A perspective view of the molecule with the atom-numbering scheme.

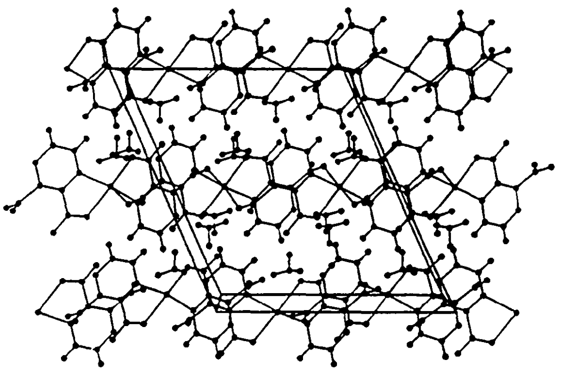

Fig. 2. Projection of the unit cell viewed along [010].

$[Mn(C_6H_2N_2O_4)_2]^{2-}$ units leading to an infinite network of hydrogen bonds along the *a* and *c* axes [H(O5)···O(4) = 1.49 (3) Å; H(O5″)···O(2) = 1.47 (3) Å].

Experimental

Crystal data

$[H_3O]_2[Mn(C_6H_2N_2O_4)_2]$
M_r = 425.17
Monoclinic
$C2/c$
a = 14.484 (2) Å
b = 8.480 (1) Å
c = 13.087 (1) Å
β = 114.753 (7)°
V = 1459.71 Å^3
Z = 4
D_x = 1.93 Mg m^{-3}
D_m = 1.92 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 86 reflections
θ = 5-13°
μ = 0.901 mm^{-1}
T = 293 K
Square bipyramid
0.3 × 0.3 × 0.3 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer
ω-θ scans
Absorption correction: none
3855 measured reflections
2039 independent reflections
1730 observed reflections [$F_o > 3\sigma(F_o)$]

R_{int} = 0.0125
θ_{max} = 30°
$h = -20 \rightarrow 20$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
Final R = 0.0332
wR = 0.0242
1730 reflections
144 parameters
Only H-atom U's refined
$w = 1.4/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.4 e Å^{-3}
$\Delta\rho_{min}$ = −0.4 e Å^{-3}

Extinction correction: *SHELX*76 (Sheldrick, 1976)
Extinction coefficient: 5.4×10^{-4}
Atomic scattering factors from *SHELX*76, except Mn (Cromer & Mann, 1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn(1)†	0.00000	0.01081 (5)	0.25000	0.0185 (1)
O(1)	0.12703 (9)	−0.0397 (1)	0.4073 (1)	0.0245 (5)
O(2)	0.18569 (9)	−0.1749 (2)	0.5680 (1)	0.0272 (5)
O(3)	0.08248 (9)	−0.2001 (1)	0.71932 (9)	0.0247 (5)
O(4)	0.0834 (1)	−0.4503 (1)	0.6691 (1)	0.0333 (5)
O(5)	0.1452 (1)	−0.5470 (2)	0.8687 (1)	0.0305 (6)
C(1)	0.1160 (1)	−0.1298 (2)	0.4772 (1)	0.0180 (6)
C(2)	0.0583 (1)	−0.3091 (2)	0.6493 (1)	0.0183 (6)
C(3)	0.0102 (1)	−0.1882 (2)	0.4522 (1)	0.0159 (6)
C(4)	−0.0150 (1)	−0.2723 (2)	0.5281 (1)	0.0166 (6)
N(1)	−0.1104 (1)	−0.3229 (2)	0.4999 (1)	0.0216 (5)
C(5)	−0.1806 (1)	−0.2849 (2)	0.3976 (1)	0.0248 (7)
C(6)	−0.1561 (1)	−0.1976 (2)	0.3229 (1)	0.0229 (6)
N(2)	−0.0612 (1)	−0.1513 (2)	0.3491 (1)	0.0184 (5)

† Occupancy factor 0.5.

Table 2. *Geometric parameters* (Å, °)

Mn(1)—O(3)	2.137 (1)	C(3)—C(4)	1.390 (2)
Mn(1)—O(1)	2.153 (1)	C(4)—N(1)	1.343 (2)
Mn(1)—N(2)	2.307 (2)	N(1)—C(5)	1.338 (2)
O(1)—C(1)	1.252 (2)	C(5)—C(6)	1.386 (3)
O(2)—C(1)	1.254 (2)	C(6)—N(2)	1.329 (2)
O(3)—C(2)	1.244 (2)	C(2)—C(5)	1.386 (2)
O(4)—C(2)	1.247 (2)	O(5)—H(O5)	1.04 (3)
C(1)—C(3)	1.510 (2)	O(5)—H(O5′)	0.90 (3)
C(2)—C(4)	1.527 (2)	O(5)—H(O5″)	1.04 (3)
C(3)—N(2)	1.349 (2)		
O(3)—Mn(1)—O(3)	82.62 (7)	O(4)—C(2)—C(4)	115.3 (1)
O(3)—Mn(1)—O(1)	106.92 (4)	N(2)—C(3)—C(4)	120.9 (1)
O(3)—Mn(1)—O(1)	90.45 (4)	N(2)—C(3)—C(1)	115.1 (1)
O(3)—Mn(1)—N(2)	88.01 (5)	C(4)—C(3)—C(1)	124.0 (1)
O(3)—Mn(1)—N(2)	158.44 (4)	N(1)—C(4)—C(3)	121.0 (1)
O(1)—Mn(1)—O(1)	157.05 (5)	N(1)—C(4)—C(2)	114.1 (1)
O(1)—Mn(1)—N(2)	73.71 (5)	C(3)—C(4)—C(2)	124.8 (1)
O(1)—Mn(1)—N(2)	92.48 (5)	C(5)—N(1)—C(4)	117.5 (2)
N(2)—Mn(1)—N(2)	106.83 (9)	N(1)—C(5)—C(6)	121.5 (1)
O(1)—C(1)—O(2)	125.4 (1)	N(2)—C(6)—C(5)	121.2 (2)
O(1)—C(1)—C(3)	118.0 (1)	C(6)—N(2)—C(3)	117.8 (2)
O(2)—C(1)—C(3)	116.5 (1)	H(O5′)—O(5)—H(O5″)	115 (2)
O(3)—C(2)—O(4)	126.4 (1)	H(O5′)—O(5)—H(O5)	104 (2)
O(3)—C(2)—C(4)	118.2 (1)	H(O5″)—O(5)—H(O5)	113 (2)

The yellow title compound was prepared by adding an aqueous solution of $MnCl_2.4H_2O$ to a solution of pyrazine-2,3-dicarboxylic acid in acetone. Crystals were obtained by recrystallization from hot dimethyl sulfoxide and their density determined by flotation in tetrachloromethane diluted with bromoform. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986) and refined with anisotropic thermal parameters (*SHELX*76; Sheldrick, 1976). All H atoms were observed on difference Fourier maps. Bond distances and angles were calculated using *ORFFE*3 (Busing, Martin & Levy, 1971). Diagrams were drawn with *SHELXTL-Plus* (Sheldrick, 1987).

We are grateful to E. M. Peters for plotting the figures and to the Université Paul Sabatier for financial support (ATUPS).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71056 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1014]

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