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Hydroxonium hydrate tris(2,4,6-triamino-1,3,5-triazin-1-ium) bis[bis(pyridine-2,6-dicarboxylato)manganate(II/III)] hydroxide pyridine-2,6-dicarboxylic acid solvate pentahydrate

Hossein Aghabozorg,[a] Zohreh Derikvand,[a] Marilyn M. Olmstead[b]* and Jafar Attar Gharamaleki[a]

[a]Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran, and [b]Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616-5292, USA
Correspondence e-mail: olmstead@chem.ucdavis.edu

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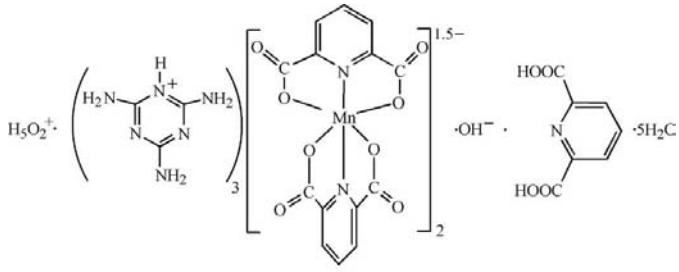
For charge balance in the title compound, $(H_5O_2)(C_3H_7N_6)_3[Mn(C_7H_3NO_4)_2]_2(OH)\cdot C_7H_5NO_4\cdot 5H_2O$, it is assumed that the metal atom site is disordered Mn^{II}/Mn^{III}, probably due to partial air oxidation of the starting Mn^{II} species. The formula unit of the complex contains a hydroxonium hydrate cation, $H_5O_2^+$, also known as the Zundel cation, with twofold symmetry. The O···O [2.445 (10) Å] and O···H distances [1.24 (2) Å] in the $H_5O_2^+$ cation indicate a strong hydrogen bond. In addition, there is a hydroxide ion that is disordered with respect to a twofold rotation axis. One of the melaminium groups and the pyridine-2,6-dicarboxylate (pydc) ligand also reside on crystallographic twofold axes. The coordination environment of the Mn ion is distorted octahedral. Three intermolecular C=O···π interactions are observed, with distances of 3.536 (4), 3.262 (4) and 3.750 (4) Å between carboxylate C=O groups and the centroids of the aromatic rings of pydc and melaminium. There are numerous O—H···O, O—H···N, N—H···O, N—H···N and C—H···O hydrogen bonds. Most of the components of the structure are organized into one plane.

Comment

Melamine, used in the synthesis of plastics, has recently been implicated in the food industry as an impurity in powdered milk and pet food products and as a causative agent in the production of kidney stones in infants and in pets. With oxalic acid, one of the main constituents of kidney fluids, a proton-transfer salt of $[melaminiumH_2][C_2O_2H]_2$ is formed (Zhang *et al.*, 2005). Melamine is also known to form $melaminiumH_2^{2+}$ salts with trifluoroacetic acid (Perpétuo & Janczak, 2006) and other strong acids. With somewhat weaker acids, such as pyridine-2,6-dicarboxylic acid ($pydcH_2$), both the mono- and diprotonated species have been described (Sharif *et al.*, 2006). It is pertinent to study these proton-transfer salts in combination with metal ions in order to model the biological species that may exist in kidney disease. The crystal structures of metal complexes involving Cd^{II} (Aghabozorg, Aghajani & Sharif, 2006), Zn^{II} (Aghajani *et al.*, 2006), Bi^{III} (Sharif, Aghabozorg & Moghimi, 2007), Pb^{II} (Sharif *et al.*, 2006), Co^{II} (Aghabozorg *et al.*, 2008) and Ni^{II} (Sharif, Aghajani & Aghabozorg, 2007) are known. In the asymmetric unit of the title compound, (I), one-and-a-half molecules of melamine are each monoprotonated and crystallize with bis(pyridine-2,6-dicarboxylato)manganate(II/III), a neutral molecule of $pydcH_2$, one-half of a $H_5O_2^+$ cation, one-half of a hydroxide anion and two-and-a-half molecules of water. Although it is beyond the scope of this report to compare all the metal complexes, it is significant that the synthesis of these complexes can be accomplished by a one-pot method, mixing acid, base and simple metal salt to form crystalline products. We were surprised to find that the product material in this case contains the Zundel cation, $H_5O_2^+$, and that the Mn atom is apparently in a disordered mixed-valent Mn^{II}/Mn^{III} state. Both Mn^{II} and Mn^{III} complexes of salts of the bis complex, $Mn(pydc)_2$, have been described previously, for example, with Mn^{II} (MacDonald *et al.*, 2004; Aghabozorg, Ghasemikhah *et al.*, 2006) and with Mn^{III} (Limburg *et al.*, 1997).



(I)

Compound (I) is depicted in Fig. 1. The Mn atom is hexacoordinated by two N atoms (N1 and N2) and four O atoms (O1, O3, O5 and O7) from carboxylate groups of two pydc groups in a distorted octahedral arrangement. The dihedral angle between these two coordinated pydc groups is 88.63 (5)°, which shows that the ligands are almost perpendicular to each other. For charge balance, it was assumed that the metal atom site is disordered Mn^{II}/Mn^{III}, probably due to partial air oxidation of Mn^{II}. However, this assumption has not been confirmed by any noncrystallographic methods. No difference-map peaks satisfied the alternative models, *i.e.* that the $melaminiumH^+$ was $melaminiumH_2^{2+}$ or that one of the coordinated carboxylate groups or water molecules was protonated.

The Mn—N and Mn—O distances (Table 1) are longer than those seen in related Mn^{III} complexes, which average 2.020 (8) and 2.01 (13) Å, respectively (Limburg *et al.*, 1997; Huang *et al.*, 2004). However, they are also shorter than the average of 34 observations [Cambridge Structural Database (CSD), *ConQuest* Version 1.10; Allen, 2002) for Mn^{II} in pydc coor-

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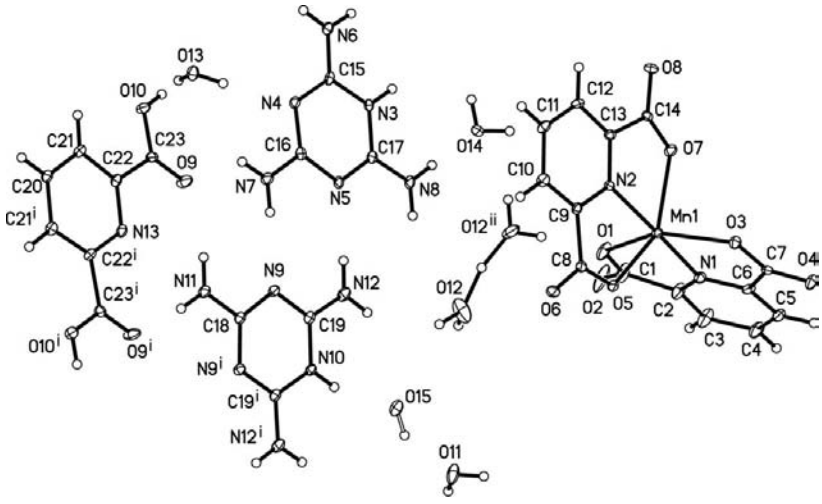

Figure 1
A view of the various constituents of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x, y, -\frac{1}{2}-z$, (ii) $-x, y, \frac{1}{2}-z$.]

dination compounds, namely 2.22 (6) and 2.30 (7) Å for Mn—N and Mn—O, respectively (CSD refcodes BIPJER, EJAMEH, IHELAI, LOYYON, LOYYUT, MABNIN, MABNOT, NEQPEF, QARZEP, SAQQUX, XEGDIW, XENJEG, MIGZEI and XIMHAD).

The formula unit of the complex contains one $H_5O_2^+$ cation that resides on a twofold rotation axis. One of the melaminiumH^+ groups and the pydc also reside on crystallographic twofold axes. In addition, there is an OH^- (O15—H15) ion that is disordered with respect to a twofold rotation axis.

There are three notable C═O$\cdots\pi$ intermolecular interactions between C═O groups and the centroids of the aromatic rings of pydc and melaminiumH^+ (Table 3). As shown in Fig. 2, the packing of the structure can be described by layers that contain almost all the consituent species. The main parts that are not in these layers are the perpendicular pydc ligands. By reference to Fig. 1, the hydrogen bonding that leads to these layers can be envisioned. A notable grouping of two melaminiumH^+ cations, water and pydc yields seven strong hydrogen bonds.

In pet food contamination studies involving dogs and cats (Filigenzi *et al.*, 2008), melamine and its metabolites are present in kidney tissue. In consideration of the number of intermolecular interactions present in this and similar structures and the rich carboxylic acid environment in the kidneys, the pathology of melamine is not at all surprising.

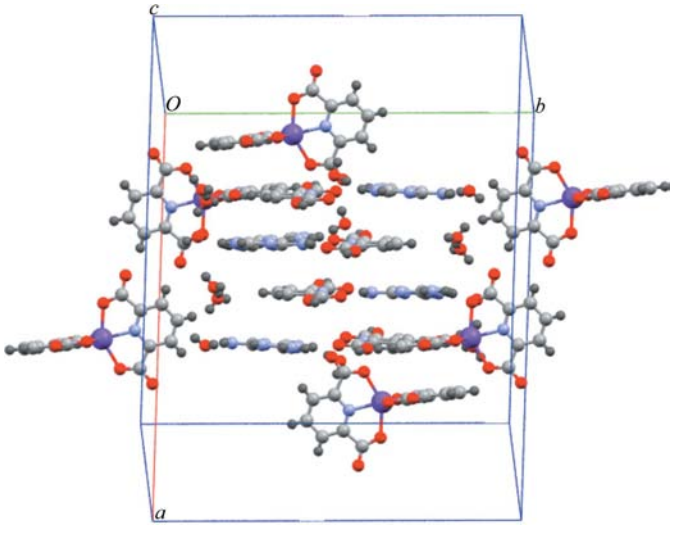

Figure 2
A packing diagram for (I), viewed perpendicular to the [101] direction, showing the presence of layers in the structure.

Experimental

The reaction between solutions of pyridine-2,6-dicarboxylic acid ($pydcH_2$; 100 mg, 1 mmol) in water (10 ml), 2,4,6-triamino-1,3,5-triazine (melamine) (110 mg, 1 mmol) in water (10 ml) and $Mn(CH_3COO)_2$ (72 mg, 0.5 mmol) in water (5 ml) in a 2:2:1 molar ratio gave pale-yellow needles after slow evaporation of the solvent at room temperature.

Crystal data

$(H_5O_2)(C_3H_7N_6)_3[Mn(C_7H_3NO_4)_2]_2(OH)\cdot C_7H_5NO_4\cdot 5H_2O$
M_r = 1462.98
Monoclinic, $C2/c$
a = 27.1406 (16) Å
b = 23.1672 (13) Å
c = 9.7838 (6) Å
β = 108.819 (3)°
V = 5822.9 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.55 mm^{-1}
T = 90 (2) K
0.55 × 0.18 × 0.08 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.754, T_{max} = 0.958
32194 measured reflections
6671 independent reflections
6153 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.189
S = 1.33
6671 reflections
484 parameters
11 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.149 (4)	Mn1—O5	2.231 (3)
Mn1—N2	2.172 (4)	Mn1—O7	2.238 (4)
Mn1—O3	2.213 (3)	Mn1—O1	2.245 (4)
N1—Mn1—N2	174.99 (15)	O3—Mn1—O7	93.41 (13)
N1—Mn1—O3	73.38 (14)	O5—Mn1—O7	144.88 (12)
N2—Mn1—O3	111.27 (13)	N1—Mn1—O1	72.91 (14)
N1—Mn1—O5	108.61 (14)	N2—Mn1—O1	102.46 (14)
N2—Mn1—O5	72.85 (13)	O3—Mn1—O1	146.27 (13)
O3—Mn1—O5	100.14 (13)	O5—Mn1—O1	89.60 (15)
N1—Mn1—O7	106.28 (14)	O7—Mn1—O1	96.86 (15)
N2—Mn1—O7	72.05 (13)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7*A*···O9	0.88	2.12	2.811 (5)	135
N7—H7*B*···N9	0.88	2.11	2.988 (6)	172
N8—H8*B*···O14	0.88	1.95	2.830 (6)	174
N10—H10*A*···O15	0.87	1.82	2.665 (9)	161
N11—H11*B*···O9	0.90	2.04	2.925 (5)	167
N12—H12*A*···N5	0.88	2.09	2.964 (6)	172
O10—H10*B*···O13	0.84 (8)	1.82 (8)	2.645 (5)	167 (11)
O13—H13*A*···N4	0.83 (6)	2.08 (2)	2.910 (5)	167 (7)
O15—H15···O11	0.861 (10)	1.98 (8)	2.767 (9)	151 (15)
N3—H3*A*···O6^{i}	0.88	1.89	2.757 (5)	168
N6—H6*A*···O4^{ii}	0.88	2.05	2.856 (5)	152
N6—H6*B*···O5^{i}	0.88	2.06	2.924 (5)	168
N10—H10*A*···O15^{iii}	0.87	1.82	2.665 (9)	161
N12—H12*B*···O1^{iv}	0.88	2.07	2.838 (6)	146
O11—H11*C*···O2^{v}	0.83 (9)	2.07 (9)	2.875 (6)	165 (10)
O12—H12*C*···O8^{vi}	0.83 (6)	1.75 (7)	2.560 (6)	162 (7)
O12—H12*D*···O2^{iv}	0.85 (5)	1.91 (7)	2.671 (6)	151 (7)
O12—H12*E*···O12^{iv}	1.24 (2)	1.24 (2)	2.445 (10)	163 (15)
O13—H13*B*···O4^{vii}	0.84 (5)	1.99 (6)	2.794 (5)	163 (7)
O14—H14*A*···O6^{i}	0.84 (4)	1.87 (2)	2.646 (5)	153 (5)
O14—H14*B*···O3^{viii}	0.84 (5)	2.06 (3)	2.841 (5)	154 (5)
C12—H12···O10^{ix}	0.95	2.45	3.236 (6)	140

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $-x, y, -z-\frac{1}{2}$; (iv) $-x, y, -z+\frac{1}{2}$; (v) $-x, -y+1, -z$; (vi) $x, y, z-1$; (vii) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (viii) $-x, y, -z+\frac{3}{2}$; (ix) $-x, -y+2, -z+1$.

C- and N-bound H atoms were positioned geometrically, with C—H = 0.95 Å and N—H = 0.88 Å, and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). O-bound H atoms were located in a difference Fourier map and allowed to refine with distance restraints of O—H = 0.84 (1) Å and H···H (in water) = 1.30 (2) Å, except for atom H12*E*, part of the $H_5O_2^+$ cation, which resides on a twofold axis and was not restrained. This atom was freely refined but displays a large isotropic displacement parameter of 0.11 Å^2 that causes an Alert A in *checkCIF* and we suggest that it is slightly disordered with respect to its position on the twofold axis. The H atom bonded to O15, part of the OH^- ion that is disordered with respect to the twofold axis, was located in a difference map and refined with a distance restraint of 0.86 (1) Å and with U_{iso}(H) = 1.2U_{eq}(O15).

Table 3
Summary of short contacts involving C═O···π interactions (Å).

C═O	Aromatic ring	O···centroid
C7═O4	(N1/C2–C6)^{i}	3.750 (4)
C8═O6	(N2/C9–C13)^{ii}	3.262 (4)
C14═O8	(N9/N10/C18/C19/N9^{iv}/C19^{iv})^{iii}	3.536 (4)

Symmetry codes: (i) $x, 1-y, \frac{1}{2}+z$; (ii) $-x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (iii) $-x, y, \frac{1}{2}-x$; (iv) $-x, y, -z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3154). Services for accessing these data are described at the back of the journal.

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