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The Crystal and Molecular Structure of 2,4,6-Tris(2'-pyridinio)-1,3,5-triazine Pentachloromanganate(III) Chloride Monohydrate

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$[C_{18}H_{15}N_6]^{3+}[MnCl_5]^{2-} \cdot Cl^- \cdot H_2O$ is monoclinic, space group $P2_1/n$, with $a = 13.27$ (2), $b = 15.31$ (1), $c = 12.10$ (1) Å, $\beta = 105.3$ (1)°, $Z = 4$. The structure was refined to $R = 0.082$ for 1339 diffractometer data. The $[MnCl_5]^{2-}$ anion is square-pyramidal, with a slight distortion towards a trigonal bipyramid, and has approximate mm symmetry. The longer axial Mn–Cl distance of 2.413 (6) Å compares with the two average equatorial distances of 2.250 (6) and 2.275 (7) Å; the Mn atom is 0.39 Å above the Cl equatorial plane. The closely planar cation contains the three pyridyl N atoms in protonated form, two of which are hydrogen-bonded to the free Cl^- ion and the third to the water molecule, which also hydrogen bonds the $[MnCl_5]^{2-}$ ion. The cations, the Cl atoms and the water molecules are contained in two sets of planes 3.18 Å apart and parallel to (201); the Mn atoms lie between these planes.

Introduction

2,4,6-Tris(2'-pyridyl)-1,3,5-triazine (tpt) has been well characterized in its interactions with transition-metal ions (Barclay, Vagg & Watton, 1977, and references therein). From acidic solutions salts have been isolated in which either the three pyridyl groups of the molecule are protonated or the molecule acts as a tridentate ligand in a protonated form (Vagg, Warrenner & Watton, 1967; Barclay, Vagg & Watton, 1977).

Unrelated to that work several reports of the isolation of chloro complexes of Mn^{3+} have appeared. The $[MnCl_6]^{3-}$ ion is stabilized by the presence of large trivalent cations (Hatfield, Fay, Pfluger & Piper, 1963; Levason, McAuliffe & Murray, 1972) although such compounds have not been investigated structurally. A series of compounds have been studied (Levason & McAuliffe, 1973) in which the $[MnCl_5]^{2-}$ ion exists. An X-ray structural analysis (Bernal, Elliot & Lalancette, 1971) has shown this species to be a distorted square-pyramidal unit in $[bipyH_2][MnCl_5]$.

The corresponding salt of tpt and Mn^{3+} has been prepared (Vagg & Watton, unpublished) of general

formula $(tptH_3)(H_2O)MnCl_6$. Its structure was investigated both to clarify the stereochemistry of the Mn atom and also as part of our overall investigations on the organic molecule.

Experimental

The compound was prepared by reaction of tpt and a 'brown solution' (Goodwin & Sylva, 1965) of $KMnO_4$ in 10 M HCl. Dark-green needles were obtained.

Over a period of days the unprotected crystals, like the bipyridine analogue (Bernal, Elliot & Lalancette, 1971), show signs of decomposition, which was arrested by mounting the crystals in a gelatin capsule prior to data collection.

Crystal data

$C_{18}H_{17}N_6Cl_6OMn$, $M_r = 601.0$, monoclinic, $a = 13.27$ (2), $b = 15.31$ (1), $c = 12.10$ (1) Å, $\beta = 105.3$ (1)°, $V = 2371.2$ Å³, $D_m = 1.70$ (by flotation), $Z = 4$, $D_c = 1.67$ g cm⁻³, $F(000) = 1208$, $\mu(Cu K\alpha) =$

11.2 cm⁻¹. Systematic absences: $0k0$ when $k = 2n + 1$ and $h0l$ when $h + l = 2n + 1$, space group $P2_1/n$. Cell parameters were fitted to the θ values of a number of high-angle reflexions measured on an equi-inclination diffractometer.

Intensities were collected from two crystals, $0.06 \times 0.12 \times 0.27$ and $0.05 \times 0.09 \times 0.30$ mm, mounted about $[010]$ and $[101]$, respectively, on an automatic Buerger-Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970) with Ni-filtered Cu radiation. Reflexions in the intervals $h0-10l$ and $hk0-5$ ($15^\circ < 2\theta < 125^\circ$) were recorded. A standard reflexion, measured at intervals of approximately 1 h, gave no indication of decomposition. Reflexions which gave counts of $\sigma(I) > 0.5I$ were edited from the data set before correcting for Lorentz, polarization and absorption effects (Blount, 1969) but not for extinction. Internal scaling yielded a set of 1339 independent reflexions.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Isotropic refinement was carried out on an IBM 360/50 computer with *ORFLS* (Busing, Martin & Levy, 1962). Anisotropic refinement was performed on a Univac 1106 computer with programs written by F. S. Stephens.

Structure determination

The structure was solved by the heavy-atom method. Full-matrix isotropic refinement was carried out, where the function minimized was $\sum w\Delta^2$ with unit weights. A difference synthesis showed the positions of the twelve H atoms of the pyridyl rings and in addition peaks in positions suggesting the protonation of the three pyridyl N atoms. H atoms were kept in these positions in subsequent calculations with $B = 5.0 \text{ \AA}^2$.

Due to the large number of parameters (284) block matrices were used during anisotropic refinement. The six matrices contained (1) the overall scale and thermal factors, and the parameters for (2) the Mn and six Cl atoms, (3) the O atom and central triazine ring and (4), (5) and (6) each of the three pyridyl rings.

Reflexions for which $|F_c| < 0.33|F_o|$ were omitted from the refinement, although all were included in the final cycle. Refinement was terminated when the maximum shift in any parameter was $< 0.25\sigma$. The final R based on the 1339 reflexions was 0.082 and R' [$= (\sum w\Delta^2 / \sum w|F_o|^{1/2})^{1/2}$] was 0.095. A final difference synthesis showed no unusual features. Atomic coordinates are given in Table 1.*

Discussion

A perspective drawing of the ionic units showing the labelling is given in Fig. 1. Bond lengths and angles are given in Table 2.

The correct formulation for the salt is $[tptH_3]^- [MnCl_5]Cl \cdot H_2O$. The Mn atom is bonded to the five Cl atoms Cl(1)–Cl(5) forming the $[MnCl_5]^{2-}$ ion. The closely planar organic cation (Table 3, plane 1) contains the three pyridyl N atoms in protonated form, two of which are hydrogen-bonded to the free Cl(6) and the

Table 1. Final atomic coordinates (fractional, $\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms) with estimated standard deviations in parentheses

	x	y	z
Mn	2240 (2)	7044 (2)	4311 (3)
Cl(1)	2628 (4)	8065 (4)	2962 (4)
Cl(2)	680 (4)	6597 (5)	3228 (5)
Cl(3)	1384 (5)	7851 (5)	5359 (5)
Cl(4)	3713 (5)	7310 (4)	5705 (5)
Cl(5)	2944 (4)	5779 (4)	3871 (5)
Cl(6)	3192 (4)	6102 (4)	-1129 (4)
O(1)	6053 (12)	6847 (10)	5590 (12)
N(1)	5283 (12)	7536 (15)	3039 (14)
N(2)	4746 (11)	8798 (12)	1949 (12)
N(3)	4204 (13)	7390 (15)	1178 (13)
N(11)	6104 (12)	8543 (11)	4904 (14)
N(21)	3389 (10)	8071 (11)	-865 (10)
N(31)	4354 (12)	5647 (12)	1330 (14)
C(1)	5214 (16)	8413 (19)	2854 (18)
C(2)	4264 (15)	8262 (20)	1093 (16)
C(3)	4741 (13)	7063 (15)	2146 (18)
C(11)	5676 (14)	8970 (18)	3887 (17)
C(12)	5776 (16)	9835 (18)	3834 (15)
C(13)	6264 (16)	10308 (15)	4822 (20)
C(14)	6652 (16)	9880 (18)	5795 (20)
C(15)	6566 (13)	8979 (19)	5838 (16)
C(21)	3780 (14)	8636 (17)	-10 (17)
C(22)	3629 (16)	9542 (18)	-214 (19)
C(23)	3111 (18)	9822 (16)	-1313 (19)
C(24)	2786 (16)	9241 (20)	-2157 (18)
C(25)	2922 (16)	8325 (17)	-1911 (16)
C(31)	4831 (14)	6100 (13)	2243 (16)
C(32)	5308 (16)	5679 (18)	3217 (16)
C(33)	5325 (17)	4779 (21)	3244 (21)
C(34)	4838 (18)	4325 (16)	2303 (23)
C(35)	4348 (16)	4765 (17)	1306 (18)
H(P11)	615	788	485
H(12)	531	1029	317
H(13)	612	1112	482
H(14)	693	1011	650
H(15)	723	860	625
H(P21)	340	735	-82
H(22)	388	1012	13
H(23)	297	1060	-160
H(24)	222	939	-290
H(25)	248	779	-262
H(P31)	410	588	65
H(32)	557	594	393
H(33)	575	439	389
H(34)	482	364	227
H(35)	400	444	58

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32828 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Mn—Cl(1)	2.413 (6)	Mn—Cl(4)	2.256 (6)
Mn—Cl(2)	2.245 (6)	Mn—Cl(5)	2.272 (7)
Mn—Cl(3)	2.278 (7)		
N(1)—C(1)	1.36 (3)	N(1)—C(3)	1.34 (2)
N(2)—C(1)	1.25 (3)	N(2)—C(2)	1.34 (3)
N(3)—C(2)	1.34 (3)	N(3)—C(3)	1.30 (2)
N(11)—C(11)	1.38 (3)	N(11)—C(15)	1.32 (2)
N(21)—C(21)	1.34 (2)	N(21)—C(25)	1.31 (2)
N(31)—C(31)	1.32 (2)	N(31)—C(35)	1.35 (3)
C(1)—C(11)	1.50 (3)	C(2)—C(21)	1.44 (3)
C(3)—C(31)	1.48 (3)		
C(11)—C(12)	1.33 (3)	C(12)—C(13)	1.40 (3)
C(13)—C(14)	1.33 (3)	C(14)—C(15)	1.39 (3)
C(21)—C(22)	1.41 (3)	C(22)—C(23)	1.39 (3)
C(23)—C(24)	1.34 (3)	C(24)—C(25)	1.44 (3)
C(31)—C(32)	1.35 (3)	C(32)—C(33)	1.38 (3)
C(33)—C(34)	1.34 (3)	C(34)—C(35)	1.38 (3)
Cl(1)—Mn—Cl(2)	97.5 (2)	Cl(1)—Mn—Cl(4)	95.3 (2)
Cl(1)—Mn—Cl(3)	104.6 (3)	Cl(1)—Mn—Cl(5)	102.7 (2)
Cl(2)—Mn—Cl(4)	167.1 (2)	Cl(3)—Mn—Cl(5)	152.7 (3)
Cl(2)—Mn—Cl(3)	88.3 (3)	Cl(4)—Mn—Cl(5)	90.0 (2)
Cl(3)—Mn—Cl(4)	87.0 (2)	Cl(2)—Mn—Cl(5)	88.6 (3)
C(1)—N(1)—C(3)	114 (2)	C(1)—N(2)—C(2)	114 (2)
C(2)—N(3)—C(3)	115 (2)	N(1)—C(1)—N(2)	127 (2)
N(2)—C(2)—N(3)	125 (2)	N(1)—C(3)—N(3)	125 (2)
N(1)—C(1)—C(11)	115 (2)	N(2)—C(1)—C(11)	117 (2)
N(2)—C(2)—C(21)	119 (2)	N(3)—C(2)—C(21)	116 (2)
N(1)—C(3)—C(31)	117 (2)	N(3)—C(3)—C(31)	118 (2)
C(1)—C(11)—N(11)	117 (2)	C(1)—C(11)—C(12)	123 (2)
C(2)—C(21)—N(21)	116 (2)	C(2)—C(21)—C(22)	124 (2)
C(3)—C(31)—N(31)	117 (2)	C(3)—C(31)—C(32)	124 (2)
N(11)—C(11)—C(12)	119 (2)	C(11)—C(12)—C(13)	120 (2)
C(12)—C(13)—C(14)	119 (2)	C(13)—C(14)—C(15)	121 (2)
C(14)—C(15)—N(11)	120 (2)	C(15)—N(11)—C(11)	121 (2)
N(21)—C(21)—C(22)	119 (2)	C(21)—C(22)—C(23)	119 (2)
C(22)—C(23)—C(24)	120 (2)	C(23)—C(24)—C(25)	120 (2)
C(24)—C(25)—N(21)	119 (2)	C(25)—N(21)—C(21)	123 (2)
N(31)—C(31)—C(32)	120 (2)	C(31)—C(32)—C(33)	120 (2)
C(32)—C(33)—C(34)	120 (2)	C(33)—C(34)—C(35)	120 (2)
C(34)—C(35)—N(31)	118 (2)	C(35)—N(31)—C(31)	123 (2)

third to the water molecule, which also hydrogen bonds to the $[\text{MnCl}_5]^{2-}$ ions. Details of these bonds are given in Table 4 and shown in Figs. 1 and 2.

The four aromatic rings in the tpt residue are planar (Table 3, planes 2–5), with the pyridyl rings (1, 2 and 3) twisted slightly around the bonds to the triazine centre (6.6, 8.4 and 4.3° respectively). The cations, with the Cl and O atoms, are contained approximately in two sets of planes 3.18 Å apart and parallel to (201); the Mn atoms lie between these planes (Fig. 2).

The $[\text{MnCl}_5]^{2-}$ ion has approximate *mm* symmetry in a distorted square pyramid with the Mn atom 0.39 Å above the equatorial Cl plane of best fit (Table 3, plane 6). The axial Mn—Cl(1) [2.413 (6) Å] is longer than the two average equatorial distances [Mn—Cl(2) and

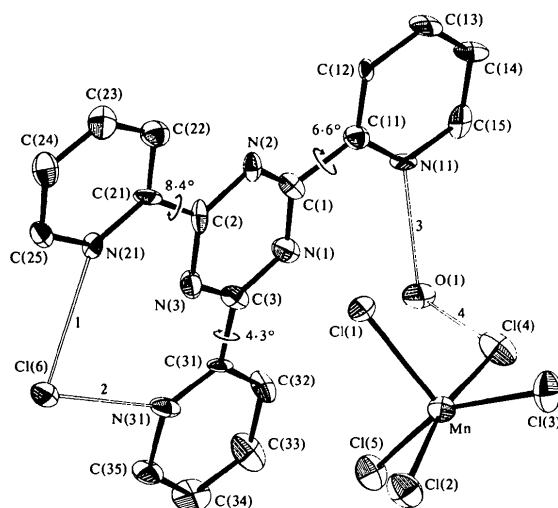


Fig. 1. Perspective drawing (Johnson, 1965) of the ionic units showing the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability. Proposed hydrogen bonds are numbered according to the details given in Table 4.

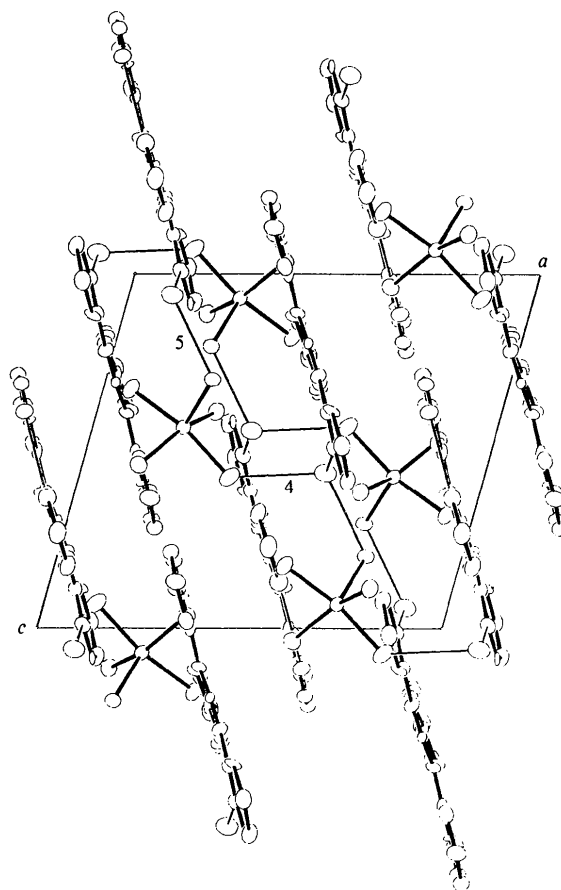


Fig. 2. Packing of the ions in the cell projected onto (010). Proposed hydrogen bonds are numbered according to the details given in Table 4.

Mn—Cl(4), ave. 2.250 (6) Å; Mn—Cl(3) and Mn—Cl(5), ave. 2.275 (7) Å]. Details of the ionic geometry are given in Table 5, where a comparison is made with the species described by Bernal, Elliott & Lalancette (1971) which has space-group-imposed *m* symmetry. The angles between the Cl planes given in Table 5 demonstrate a slight distortion towards a trigonal bipyramid in both cases — this is more

pronounced in the title compound. These angles compare with the 90 and 180° expected for an undistorted square pyramid, and the 120° for a trigonal bipyramid. The latter geometry would contain the Mn atom in each of the planes 7–12.

The *tpt* molecular dimensions are comparable with those of the coordinated ligand (Barclay, Vagg & Watton, 1977), although the angular distortion due to

Table 3. *Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$, where X' , Y' and Z' are orthogonal coordinates related to the atomic coordinates X , Y and Z by $X' = X \sin \beta$, $Y' = Y$ and $Z' = Z + X \cos \beta$*

Deviations (Å) of relevant atoms from the planes are given in square brackets.

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane 1: C(1)—C(3), N(1)—N(3), C(11)—C(15), C(21)—C(25), C(31)—C(35), N(11)—N(31)	0.8568	-0.0180	-0.5154	4.5943
[C(1), N(1), C(24), N(21), C(33) 0.05; C(2) -0.06; C(3), C(23) -0.07; C(4), C(14), C(31), C(35) 0.01; N(3) -0.16; C(11), N(31) -0.02; C(12) 0.12; C(13) 0.11; C(15) -0.10; N(11), C(22) -0.09; N(21) 0.001; C(32) 0.02; C(34) 0.03; Cl(6) 0.02; O(1) -0.54]				
Plane 2: C(1)—C(3), N(1)—N(3)	0.8183	-0.0605	-0.5716	3.7669
[C(1) -0.017; C(2) 0.030; C(3) -0.004; N(1) 0.023; N(2) -0.010; N(3) -0.022]				
Plane 3: C(11)—C(15), N(11)	0.8731	-0.0985	-0.4775	3.7101
[C(11) -0.016; C(12) 0.012; C(13) -0.003; C(14), C(15) -0.002; N(11) 0.011; O(1) -0.196]				
Plane 4: C(21)—C(25), N(21)	0.8767	0.0378	-0.4795	5.3603
[C(21) 0.021; C(22) -0.003; C(23) -0.017; C(24) 0.019; C(25) -0.001; N(21) -0.019; Cl(6) -0.235]				
Plane 5: C(31)—C(35), N(31)	0.8480	-0.0058	-0.5300	4.6395
[C(31) 0.009; C(32) -0.007; C(33), C(35) 0.006; C(34) -0.005; N(31) -0.008; Cl(6) 0.087]				
Plane 6: Cl(2)—Cl(5)	0.1813	0.6553	-0.7333	3.9430
[Cl(2), Cl(4) 0.143; Cl(3) -0.145; Cl(5) -0.141; Mn 0.394]				
Plane 7: Cl(1), Cl(2), Cl(4)	-0.4572	0.7327	0.5041	8.8519
[Mn -0.027]				
Plane 8: Cl(2), Cl(3), Cl(4)	0.1192	0.7434	-0.6581	5.1983
[Mn 0.24]				
Plane 9: Cl(2), Cl(4), Cl(5)	0.2381	0.5603	-0.7933	2.9562
[Mn 0.25]				
Plane 10: Cl(1), Cl(3), Cl(5)	0.8706	0.2242	0.4379	6.8641
[Mn -0.009]				
Plane 11: Cl(2), Cl(3), Cl(5)	0.2907	0.6805	-0.6726	4.6593
[Mn 0.53]				
Plane 12: Cl(3), Cl(4), Cl(5)	0.0689	0.6210	-0.7808	2.9014
[Mn 0.53]				

Table 4. *Proposed hydrogen bonds; donor-acceptor distances (Å) are given, with estimated standard deviations in parentheses*

Bond		Acceptor at	
1	N(21)—H(P21)···Cl(6)	(<i>x, y, z</i>)	3.04 (2)
2	N(31)—H(P31)···Cl(6)	(<i>x, y, z</i>)	3.05 (2)
3	N(11)—H(P11)···O(1)	(<i>x, y, z</i>)	2.73 (2)
4	O(1)···Cl(4)	(<i>x, y, z</i>)	3.22 (2)
5	O(1)···Cl(1)	($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$)	3.08 (2)

coordination is absent. The structure of the central ring [ave. C—N 1.32 (3) Å, C—N—C 114 (2), N—C—N 126 (2)°] is similar to that of both coordinated tpt [1.35 (3) Å, 117 (3) and 123 (2)°] and unsubstituted triazine [1.319 (5) Å, 113.2 (4) and 126.8 (4)°, Wheatley, 1955]. Although the molecules lie on planes 3.18 Å apart they pack such that the shortest non-bonding contact between tpt residues is 3.69 Å. No severe steric interactions occur between atoms in adjacent planes.

We thank Professor H. C. Freeman of the University of Sydney for making his diffractometer available for the data collection, and Dr F. S. Stephens of this School for helpful discussions.

Table 5. *Comparison of [MnCl₅]²⁻ ion geometries*

Data in parentheses are corresponding values calculated from molecular dimensions given by Bernal, Elliott & Lalancette (1971).

	[tptH ₃][MnCl ₅] Cl·H ₂ O (This work)	[bipyH ₂][MnCl ₅] (Bernal <i>et al.</i> , 1971)
Axial Mn—Cl bond length (Å)	2.413 (8)	2.583 (6)
Equatorial Mn—Cl bond lengths (Å)	2.245 (6)–2.278 (7)	2.241 (8)–2.336 (8)

Dihedral angles (°) between planes defined in Table 3

Planes 7 and 8	99.1	(93.9)
7 and 9	95.6	(93.9)
8 and 9	165.2	(172.1)
10 and 11	96.4	(91.5)
10 and 12	98.2	(96.0)
11 and 12	165.4	(172.5)

Deviations (Å) of Mn atoms from planes defined in Table 3

Plane 6	0.39	(0.29)
7	0.03	(0.00)
8	0.24	(0.21)
9	0.25	(0.21)
10	0.01	(0.04)
11	0.53	(0.36)
12	0.53	(0.36)

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