Coordination polymers of Mn(II) with the ligand pyrazine-2,3,5,6-tetracarboxylic acid

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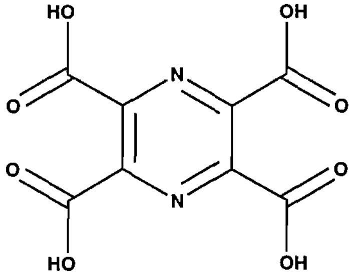
Abstract

Two coordination polymers of Mn(II) with the ligand pyrazine-2,3,5,6-tetracarboxylic acid (H_4pztc) have been prepared. The reaction of $MnSO_4$ with H_4pztc (ratio 1:1) carried out at 50 °C gave a zig-zag polymer structure with the ligand coordinated in a pseudo bis(tridentate) fashion (**1**) (crystal data: $C_8H_{10}N_2O_{12}Mn$, tetragonal, space group $I4_1/a$, $a=b=13.934(1)$, $c=13.578(1)$ Å, $Z=8$, 1670 reflections with $I>3\sigma(I)$, $R=0.029$). The reaction of an excess of $MnSO_4$ with H_4pztc (ratio 3:1) at room temperature gave the salt $[Mn(H_2O)_6][H_2pztc]$ (**2**) (crystal data: $C_8H_{14}N_2O_{14}Mn$, monoclinic, space group $A2/n$, $a=6.83(1)$, $b=9.918(1)$, $c=22.051(2)$ Å, $\beta=102.91(2)°$, $Z=4$, 1547 reflections with $I>3\sigma(I)$, $R=0.026$). The anion possesses a strong intramolecular H bond and is found coordinated to the Mn atom in polymer **1**. The reaction of $MnSO_4$ with H_4pztc (ratio 1:1) carried out at 50 °C in the presence of the equimolar buffer CH_3COOK/CH_3COOH, gave a column type polymer with the ligand coordinated in a mono(tridentate)-bis(monodentate) fashion (**3**) (crystal data: $C_8H_7N_2O_{11.25}K_2Mn$, monoclinic, space group $I2/a$, $a=18.207(2)$, $b=8.335(1)$, $c=19.185(3)$ Å, $\beta=103.66(1)°$, $Z=8$, 1539 reflections with $I>2\sigma(I)$, $R=0.041$). The reaction of H_4pztc with $ZnCl_2$ (ratio 1:1) in the presence of the same equimolar buffer solution lead to the formation of the isomorphous polymer Zn-**3** (crystal data: $C_8H_7N_2O_{11.25}K_2Zn$, monoclinic, space group $I2/a$, $a=18.194(1)$, $b=8.264(1)$, $c=18.924(1)$ Å, $\beta=103.92(1)°$, $Z=8$, 2567 reflections with $I>3\sigma(I)$, $R=0.031$).

Key words: Crystal structures; Manganese complexes; Polymer complexes

Introduction

The design and evaluation of coordination compounds which are able to build extended chain, layer or three-dimensional structures has many interesting aspects. One goal in this field is to develop synthetic routes for 'molecular engineering' of new compounds. A second goal is to develop molecular based ferromagnets on the basis of three-dimensional structures. The ligand pyrazine-2,3,5,6-tetracarboxylic acid (H_4pztc) was first synthesised by Wolff in 1887 [1] and its Na^+, K^+ and Ba^{2+} salts, as well as its Ag(I) complex, have been known since 1893 [2]. We have investigated the potentiality of this bis(tridentate) binucleating ligand for the formation of quasi-linear coordination polymers. A number of structurally different polymeric materials has been obtained by reacting an aqueous solution of MCl_2 or MSO_4, where M = Mn(II), Fe(II), Co(II) and Zn(II), with one equivalent of H_4pztc, and in other cases Mn(II), Cu(II) and Zn(II) salts with one equivalent of H_4pztc in the presence of a buffer [3]. The first structure of one such quasi-linear polymer from an aqueous solution, namely {[μ-(2,5-dicarboxypyrazine-3,6-dicarboxylato)-*trans*-diaquairon(II)dihydrate]}$_\infty$, with the ligand coordinating in a bis(bidentate) fashion, was published in 1986 [4]. It is isomorphous with the Co(II) and Zn(II) polymers produced under the same conditions. The structures of two different Cu(II) polymers, one zig-zag, formed in the presence of a K^+ buffer, and the other quasi-linear, formed in the presence of a Mg^{2+} buffer, have been described elsewhere [5]. The structures of a zig-zag Mn(II) polymer (**1**), from an



pyrazine-2,3,5,6-tetracarboxylic acid

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aqueous solution and a column type Mn(II) polymer (**3**), formed in the presence of a K^+ buffer solution, will be described here. The latter is isomorphous with the Zn(II) (Zn-**3**) polymer produced under similar conditions.

Experimental

IR spectra were recorded on a Perkin-Elmer IR 521 spectrometer using CsBr pellets, C, H and N microanalyses were carried out by the 'Organische-chemisches Mikrolabor' of the ETH in Zurich. The thermogravimetric measurements were carried out using a Mettler TA3000 with a TC10 microprocessor and a TG50 connected to a Mettler balance M3. The susceptibility measurements were carried out using the moving sample technique [6].

Synthesis of 2,3,5,6-tetracarboxylic acid (H_4pztc)

The ligand pyrazine-2,3,5,6-tetracarboxylic acid (H_4pztc) is most easily obtained by Wolff's original synthesis [1, 2]; the oxidation of tetramethylpyrazine under strongly basic conditions. An alternative synthesis is possible following the method of Chattaway and Humphrey [7]; the oxidation of quinaloxine-2,3-dicarboxylic acid.

The syntheses of the complexes were carried out under nitrogen to prevent oxidation of the Mn(II). The $MnSO_4$ used was Fluka puriss. For the microanalyses Mn was dosed by colorimetry using MnO_4^- at $\lambda = 544$ nm.

Synthesis of $\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (1)

A solution of 0.33 g (1.95 mmol) of $MgSO_4$ in 5 ml of H_2O was added to a solution of 0.50 g (1.95 mmol) of H_4pztc in 10 ml of H_2O under a stream of N_2 at 50 °C. The reaction mixture was stirred for 10 min and then left to cool to r.t. Yellow crystals were formed after 24 h. Yield 0.24 g (34%).

IR (KBr, cm^{-1}): C=O; $\nu = 1705$, 1590. *Anal.* Calc.: C, 25.21; H, 2.64; N, 7.35; Mn, 14.42. Found: C, 25.71; H, 2.15; N, 7.44; Mn, 14.99%.

Synthesis of $[Mn(H_2O)_6][H_2pztc]$ (2)

A solution of 0.99 g (5.85 mmol) of $MgSO_4$ in 5 ml of H_2O was added to a solution of 0.50 g (1.95 mmol) of H_4pztc in 10 ml of H_2O under a stream of N_2 at 20 °C. The reaction mixture was stirred for 10 min and then left at r.t. for 4 days. Large prism like almost colourless crystals were formed. Yield 0.53 g (65%).

IR (KBr, cm^{-1}): C=O; $\nu = 1740$, 1590. *Anal.* Calc.: C, 23.03; H, 3.38; N, 6.72; Mn, 13.17. Found: C, 23.13; H, 3.11; N, 6.73; Mn, 13.05%.

Synthesis of $\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (3)

A solution of 0.33 g (1.95 mmol) of $MgSO_4$ in 25 ml of H_2O was added to a solution of 0.50 g (1.95 mmol) of H_4pztc in 20 ml of H_2O under a stream of N_2 at 50 °C. 10 ml of a 2 M solution of the equimolar buffer CH_3COOK/CH_3COOH were added in order to obtain a pH of approximately 4. The reaction mixture was stirred and then left to cool. After 3 days yellow needle-like crystals were formed. Yield 0.67 g (78%).

IR (KBr, cm^{-1}): C=O; $\nu = 1610$. *Anal.* Calc.: C, 21.87; H, 1.38; N, 6.38; Mn, 12.51. Found: C, 21.60; H, 1.31; N, 6.22; Mn, 12.33%.

Synthesis of $\{K_2[Zn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (Zn-3)

A solution of 0.53 g (3.89 mmol) of $ZnCl_2$ in 5 ml of H_2O was added to a solution of 1.00 g (3.90 mmol) of H_4pztc in 20 ml of H_2O at 20 °C. 30 ml of a 2 M solution of the equimolar buffer CH_3COOK/CH_3COOH were added in order to obtain a pH of approximately 4.8. The reaction mixture was stirred for 10 min and then left to cool. After 1 week colourless crystals were formed. Yield 1.10 g (63%).

IR (KBr, cm^{-1}): C=O; $\nu = 1610$. *Anal.* Calc.: C, 21.37; H, 1.34; N, 6.23; K, 17.39; Zn, 14.54. Found: C, 21.40; H, 0.75; N, 6.33; K, 17.88; Zn, 14.11%.

X-ray data collection, structure solution and refinement

Intensity data were collected at room temperature on a Stoe AED2 4-circle diffractometer using Mo $K\alpha$ graphite monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved by Patterson and difference Fourier syntheses using the NRCVAX [8] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [8] are from International Tables for X-ray Crystallography [9]. The H atoms were located from difference maps and were either refined isotropically or in certain cases (water molecules) held fixed ($U_{iso} = 0.075$ Å^2). The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares. Crystal data, details of data collection and structure refinement for **1**, **2**, **3** and Zn-**3** are given in Table 1. Atomic parameters and equivalent isotropic thermal parameters are given in Table 2. Selected bond distances and angles are given in Table 3. The numbering schemes used are illustrated in the PLUTO [10] plots of Figs. 3, 5, 7 and 9. The same programme was used to draw the packing diagrams (Figs. 4, 6 and 8); see also 'Supplementary material'.

Results and discussion

When an excess of $MnSO_4\cdot H_2O$ (ratio 3:1) was added to H_4pztc at 20 °C it lead to the formation of salt **2**, cation $[Mn(H_2O)_6]^{2+}$ and anion $[H_2pztc]^{2-}$. At 50 °C

TABLE 1. Crystal data, details of data collection and structure refinement of $\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (**1**), $[Mn(H_2O)_6][H_2pztc]$ (**2**), $\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**) and $\{K_2[Zn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (Zn-**3**)

Formula	$C_8H_6N_2O_{10}Mn\cdot 2H_2O$	$C_8H_2N_2O_8{}^{2-}Mn(H_2O)_6{}^{2+}$	$C_8H_2N_2O_9K_2Mn\cdot 2.25H_2O$	$C_8H_2N_2O_9K_2Zn\cdot 2.25H_2O$
Molecular weight	381.1	417.1	444.3	452.2
Crystal color	yellow	colourless	yellow	colorless
Crystal habit	blocks	blocks	needles	needles
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$I4_1/a$	$A2/n$	$I2/a$	$I2/a$
Z	8	4	8	8
D_{calc} (g cm^3)	1.920	1.888	2.086	2.175
μ(Mo Kα) (cm^{-1})	10.3	9.4	15.6	7.5
Crystal size (mm)	0.42	0.42	0.27	0.57
	0.42	0.27	0.15	0.23
	0.27	0.15	0.11	0.23
Cell parameters: least-squares fit of				
N reflections	16	13	18	10
2θ range (°)	30–45	30–40	25–35	29–48
a (Å)	13.934(1)	6.883(1)	18.207(2)	18.194(1)
b (Å)	13.934(1)	9.918(1)	8.335(1)	8.264(1)
c (Å)	13.578(1)	22.051(2)	19.185(3)	18.924(1)
β (°)		102.91(1)	103.66(1)	103.92(1)
V (Å^3)	2636.3	1467.3	2829.1	2761.8
Scan method	ω/θ	ω/θ	ω/θ	ω/θ
θ_{max} (°)	30.0	27.5	25.0	27.5
h,k,l Range	+19, +19, +19	±8, +12, +28	±21, +9, +22	±23, +10, +24
No. reference reflections	4	5	3	3
variation (%)	2.5	2.6	1	5
Refinement				
No. unique reflections	1913	1678	2456	3121
No. reflections in refinement	1670	1547	1539	2567
$I > x\sigma(I)$, where $x=$	3.0	3.0	2.0	3.0
No. parameters refined	125	143	222	230
$R_f{}^a$	0.029	0.026	0.041	0.031
$R_w{}^b$	0.053	0.038	0.054	0.054
k^c	0.0015	0.00025	0.0025	0.002
Max. shift/sigma ratio	0.107	0.033	0.002	0.065
Residual density (e Å^3)	+0.35	+0.31	+0.45	+0.92
	−0.51	−0.58	−0.50	−0.65

$^aR_f=\Sigma(F_o-F_c)/\Sigma F_o$. $^bR_w=[\Sigma w(F_o-F_c)^2/\Sigma wF_o{}^2]^{1/2}$. $^cw^{-1}=\sigma^2(F_o)+k(F_o)^2$.

a mixture of polymer **1** and salt **2** was generally obtained. Lowering the temperature to 20 °C favoured the formation of **2**.

Infrared spectra

The IR spectrum of **1** showed two intense bands at 1705 and 1590 cm^{-1} which indicated the presence of protonated and deprotonated carboxylate groups. A broad band at 2000 cm^{-1} was also observed, indicating the possible presence of H bonding. The IR spectrum of **2** was very similar to that of **1**. In the case of **3** only one band was present in the ν(C=O) region at 1610 cm^{-1}, indicating the presence of deprotonated carboxylate groups only.

Thermogravimetric analyses

1: loss of 4 water molecules at 139 °C; loss of two molecules of CO_2 at 229 °C, decomposition at 389 °C.

2: loss of three water molecules at 63 °C, loss of another three water molecules at 135 °C, loss of two molecules of CO_2 at 237 °C, decomposition occurred at 385 °C.

3: loss of three water molecules at 127 °C, decomposition occurred at 321 °C.

The loss of CO_2 from **1** and **2** indicated the presence of protonated carboxylate groups, as expected from the IR spectra. In **3** there was no loss of CO_2 indicating that all four carboxylic groups were deprotonated and possibly coordinated. The residue in each case was Mn_2O_3.

Magnetic susceptibility

The magnetic susceptibility measurements for **1** and **3** were carried out over the temperature range 1.5–285 K. The graphical representations of χ_A^{-1} as a function of T (K) showed a deviation from the Curie law, Figs. 1 and 2. The effective magnetic moment μ_{eff} decreases

TABLE 2. Atomic parameters and equivalent isotropic thermal parameters

Atom	x	y	z	B_{iso}[a]
$\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (**1**)				
Mn	1/2	1/4	0.11585(2)	2.098(15)
OW1	0.58660(11)	0.17248(10)	0.22588(12)	4.13(6)
OW2	0.69801(12)	0.28166(14)	0.36327(12)	4.32(7)
N1	0.49581(7)	0.08933(7)	0.04030(8)	1.58(3)
O1	0.61404(8)	0.22897(7)	0.00230(10)	3.01(4)
O2	0.71105(7)	0.13871(7)	−0.08512(10)	2.79(4)
O3	0.37492(9)	0.14407(8)	0.17284(11)	3.46(4)
O4	0.28535(9)	0.01482(9)	0.16427(12)	4.11(6)
C1	0.63510(9)	0.15186(8)	−0.03643(10)	1.95(4)
C2	0.56603(8)	0.06789(8)	−0.02222(9)	1.55(4)
C3	0.42955(8)	0.02457(8)	0.06412(9)	1.59(3)
C4	0.35854(10)	0.06469(10)	0.13922(11)	2.36(5)
HO4	0.285(3)	−0.039(3)	0.1235(22)	8.1(10)
$[Mn(H_2O)_6][H_2pztc]$ (**2**)				
Mn	1/4	0.45689(3)	3/4	1.58(1)
OW1	1/4	0.2381(1)	3/4	2.45(6)
OW2	0.4551(2)	0.4337(1)	0.6866(0)	1.94(4)
OW3	0.0052(2)	0.4719(1)	0.6692(1)	2.90(5)
OW4	1/4	0.6724(2)	3/4	3.12(7)
N1	0.4065(2)	0.0186(1)	0.9389(1)	1.45(4)
O1	0.3903(2)	0.3653(1)	0.9731(0)	2.31(4)
O2	0.2154(2)	0.2424(1)	0.8974(0)	2.29(4)
O3	0.5653(2)	0.3310(1)	1.0791(0)	3.10(5)
O4	0.5898(2)	0.1673(1)	1.1478(0)	2.73(5)
C1	0.5216(2)	0.1024(1)	1.0415(1)	1.38(4)
C2	0.4267(2)	0.1219(1)	0.9787(1)	1.33(4)
C3	0.5600(2)	0.2075(1)	1.0940(1)	1.79(5)
C4	0.3357(2)	0.2517(1)	0.9468(1)	1.57(4)
HO1	0.483(4)	0.352(3)	1.016(1)	6.3(7)
$\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**)				
Mn	0.20618(4)	0.51277(10)	0.61503(4)	1.45(3)
O1	0.30562(22)	0.6750(5)	0.65264(20)	1.87(15)
O2	0.40355(21)	0.7288(5)	0.74517(21)	2.41(18)
O3	0.11800(22)	0.6902(5)	0.60455(22)	1.99(16)
O4	0.05193(21)	0.9172(5)	0.58938(22)	2.00(16)
O5	0.28554(22)	0.3377(5)	0.59110(20)	1.91(16)
O6	0.37064(25)	0.1437(5)	0.59464(23)	2.53(18)
O7	0.12919(22)	0.3378(5)	0.65270(20)	1.83(15)
O8	0.09480(22)	0.2368(5)	0.74904(21)	2.50(18)
N1	0.24102(23)	0.4965(5)	0.73261(20)	1.17(16)
N2	0.28549(25)	0.4790(5)	0.87894(22)	1.48(17)
C1	0.3014(3)	0.5792(6)	0.7672(3)	1.12(19)
C2	0.3233(3)	0.5705(6)	0.8421(3)	1.18(19)
C3	0.2249(3)	0.3968(6)	0.8426(3)	1.21(19)
C4	0.2018(3)	0.4067(6)	0.7685(3)	1.38(21)
C5	0.3410(3)	0.6704(6)	0.7183(3)	1.39(21)
C6	0.1102(3)	0.8374(7)	0.6139(3)	1.49(22)
C7	0.3153(3)	0.2027(7)	0.6111(3)	1.56(21)
C8	0.1352(3)	0.3184(6)	0.7191(3)	1.42(20)
OW	0.14844(24)	0.4766(5)	0.50562(20)	2.47(17)
K1	0.51726(7)	0.47985(16)	0.80229(7)	2.25(5)
K2	0.05863(8)	0.20512(18)	0.52120(7)	2.79(6)
OW1	0.0165(3)	0.4432(6)	0.3524(3)	3.72(25)
OW2	−0.0687(3)	0.2703(7)	0.5825(3)	3.97(23)
OW3[b]	1/4	0.8036(22)	1/2	7.6(14)
$\{K_2[Zn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (Zn-**3**)				
Zn	0.20537(2)	0.50869(3)	0.61703(2)	1.338(15)
O1	0.30132(11)	0.67364(23)	0.64591(10)	1.71(7)
O2	0.40019(11)	0.7340(3)	0.73833(11)	2.11(8)
O3	0.11915(10)	0.68160(23)	0.60948(11)	1.68(7)
O4	0.05293(10)	0.91110(24)	0.59173(10)	1.77(7)
O5	0.28354(11)	0.34106(23)	0.59070(11)	1.75(7)
O6	0.37026(11)	0.1489(3)	0.59561(12)	2.41(8)
O7	0.12815(11)	0.33347(24)	0.64926(10)	1.73(7)
O8	0.09423(11)	0.2322(3)	0.74671(11)	2.29(8)
N1	0.23947(12)	0.49549(22)	0.72891(12)	1.07(7)
N2	0.28553(13)	0.4806(3)	0.87729(12)	1.32(8)
C1	0.29903(13)	0.5804(3)	0.76288(13)	1.03(8)
C2	0.32155(13)	0.5747(3)	0.83892(13)	1.09(8)
C3	0.22474(13)	0.3963(3)	0.84088(13)	1.11(8)
C4	0.20083(13)	0.4046(3)	0.76557(13)	1.09(8)
C5	0.33756(15)	0.6717(3)	0.71175(14)	1.32(9)
C6	0.11100(14)	0.8315(3)	0.61707(13)	1.24(8)
C7	0.31381(14)	0.2057(3)	0.61186(13)	1.31(8)
C8	0.13483(14)	0.3152(3)	0.71656(14)	1.28(8)
OW	0.15463(14)	0.4861(3)	0.50989(12)	2.24(9)
K1	0.51668(3)	0.48678(7)	0.80020(4)	2.025(24)
K2	0.06131(4)	0.20038(9)	0.51990(3)	2.61(3)
OW1	0.01733(13)	0.4459(3)	0.35506(14)	3.16(11)
OW2	−0.07085(15)	0.2617(4)	0.57644(14)	3.97(12)
OW3[b]	1/4	0.8187(18)	1/2	9.4(18)

B_{iso} is the mean of the principal axes of the thermal ellipsoids. [b] Occupancy 0.25.

regularly as a function of temperature to approximately 10 K (Figs. 1 and 2). At lower temperatures μ_{eff} for **1** showed a large dispersion in the observed points which were impossible to interpret. In the case of **3** μ_{eff} continues to decrease to 1.7 K. This result could indicate an antiferromagnetic coupling for **3**. A least-squares fit of eqn. (1) gave $g \cong 1.90$ for both **1** and **3**.

$$1/\chi_A = 3kT/N_{av}g^2\mu_B{}^2S(S+1) \qquad (1)$$

For a paramagnetic sample of Mn(II) a perfect behaviour according to Curie's law would give a value of $g = 2.0$. The experimental value found is in agreement with this comportment.

Selected bond distances and angles in **1**, **2**, **3** and Zn-**3** are given in Table 3.

Structures

$\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (1)

The reaction of $MnSO_4\cdot H_2O$ with H_4pztc in a metal to ligand ratio of 1:1 (pH 2.98) at 50 °C gave yellow needles, the structure analysis of which indicated that it is a zig-zag polymer, **1**. As one passes along the polymer chain the ligands are at right-angles to one another, see Fig. 3. The Mn(II) atom sits on a two-fold axis while the ligand is situated about a centre of symmetry. The Mn(II) atom is octa-coordinate with

TABLE 3. Selected distances (Å) and angles (°) and short intra and intermolecualr metal...metal distances

$\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O)\}_\infty$ (**1**)	
Mn–OW1	2.203(1)
Mn–N1	2.463(1)
Mn–O1	2.233(1)
Mn–O3	2.411(1)
O4–HO4	0.93(4)
HO4...O2^{a}	1.49(4)
O4...O2^{a}	2.194(2)
Mn...Mn^{i}	7.644(1)
Mn...Mn^{ii}	6.541(1)
Mn...Mn^{iii}	7.038(1)
OW1–Mn–O1^{b}	94.62(7)
OW1–Mn–N1	81.36(5)
OW1–Mn–N1^{b}	135.64(4)
OW1–Mn–O1	90.81(6)
OW1–Mn–O1^{b}	157.23(4)
OW1–Mn–O3	83.00(5)
OW1–Mn–O3^{b}	71.74(4)
N1–Mn–N1^{b}	130.78(4)
N1–Mn–O1	67.05(3)
N1–Mn–O1^{b}	79.33(4)
N1–Mn–O3	63.91(3)
N1–Mn–O3^{b}	135.00(4)
O1–Mn–O1^{b}	92.68(5)
O1–Mn–O3	130.95(4)
O1–Mn–O3^{b}	77.74(5)
O3–Mn–O3^{b}	142.56(5)
O4–HO4...O2^{a}	163(3)
$[Mn(H_2O)_6][H_2pztc]$ (**2**)	
Mn–OW1	2.170(2)
Mn–OW2	2.209(1)
Mn–OW3	2.167(1)
Mn–OW4	2.137(2)
O1–HO1	1.02(3)
HO1...O3	1.40(3)
O1...O3	2.403(2)
Mn...Mn^{iv}	5.356(1)
Mn...Mn^{v}	6.756(1)
Mn...Mn^{vi}	6.883(1)
OW1–Mn–OW2	84.03(3)
OW1–Mn–OW3	93.94(3)
OW1–Mn–OW4	180
OW2–Mn–OW2c	168.07(4)
OW2–Mn–OW3	88.65(5)
OW2–Mn–OW3^{c}	92.16(5)
OW2–Mn–OW4	95.97(3)
OW3–Mn–OW3^{c}	172.13(5)
OW3–Mn–OW4	86.06(3)
O1–HO1...O3	165(3)
$\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**)	
Mn–O1	2.238(4)
Mn–O3	2.157(4)
Mn–O5	2.178(4)
Mn–O7	2.257(4)
Mn–N1	2.198(4)
Mn–OW	2.135(4)
Mn...Mn^{vii}	7.762(2)
Mn...Mn^{viii}	5.035(2)
Mn...Mn^{ix}	6.411(2)
Mn....Mn^{x}	6.682(2)
O1–Mn–O3	98.25(15)
O1–Mn–O5	86.92(15)
O1–Mn–O7	143.47(14)
O1–Mn–N1	72.00(15)
O1–Mn–OW	125.11(16)
O3–Mn–O5	162.98(15)
O3–Mn–O7	88.17(15)
O3–Mn–N1	99.56(16)
O3–Mn–OW	79.77(15)
O5–Mn–O7	97.34(15)
O5–Mn–N1	97.46(15)
O5–Mn–OW	83.99(15)
O7–Mn–N1	71.47(15)
O7–Mn–OW	91.42(16)
N1–Mn–OW	162.88(17)
$\{K_2[Zn(pztc)(H_2O)\}\cdot 2.25H_2O\}_\infty$ (Zn-**3**), isomorphous with **3**	
Zn–O1	2.1785(19)
Zn–O3	2.1012(19)
Zn–O5	2.1286(19)
Zn–O7	2.2033(19)
Zn–N1	2.0610(22)
Zn–OW	2.0241(22)
Zn...Zn^{vii}	7.717(1)
Zn...Zn^{viii}	5.071(1)
Zn...Zn^{ix}	6.320(1)
Zn...Zn^{x}	6.505(1)
O1–Zn–O3	97.56(7)
O1–Zn–O5	85.74(8)
O1–Zn–O7	150.19(7)
O1–Zn–N1	75.54(8)
O1–Zn–OW	117.00(9)
O3–Zn–O5	163.05(8)
O3–Zn–O7	87.16(8)
O3–Zn–N1	98.12(8)
O3–Zn–OW	80.88(8)
O5–Zn–O7	98.25(7)
O5–Zn–N1	98.80(8)
O5–Zn–OW	82.81(8)
O7–Zn–N1	74.65(7)
O7–Zn–OW	92.81(9)
N1–Zn–OW	167.46(9)

Symmetry operations: $^{a}1-x, -y, -z$; $^{b}1-x, 0.5-y, z$; $^{c}0.5-x, y, 1.5-z$; $^{i}1-x, -y, -z$; $^{ii}0.25+y, 0.75-x, -0.25-z$; $^{iii}0.25+y, 0.75-x, 0.75-z$; $^{iv}-x, 0.5-y, 1.5-z$; $^{v}-x, 1.5-y, 1.5-z$; $^{vi}1+x, y, z$; $^{vii}-x, 1-y, 1-z$; $^{viii}0.5-x, y, 1-z$; $^{ix}0.5-x, 1.5-y, 1.5-z$, $^{x}0.5-x, 0.5-y, 1.5-z$.

^{a,b,c,i} and ^{vii} are intramolecular distances.

four short and four long bonds. The ligand is only partially deprotonated. The shorter bonds involve the O atoms, O1, of the deprotonated carboxylate groups and the water molecules, OW1. The longer bonds involve the pyrazine N atoms, N1, and the carbonyl O atoms, O3, of the protonated carboxylate groups. Hence, the ligand is coordinated in a pseudo bis(tridentate) manner and is relatively planar. The deprotonated and the protonated carboxylic groups are inclined to the planar pyrazine ring by 7.02(10) and 6.52(11)°, respectively, and by 9.99(9)° to one another. The OH function of

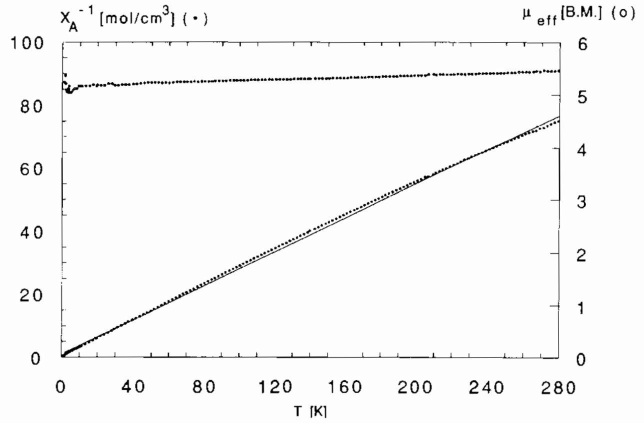

Fig. 1. χ_A^{-1} as a function of T (K) and μ_{eff} as a function of T (K) for $\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (**1**).

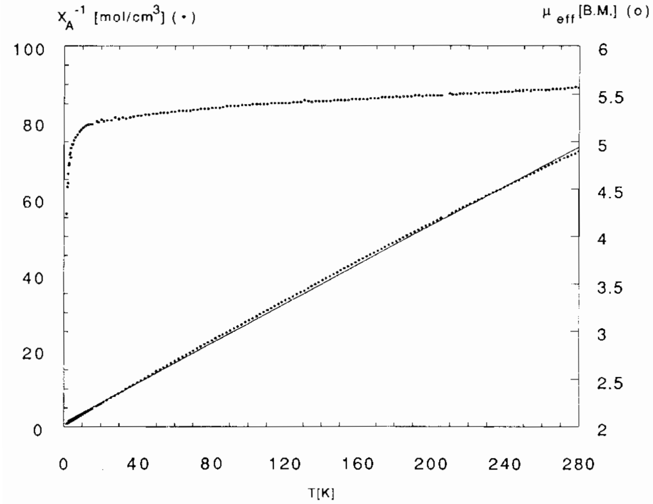

Fig. 2. χ_A^{-1} as a function of T (K) and μ_{eff} as a function of T (K) for $\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**).

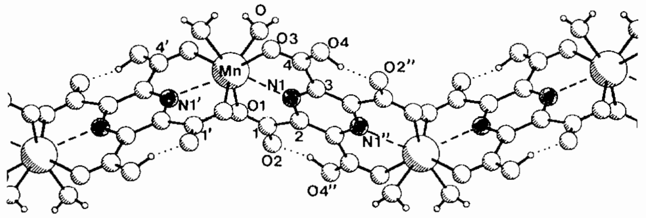

Fig. 3. PLUTO [10] plot of $\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (**1**).

the protonated carboxylate group is involved in a strong intramolecular hydrogen bond with the carbonyl oxygen of the coordinated CO_2^- group (O4–H(O4)...O2), see Table 3. In the crystal the zig-zag polymer chains are interlaced and run in two mutually perpendicular directions parallel to the *a* and *b* axes, Fig. 4. The chains are linked by a hydrogen bonding network involving the coordinated water molecules, OW1, the water molecule of crystallisation, OW2, and atom O3 of the protonated carboxylate group.

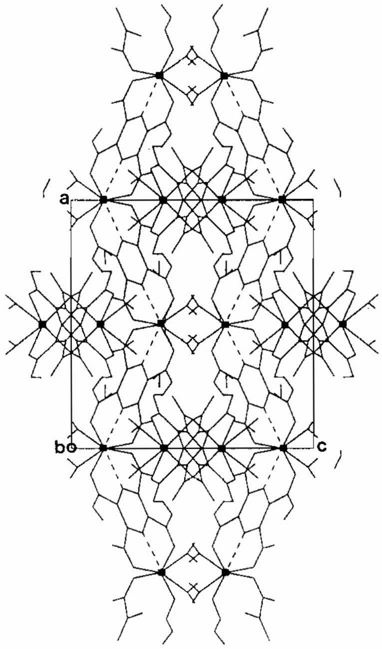

Fig. 4. Crystal packing in $\{[Mn(H_2pztc)(H_2O)_2]\cdot 2H_2O\}_\infty$ (**1**); ■, Mn atoms.

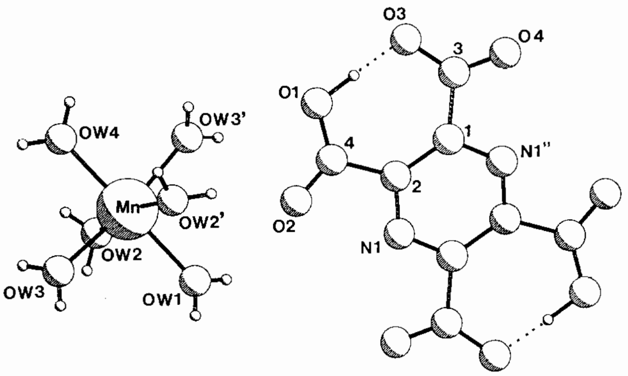

Fig. 5. PLUTO [10] plot of $[Mn(H_2O)_6][H_2pztc]$ (**2**).

$[Mn(H_2O)_6][H_2pztc]$ (2)

The reaction of $MnSO_4\cdot H_2O$ with H_4pztc in a metal to ligand ratio of 3:1 (pH 3.18) at 20 °C gave elongated colourless prisms, the structure analysis of which indicated that it is a salt composed of the cation $[Mn(H_2O)_6]^{2+}$ and the anion $[H_2pztc]^{2-}$, Fig. 5. The cation possesses C_2 symmetry and the anion C_i symmetry. There is a strong intramolecular H bond in the anion, O1–HO1...O3, the geometry of which resembles that of the ligand in **1**, see Table 3. However the anion is much less planar than its coordinated form found in **1**. The deprotonated and the protonated carboxylate groups are inclined to the planar pyrazine ring by 22.53(13) and 19.33(6)°, respectively, and by 31.32(15)° to one another. In the crystal both the cations and the anions stack up the *a* axis, Fig. 6. They are linked by an extensive three-dimensional H-bonding network in-

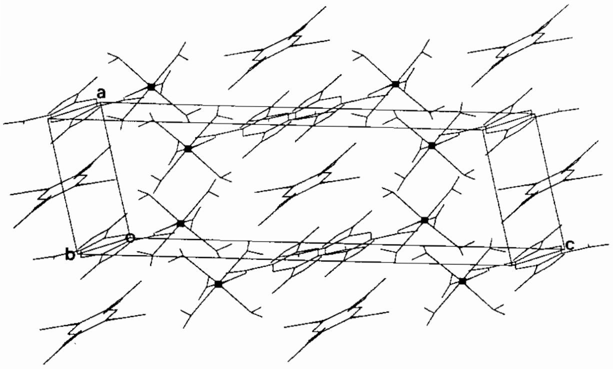

Fig. 6. Crystal packing in $[Mn(H_2O)_6][H_2pztc]$ (**2**); ■, Mn atoms.

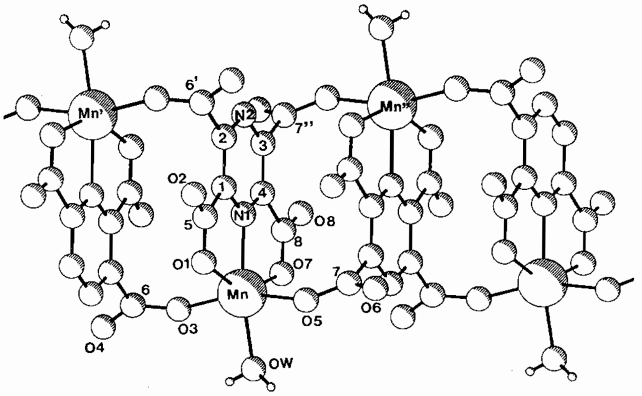

Fig. 7. PLUTO [10] plot of $\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**).

volving atoms O2, O3 and O4 of the anion and the water molecules, OW1, 2, 3 and 4, of the cation.

$\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (3) and $\{K_2[Zn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (Zn-3)

The reaction of MSO_4 or MCl_2 with H_4pztc in a metal to ligand ratio of 1:1 in the presence of a potassium acetate/acetic acid buffer solution resulted in the formation of a column type polymer **3** (Fig. 7) and Zn-**3**. The ligand is completely deprotonated as suggested by the IR spectra and the thermogravimetric measurements. The metal atoms are hexa-coordinate and while one side of the ligand is coordinated in a tridentate manner the opposite side coordinates in a bis(monodentate) manner linking the molecules related by a centre of symmetry to form the column. On this side of the ligand the pyrazine N atom, N2, is not coordinated and is not protonated. The distorted coordination sphere of the metal is completed by a water molecule, OW1. In both **3** and Zn-**3** the carboxylate groups at C2 and C3 are rotated with respect to the best plane through the pyrazine ring by approximately 80°. Along the column the ligands are separated by *c.* 4.1 Å. In the crystal the columns stack up the *b* axis and the channels between the columns are occupied by K^+ ions and water molecules, Fig. 8. An extensive H-bonding network links the polymer chains via the K^+ cations and the water molecules.

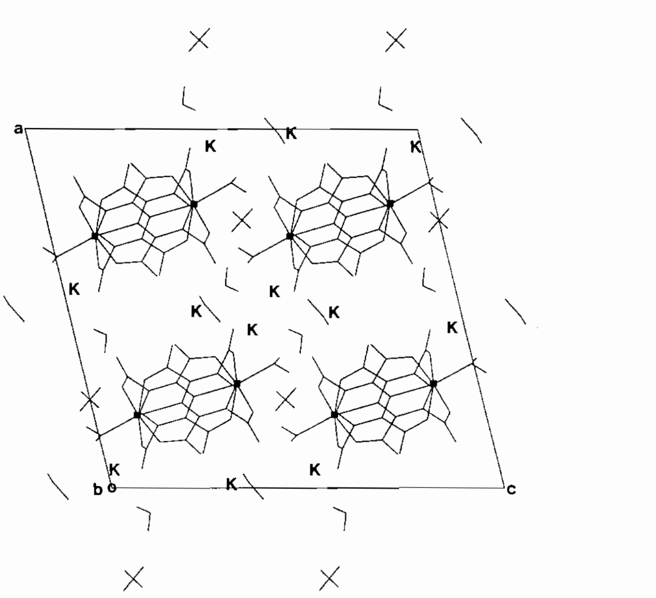

Fig. 8. Crystal packing in $\{K_2[Mn(pztc)(H_2O)]\cdot 2.25H_2O\}_\infty$ (**3**); ■, Mn atoms; K, potassium cations.

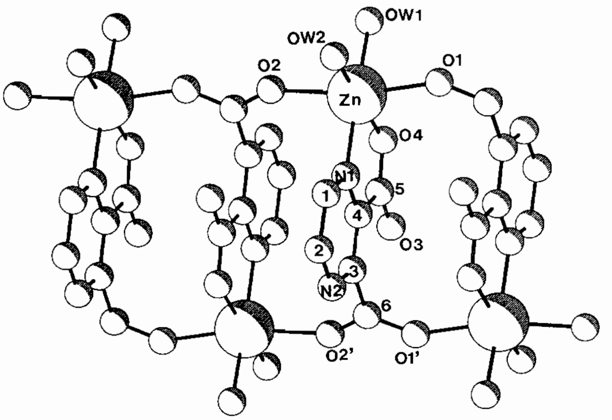

Fig. 9. PLUTO [10] plot of $\{[Zn(pzdc)(H_2O)_2]\cdot H_2O\}_\infty$ (**4**).

This column type stacking observed in **3** and Zn-**3** is reminiscent of that observed for polymer **4**, produced by the reaction of pyrazine-2,3-dicarboxylic acid (H_2pzdc) with zinc acetate [11], Fig. 9. Here, one of the two adjacent carboxylate groups rotates out of plane of the pyrazine ring by 85.4° and coordinates to two different symmetry related molecules. The distance of *c.* 3.2 Å separating the ligands along the column is much shorter than that in **3** or Zn-**3**. In **4** the Zn–N_{pz} distance of 2.145 Å is much longer than the same distance in Zn-**3** (2.061 Å). This is compensated for by the shorter Zn–O chelate (2.060 Å) and bridging (2.154 and 2.124 Å) distances in **4** as compared to those in Zn-**3**, Table 3.

To date there are only three Mn(II)–pyrazine complexes reported in the Cambridge Crystallographic Data

Base [12]. The first two involve the ligand bis(pyrazine-2-methyl)ethylenediamine [13, 14]. The third compound, diaqua-bis(pyrazinecarboxylato-*N*,*O*)-Mn^{II} (**5**) [15], involves the ligand pyrazine-2-carboxylic acid. The bond distances and angles involving the Mn atoms in compounds **1**, **3** and **5** differ quite considerably. The $Mn–N_{pz}$ distance in **5**, 2.307 Å, lies between the distances found for **1** and **3**, 2.463 and 2.198 Å, respectively. The chelate Mn–O distance of 2.135 Å in **5** is similar to that found for the bridging Mn–O distances in **3**, 2.157 and 2.178 Å. However, the chelating Mn–O distances in **1** and **3** are similar and notably longer, 2.233–2.257 Å, than the bridging distances. The $Mn–O_{water}$ distances in **1** and **5** are similar, 2.203 and 2.186 Å, respectively, and longer than that observed in **3**, 2.135 Å. The chelating bite angle $N_{pz}–Mn–O_{carboxylato}$ in **5**, 74.6°, is similar to that observed in **3** (72.0 and 71.5°), but much larger than that observed in **1** (67.1 and 63.9°).

Conclusions

The ligand pyrazine-2,3,5,6-tetracarboxylic acid has proved to be an extremely flexible ligand in coordination chemistry with 3^d metals and zinc. Bis(tridentate) binuclear coordination is probably not possible due to the steric hindrance which would arise between the carbonyl groups. However, pseudo bis(tridentate), bis(bidentate) and mono(tridentate)/bis(monodentate) binuclear coordination modes have been found and quasi-linear, zig-zag and column type polymers have been produced. The actual mode of coordination of H_4pztc depends not only on the metal used but also on the temperature and the pH of the solution. The manner in which ligands with adjacent carboxylic acid groups coordinate is being used to design new ligands and to construct three-dimensional coordination polymers. We shall report on our efforts in this direction at a later date.

Supplementary material

Complete tables of atomic fractional coordinates and distances and angles for **1**, **2**, **3** and Zn-**3** have been deposited with the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EW, UK. Further crystallographic, thermogravimetric and magnetic susceptibility data are available from the author H.St.-E.

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