Synthesis and Crystal Structures of Complexes of Mn^{II}, Cu^{II} and Zn^{II} with the New Bis(tridentate) Chelate 2,3,5,6-Tetrakis(aminomethyl)pyrazine†

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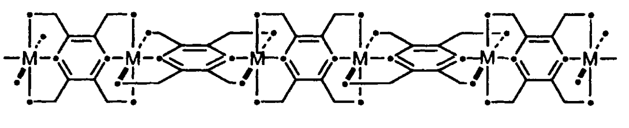
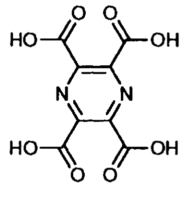
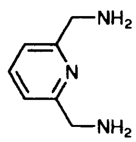
The new bis(tridentate) chelate 2,3,5,6-tetrakis(aminomethyl)pyrazine (tampyz) has been prepared. It forms a quasi-linear one-dimensional polymeric complex with $MnCl_2$ in water, $[\{Mn(tampyz)Cl_2{\cdot}2H_2O\}_\infty]$. The crystal structure reveals that it is the first infinite co-ordination polymer with a regular metal–ligand arrangement where the metal atom is fully co-ordinated by all six functional groups of the ligand. The binuclear complex $[Cu_2(tampyz)Cl_2]Cl_2{\cdot}2.25H_2O$ was obtained by the reaction of $Cu(O_3SC_6H_4Me\text{-}p)_2{\cdot}5H_2O$ and $[H_4tampyz]Cl_4$ in water, and its crystal structure determined. The copper atoms can be considered to be either four-co-ordinate in a square-planar environment, or six-co-ordinate with two weak apical Cu···Cl bonds so forming a ladder-type polymer. The binuclear complex $[Cl_2Zn(tampyz)ZnCl_2]$ was prepared by the reaction of $ZnCl_2$ and tampyz in water. Its crystal structure reveals that the zinc atoms are five-co-ordinate in a trigonal-bipyramidal arrangement. The two Zn–Cl bonds are equivalent, as expected for a d^{10} complex.

We have investigated the possibility of using tetrasubstituted pyrazine derivatives, with functional groups branched in the β position, to synthesise a 'columnane'. That is, a new quasi-linear co-ordination polymer with the bis(tridentate) ligand acting as a bridging planar chelate. Pyrazine tetracarboxylic acid ($H_4pyztca$)[1] is a known example of such a ligand but while co-ordination polymers[2] have been synthesised with Fe^{II},[3] Mn^{II} and Zn^{II},[4] and Cu^{II},[5] bis(tridentate) co-ordination of this ligand has not been observed. Based on previous knowledge concerning the co-ordination chemistry of 3d metals and zinc with the tridentate ligand 2,6-bis(aminomethyl)pyridine (bampy)[6] it was decided to synthesise the new bis(tridentate) pyrazine analogue 2,3,5,6-tetrakis(aminomethyl)pyrazine (tampyz).[7] Recently Constable and Cargill Thompson[8] have proposed the formation of a similar one-dimensional linear polymer structure using bis(tridentate) 'back to back' 2,2′:6′,2″-terpyridine ligands, which also give rise to linear connectivity at the ligand.

Here we report on the synthesis of tampyz, and on the synthesis and characterization of a manganese(II) polymer complex and binuclear complexes of Cu^{II} and Zn^{II}.


Columnane


$H_4pyztca$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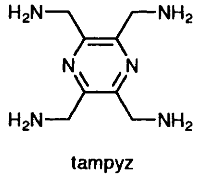
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Results and Discussion

Synthesis of 2,3,5,6-Tetrakis(aminomethyl)pyrazine.—Attempts to obtain this compound by either hydride or molecular hydrogen reduction of the known tetracyanopyrazine were unsuccessful.[7] The IR spectra of the solids collected indicated the presence of unreacted nitrile. Furthermore they were highly coloured indicating possible polymerization. The aminomethyl pyrazine derivative was prepared by the hydrolysis of a pyrazine azidomethyl analogue.[9] The synthesis was carried out according to Scheme 1.

Bromination of tetramethylpyrazine **I**[10] gave a poor yield (10%) of 2,3,5,6-tetrakis(bromomethyl)pyrazine **II**, owing to the different halogenated products which could be formed. This step was followed by thin-layer chromatography. After 24 h five large spots were identified as new materials which form an oil after evaporation of the solvent. Compound **II** was isolated by crystallization of the oily residue. 2,3,5,6-Tetrakis(azidomethyl)pyrazine **III** was obtained in high yield (82%) by substitution of bromide by azido using NaN_3. It was recrystallized carefully from methanol. **CAUTION**: azides can be explosive! The catalytic hydrogenation of **III** with Pd/C yielded the corresponding amine tampyz. Subsequent addition of a methanolic HCl solution gave the corresponding amine salt $[H_4tampyz]Cl_4$.

Titration of $[H_4tampyz]Cl_4$.—The four p*K* values of the hydrochloride $[H_4tampyz]Cl_4$ were determined by pH potentiometry. The values given in Scheme 2 are within the range expected for primary amines in the β position with respect to the aromatic ring.

Structures.—The manganese(II) polymeric complex $[\{Mn(tampyz)Cl_2{\cdot}2H_2O\}_\infty]$ was obtained from $MnCl_2{\cdot}3.78H_2O$

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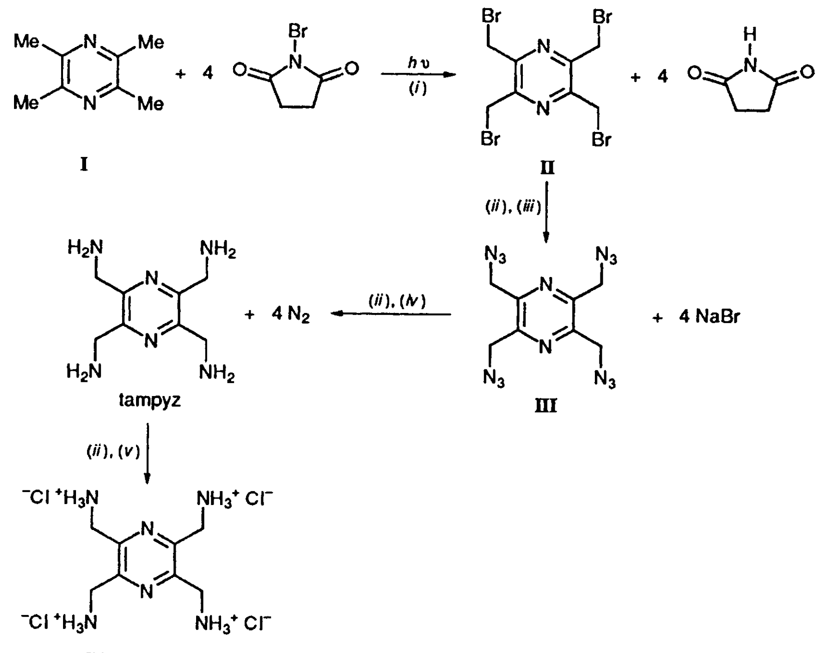
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviiii.



Scheme 1 (*i*) $(PhCO)_2O_2$, CCl_4; (*ii*) MeOH; (*iii*) $4NaN_3$, 50 °C; (*iv*) $4H_2$, Pd/C; (*v*) 4HCl

$$H_4tampyz^{4+} \rightleftharpoons H_3tampyz^{3+} + H^+ \qquad pK_1 = 7.412 \pm 0.008$$

$$H_3tampyz^{3+} \rightleftharpoons H_2tampyz^{2+} + H^+ \qquad pK_2 = 8.267 \pm 0.007$$

$$H_2tampyz^{2+} \rightleftharpoons Htampyz^{+} + H^+ \qquad pK_3 = 9.027 \pm 0.007$$

$$Htampyz^{+} \rightleftharpoons tampyz + H^+ \qquad pK_4 = 9.764 \pm 0.004$$

Scheme 2 Literature values: 2-aminomethylpyridine, $pK_1 = 8.70$;[11] 3-aminomethylpyridine, $pK_2 = 9.12$;[12] 2,6-bis(aminomethyl)pyridine, $pK_1 = 8.82$, $pK_2 = 9.28$;[6] 2-amino-3-methylaminopyrazine, $pK_2 = 8.40$[13]

and free tampyz in water, as yellow crystals. Thermogravimetric analysis showed a weight loss between 90 and 180 °C corresponding to two water molecules per Mn^{2+} ion. The determination of the contents of Mn and tampyz by UV and VIS spectroscopy indicated a 1:1 metal-to-ligand ratio. Accordingly, there are two possible compositions for this complex, either mono- or poly-nuclear. This problem was resolved by X-ray crystallographic analysis. The complex was found to be a columnane. It is an extended quasi-linear chain polymer with the bis(tridentate) ligands, tampyz, and the metal atoms arranged alternately, Fig. 1(*a*). As a consequence of the conformational strain involved around the metal centre, the polymeric chain adopts a wave form. The Mn^{2+} ion sits on a two-fold rotation axis and the pyrazine ring is situated about a centre of symmetry, Fig. 1(*b*). The maganese environment is a very distorted octahedron with relatively long co-ordination bonds, $Mn-N_{pyz}$ being 2.216(2) Å and $Mn-N_{amine}$ 2.314(3) and 2.253(3) Å, see Table 1. The two chelate rings are highly strained with angles N(1)–Mn–N(2) and N(1)–Mn–N(3) being 73.08(9) and 74.64(9)°, respectively. The N(2) chelate ring has a C_s [C(4)] envelope conformation while the N(3) chelate ring has a C_s(Mn) envelope conformation. In the crystal parallel chains are held together by weak hydrogen bridges between the water molecules and the Cl^- ions, and the amine protons, Fig. 2. The mean Cl ··· H(N) and Cl ··· N distances are 2.59 and 3.388 Å, respectively, mean Cl ··· H(water) and Cl ··· O(water) distances are 2.54 and 3.238 Å, and mean O(water) ··· H(N) and O(water) ··· N distances are 2.41 and 3.207 Å, respectively. The intrachain Mn ··· Mn($\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$) distance is 7.149(1) Å while the shortest interchain Mn ··· Mn($1 - x$, $1 - y$, $-z$) distance is 6.975(2) Å.

The binuclear complex $[Cu_2(tampyz)Cl_2]Cl_2 \cdot 2.25H_2O$ was obtained from $Cu(O_3SC_6H_4Me\text{-}p)_2 \cdot 5H_2O$ and $[H_4tampyz]Cl_4$ in water as greenish blue crystals. It has crystallographic D_{2h} (*mmm*) symmetry, Fig. 3. The copper(II) ions can be considered to be four-co-ordinate with a square-planar environment or six-co-ordinate with two equivalent *trans* apical Cu ··· Cl(2) bonds of 2.871(1) Å, see Table 2. The intramolecular Cu ··· Cu($-x$, $-y$, $-z$) distance is 6.557(1) Å. The $Cu-N_{pyz}$ distances are 1.945(4) Å and the $Cu-N_{amine}$ distances are 2.036(3) Å. The binuclear complexes are linked by two parallel Cu ··· Cl(2) ··· Cu bridges to form a ladder-type polymer structure (Fig. 4) with an intermolecular Cu ··· Cu($1 + x$, y, z) distance of 5.716(1) Å. In the crystal the ladders stack up the *a* axis with an interladder Cu ··· Cu ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$) distance of only 5.536(1) Å.

The binuclear complex $[Cl_2Zn(tampyz)ZnCl_2]$ was obtained from $ZnCl_2$ and free tampyz in water as white crystals. Thermogravimetric analysis showed no weight loss up to 340 °C indicating the absence of water in the crystals. This was consistent with the structure of the binuclear complex. The four chloride counter ions are directly bound to the metal centre to neutralize the two Zn^{2+} ions. The complex has crystallographic C_{2h} (2/*m*) symmetry, Fig. 5. The zinc(II) ions are five-co-ordinate with distorted trigonal-bipyramidal geometries. The intramolecular Zn ··· Zn($1 - x$, $-y$, $-z$) distance is 6.850(1) Å. The $Zn-N_{pyz}$ distances are 2.084(3) Å and the $Zn-N_{amine}$ distances are 2.188(3) Å, Table 3. The atoms Cl(1), Cl(2) and N(1) occupy the equatorial positions of the trigonal bipyramid. The Zn–Cl distances are equivalent, within experimental error, as expected for a d^{10} complex. In the crystal the molecules are inclined to the *bc* plane by *ca.* 45° and stack up the *a* axis, Fig. 6. There are two short intermolecular Zn ··· Zn distances of 5.575(1) Å ($-x$, $-y$, $-z$) and 5.802(1) Å ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$).

In Table 4 various M–N bond distances and N–M–N bond angles are compared for complexes of Mn^{II}, Cu^{II} and Zn^{II} with tampyz, $H_4pyztca$[4,5] and the pyridine analogue bampy.[6] It can be seen that apart from one exception (the $Cu-N_{pyz}$ distances in complexes with $H_4pyztca$[5]) the geometries about the metal centres are very similar. The most strained geometry each time

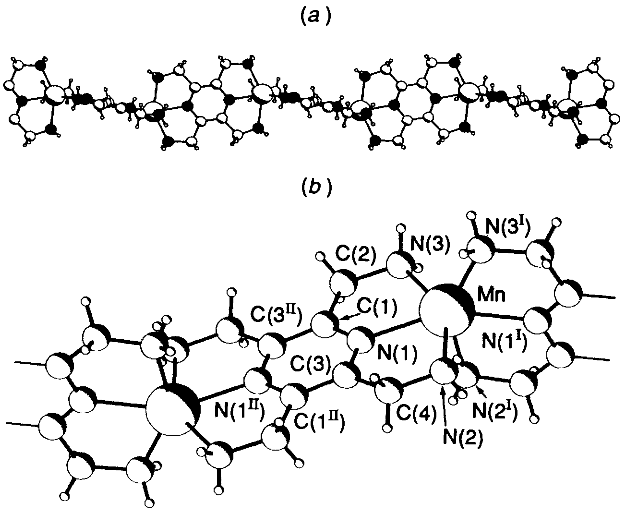


Fig. 1 Perspective views of (*a*) the polymer chain of [{Mn(tampyz)-$Cl_2 \cdot 2H_2O$}$_\infty$] (Mn atoms are large open circles, N atoms are small shaded circles) and (*b*) a small part of the complex viewed perpendicular to the two-fold axis

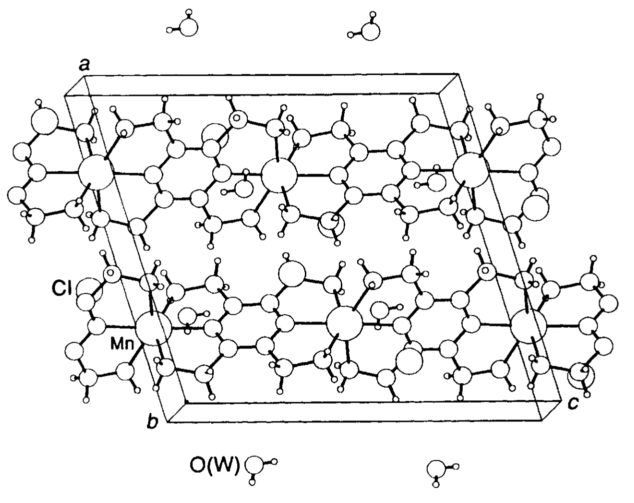


Fig. 2 Packing diagram for [{Mn(tampyz)$Cl_2 \cdot 2H_2O$}$_\infty$]

Table 1 Selected bond lengths (Å) and angles (°) for [{Mn(tampyz)-$Cl_2 \cdot 2H_2O$}$_\infty$]

Mn–N(1)	2.216(2)	N(2)–C(4)	1.465(4)
Mn–N(2)	2.314(3)	N(3)–C(2)	1.470(4)
Mn–N(3)	2.253(3)	C(1)–C(2)	1.504(4)
N(1)–C(1)	1.339(4)	C(1)–C(3^{II})	1.390(4)
N(1)–C(3)	1.333(4)	C(3)–C(4)	1.511(4)
N(1)–Mn–N(1^{I})	154.0(1)	C(1)–N(1)–C(3)	120.2(3)
N(1)–Mn–N(2)	73.1(1)	Mn–N(2)–C(4)	115.3(2)
N(1)–Mn–N(2^{I})	88.8(1)	Mn–N(3)–C(2)	114.9(2)
N(1)–Mn–N(3)	74.6(1)	N(1)–C(1)–C(2)	117.6(3)
N(1)–Mn–N(3^{I})	122.3(1)	N(1)–C(1)–C(3^{II})	119.6(3)
N(2)–Mn–N(2^{I})	91.9(1)	C(2)–C(1)–C(3^{II})	122.8(3)
N(2)–Mn–N(3)	147.7(1)	N(3)–C(2)–C(1)	113.3(3)
N(2)–Mn–N(3^{I})	89.4(1)	N(1)–C(3)–C(1^{II})	120.1(3)
N(3)–Mn–N(3^{I})	106.3(1)	N(1)–C(3)–C(4)	117.7(3)
Mn–N(1)–C(1)	118.8(2)	C(1^{II})–C(3)–C(4)	122.2(3)
Mn–N(1)–C(3)	120.8(2)	N(2)–C(4)–C(3)	112.1(3)

Symmetry operations: I $\frac{1}{2} - x, y, -z$; II $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$.

is that involving the manganese atom with a N–M–N chelate angle of less than 74°.

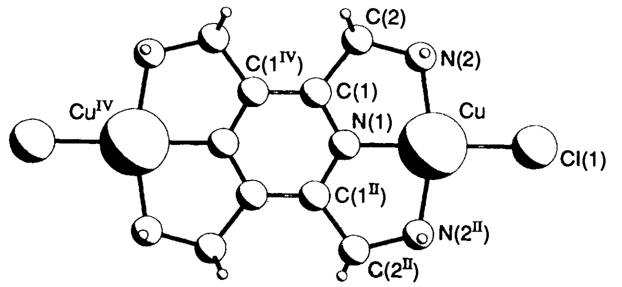


Fig. 3 Perspective view of the cation [Cu_2(tampyz)Cl_2]$^{2+}$

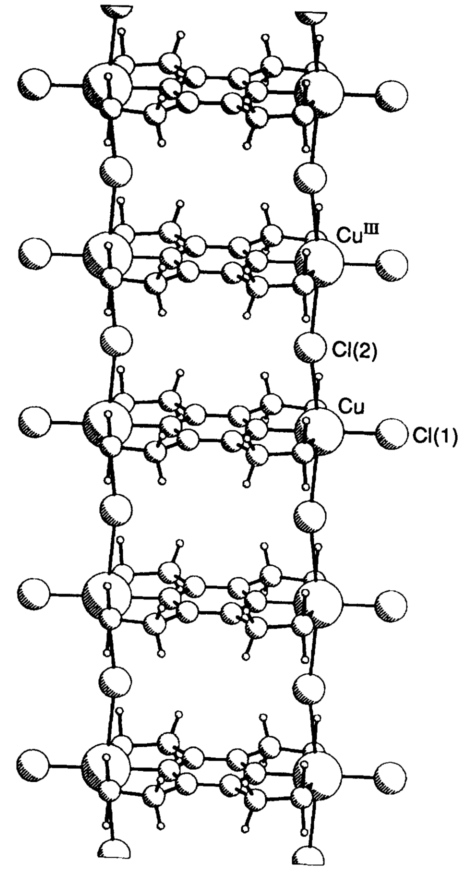


Fig. 4 Perspective view of [Cu_2(tampyz)Cl_2]Cl_2, showing the ladder-type polymer structure

The magnetic and electrical behaviour of these one-dimensional polymeric complexes is of particular interest. Work on this aspect is currently underway.

Experimental

Melting points were determined on a Culatti apparatus and are corrected. The IR spectra were recorded on a Perkin-Elmer 521 spectrometer. Thermogravimetric measurements were performed on a Mettler TA 3000 instrument, with a TC 10 processor and a TG 50 unit coupled with a Mettler M3 microbalance. Proton and ^{13}C NMR spectra were recorded on a Brucker WP 200 spectrometer, mass spectra on a triple quadrupole Nermag R 30-10, and UV/VIS spectra on a Uvikon 810/820 spectrometer. The elemental analyses were performed by the Organische-chemisches Mikrolabor at the Eidgenössische Technische Hochschule Zürich. pH-Potentiometric titrations were carried out using a Metrohm titration station comprised of a Metrohm 605 pH-meter, a Metrohm 655 Dosimat and an Orion B102SC combined electrode. The instrument was

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_2(tampyz)Cl_2]Cl_2{\cdot}2.25H_2O$

Cu–Cl(1)	2.243(1)	N(1)–C(1)	1.334(3)
Cu · · · Cl(2)	2.871(1)	N(1)–C(1^{II})	1.334(3)
Cl(2) · · · Cu^{III}	2.871(1)	N(2)–C(2)	1.449(5)
Cu–N(1)	1.945(4)	C(1)–C(1^{IV})	1.382(6)
Cu–N(2)	2.036(3)	C(1)–C(2)	1.509(4)
Cl(1)–Cu–Cl(2)	95.4(1)	Cu–Cl(2)–Cu^{III}	169.2(1)
Cl(1)–Cu–N(1)	180.0(0)	Cu–N(1)–C(1)	118.8(2)
Cl(1)–Cu–N(2)	98.4(1)	C(1)–N(1)–C(1^{II})	122.4(3)
Cl(2)–Cu–Cl(2^{I})	169.2(1)	Cu–N(2)–C(2)	113.4(2)
Cl(2)–Cu–N(1)	84.6(1)	N(1)–C(1)–C(1^{IV})	118.8(3)
Cl(2)–Cu–N(2)	89.2(1)	N(1)–C(1)–C(2)	115.1(3)
N(1)–Cu–N(2)	81.6(1)	C(1^{IV})–C(1)–C(2)	126.1(3)
N(2)–Cu–N(2^{II})	163.2(1)	N(2)–C(2)–C(1)	111.2(3)

Symmetry operations: I $-1 + x, y, z$; II $x, -y, z$; III $1 + x, y, z$; IV $-x, y, -z$.

Table 3 Selected bond lengths (Å) and angles (°) for $[Cl_2Zn(tampyz)ZnCl_2]$

Zn–Cl(1)	2.302(1)	N(1)–C(1)	1.328(3)
Zn–Cl(2)	2.289(1)	N(2)–C(2)	1.458(4)
Zn–N(1)	2.084(3)	C(1)–C(1^{II})	1.392(6)
Zn–N(2)	2.188(3)	C(1)–C(2)	1.504(4)
Cl(1)–Zn–Cl(2)	119.6(1)	Zn–N(1)–C(1)	119.1(2)
Cl(1)–Zn–N(1)	115.4(1)	C(1)–N(1)–C(1^{I})	121.7(3)
Cl(1)–Zn–N(2)	98.3(1)	Zn–N(2)–C(2)	113.7(2)
Cl(2)–Zn–N(1)	125.1(1)	N(1)–C(1)–C(1^{II})	119.2(3)
Cl(2)–Zn–N(2)	94.6(1)	N(1)–C(1)–C(2)	117.6(3)
N(1)–Zn–N(2)	77.3(1)	C(1^{II})–C(1)–C(2)	123.3(3)
N(2)–Zn–N(2^{I})	153.8(1)	N(2)–C(2)–C(1)	111.9(3)

Symmetry operations: I $x, -y, z$; II $1 - x, y, -z$.

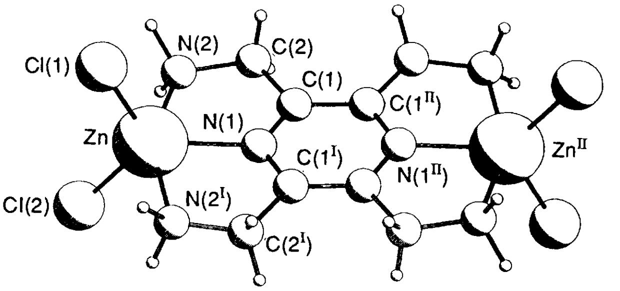


Fig. 5 Perspective view of the dinuclear complex $[Cl_2Zn(tampyz)ZnCl_2]$

calibrated with repeated titrations of the known monoacid tris(hydroxymethyl)aminomethane (Tris) under the same ionic strength conditions as for $[H_4(tampyz)]Cl_4$.

X-Ray Crystallography.—Intensity data were measured on a Stoe AED2 four-circle diffractometer at room temperature, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Further details are given in Table 5. Numerical absorption corrections were applied in the case of the complexes of Cu^{II} and Zn^{II} using the program SHELX 76.[14] The program system NRCVAX[15] was used to solve all three structures by Patterson and Fourier methods, and in all further calculations. Hydrogen atoms were located in difference maps and refined isotropically for all three structures. It was not possible to locate the water H atoms in the case of the copper(II) complex. Weighted full-matrix least-squares refinement on F was used in all cases with the weighting scheme $w^{-1} = \sigma^2(F_o) + k(F_o)^2$. Residuals are defined by $R = \Sigma(F_o - F_c)/\Sigma F_o$ and $R' = [\Delta w(F_o - F_c)^2/\Sigma w F_o^{\,2}]^{\frac{1}{2}}$. Complex neutral-atom scattering factors in NRCVAX are taken from ref. 16. Figs. 1–6 were prepared using the program PLUTO.[17] Final atomic coordinates for the three complexes are given in Tables 6–8.

Table 4 A comparison of average M–N bond distances (Å) and N–M–N bond angles (°) in the complexes of 2,3,5,6-tetrakis(aminomethyl)pyrazine, pyrazine-2,3,5,6-tetracarboxylic acid[4,5] and 2,6-bis(aminomethyl)pyridine[6]

	Mn^{II}	Cu^{II}	Zn^{II}
M–N$_{pyz}$	2.216	1.945	2.084
	2.198[4]	2.139[5]	2.061[4]
M–N$_{py}$[6]	2.218	1.931	2.095
M–N$_{amine}$	2.284	2.036	2.188
M–N$_{amine}$[6]	2.290	2.016	2.218
N$_{pyz}$–M–N$_{amine}$	73.86	81.59	77.32
N$_{py}$–M–N$_{amine}$[6]	73.39	81.73	76.85

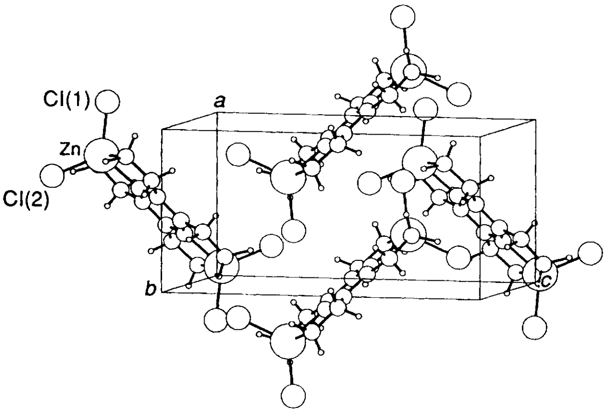


Fig. 6 Packing diagram for $[Cl_2Zn(tampyz)ZnCl_2]$

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles. Structure factor tables, and tables of hydrogen bonding and least-squares planes for the manganese(II) complex, are available on request from H. St.-E.

Potentiometric Titrations.—The salt $[H_4(tampyz)]Cl_4$ was titrated automatically with 0.4 mol dm^{-3} NaOH, I = 0.5 mol dm^{-3} KNO$_3$, at 25.0 ± 0.1 °C, ligand concentration C_L = 1.88 × 10^{-3} mol dm^{-3}, after degassing with N$_2$ for 15 min. The titration curves were evaluated using the program TITFIT.[18] The following average logarithmetic formation constants were obtained: $[HL]^+$, 9.764 ± 0.004; $[H_2L]^{2+}$, 18.791 ± 0.003; $[H_3L]^{3+}$, 27.058 ± 0.004; $[H_4L]^{4+}$, 34.470 ± 0.004.

Syntheses.—2,3,5,6-*Tetrakis(bromomethyl)pyrazine* **II**. 2,3,5,6-Tetramethylpyrazine **I** (230 g, 1.3 mol; purum, Fluka), freshly recrystallized *N*-bromosuccinimide (230 g, 1.3 mol) and CCl$_4$ (1.5 l) were introduced into a three-necked flask (2 l). The mixture was stirred and irradiated with two 300 W lamps for 4 h. As soon as the mixture began to boil a catalytic amount of benzoyl peroxide (1 g dissolved in the minimum of CHCl$_3$) was added to initiate the reaction. The reaction was complete when the succinimide was observed floating on the surface of the solvent. The succinimide was then filtered off and the filtrate cooled overnight, whereupon more succinimide crytallized. This was also filtered off. The filtrate was evaporated and the residual oil dissolved in an equal volume of dimethyl ether. Light petroleum (b.p. 60–80 °C) was then added dropwise at room temperature (r.t.) in order to crystallize the bromo compound. Recrystallization of crude 2,3,5,6-tetrakis(bromomethyl)pyrazine from toluene–light petroleum gave 13 g of pure compound (10%), m.p. 142.6 °C (Found: C, 21.25; H,

Table 5 Crystal data, details of data collection and structure refinement

Compound	$[\{Mn(tampyz)Cl_2{\cdot}2H_2O\}_\infty]$	$[Cu_2(tampyz)Cl_2]Cl_2{\cdot}2.25H_2O$	$[Cl_2Zn(tampyz)ZnCl_2]$
Formula	$C_8H_{16}Cl_2MnN_6{\cdot}2H_2O$	$C_8H_{16}Cl_4Cu_2N_6{\cdot}2.25H_2O$	$C_8H_{16}Cl_4N_6Zn_2$
M_r	358.13	510.19	468.82
Crystal colour/habit	Yellow lozenges	Blue blocks	Cream plates
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*I*2/*a*	*Immm*	*Pnmn*
Z	4	2	2
D_c/g cm^{-3}	1.623	2.015	1.922
μ(Mo-Kα)/cm^{-1}	12.4	31.9	37.0
Crystal size/mm	0.38 × 0.38 × 0.08	0.38 × 0.30 × 0.23	0.34 × 0.19 × 0.08
Least-squares fit of *N* reflections	28	46	29
2θ range/°	18–30	21–39	20–35
a/Å	13.039(4)	5.716(1)	6.940(1)
b/Å	8.441(2)	8.415(1)	8.698(1)
c/Å	13.866(2)	17.483(1)	13.423(1)
β/°	106.18(1)		
U/Å^3	1465.7(6)	840.9(2)	810.3(2)
Scan method	ω–θ	ω–θ	ω–θ
θ_{max}/°	25.0	27.5	27.5
h, *k*, *l* range	−15 to 14, 0–10, 0–16	−7 to 7, 0–10, 0–22	0–8, 0–11, 0–17
Transmission		0.47–0.62	0.54–0.77
No. of reference reflections	3	4	3
variation (%)	< 1	< 1	1
No. unique reflections	1289	580	992
No. reflections refined [$I > 2.5\sigma(I)$]	1016	533	833
No. of refined parameters	127	54	68
R	0.038	0.035	0.031
R'	0.052	0.053	0.045
Weighting parameter *k*	0.0014	0.0015	0.001
Goodness of fit	1.15	1.28	1.18
Maximum shift/e.s.d.	0.035	0.026	0.033
Maximum, minimum electron density/e Å^{-3}	+0.38, −0.41	+0.61, −0.69	+0.70, −0.34

Table 6 Positional parameters for $[\{Mn(tmpyz)Cl_2{\cdot}2H_2O\}_\infty]$

Atom	*x*	*y*	*z*
Mn	1/4	0.353 21(8)	0
N(1)	0.245 65(19)	0.294 2(3)	0.154 56(18)
N(2)	0.119 0(3)	0.162 7(4)	−0.014 21(21)
N(3)	0.371 7(3)	0.513 3(4)	0.101 35(20)
C(1)	0.318 83(24)	0.358 6(3)	0.232 17(23)
C(2)	0.393 1(3)	0.479 9(4)	0.209 16(25)
C(3)	0.176 76(23)	0.187 4(3)	0.170 50(21)
C(4)	0.095 5(3)	0.120 2(4)	0.079 83(24)
Cl(1)	0.385 91(7)	0.658 13(12)	−0.118 32(7)
O(W)	−0.181 7(3)	0.119 6(4)	0.137 4(3)

Table 7 Positional parameters for $[Cu_2(tampyz)Cl_2]Cl_2{\cdot}2.25H_2O$

Atom	*x*	*y*	*z*
Cu	0	0	0.187 51(3)
Cl(1)	0	0	0.315 83(6)
Cl(2)	1/2	0	0.172 00(10)
N(1)	0	0	0.076 27(21)
N(2)	0	0.239 4(4)	0.170 49(16)
C(1)	0	0.138 9(3)	0.039 54(17)
C(2)	0	0.283 8(4)	0.090 38(20)
O(W1)	1/2	1/2	0
O(W2)	1/2	0.183 4(20)	0
O(W3)*	0	1/2	0.171(4)

* Occupancy 0.25.

Table 8 Positional parameters for $[Cl_2Zn(tampyz)ZnCl_2]$

Atom	*x*	y	z
Zn	0.167 73(7)	0	0.188 68(4)
Cl(1)	0.301 06(16)	0	0.345 71(10)
Cl(2)	−0.160 17(15)	0	0.171 21(10)
N(1)	0.364 5(5)	0	0.071 41(25)
N(2)	0.199 9(4)	0.245 0(3)	0.155 8(3)
C(1)	0.429 6(4)	0.133 3(3)	0.036 93(22)
C(2)	0.346 0(5)	0.277 9(4)	0.080 6(3)

1.70; Br, 71.05; N, 6.40. Calc. for $C_8H_8Br_4N_2$: C, 21.25; H, 1.80; Br, 70.75; N, 6.40%); ν_{max}(CsBr disc) 3035, 2980, 1440, 1405, 1220, 785, 630, 541 and 443 cm^{-1}. NMR ($CDCl_3$): ^1H (200 MHz) δ 4.72 (s); ^{13}C, δ 28.77 (t), 150.42 (s). UV_{max}(methanol) 277 nm (ε = 8800 dm^3 mol^{-1} cm^{-1}). Mass spectrum: *m*/*z* 452 (quintet, 4 Br), 373 (quartet, 3 Br), 292 (triplet, 2 Br), 213 (doublet, 1 Br) and 92 ($C_6H_6N^+$, azatropylium).

2,3,5,6-*Tetrakis*(*azidomethyl*)*pyrazine* **III**. 2,3,5,6-Tetrakis(bromomethyl)pyrazine **II** (33 mmol, 15 g), sodium azide (134 mmol, 8.7 g; purum, Fluka) and absolute methanol (200 cm^3) were placed under nitrogen in a three-necked flask. The mixture was warmed to 50 °C under a slight nitrogen flow. The reaction was monitored by thin-layer chromatography. When it was complete, the solvent was carefully evaporated under reduced pressure, but not to dryness. The brownish paste was suspended in ether and the undissolved sodium bromide extracted with water. The ether phase was then collected and dried over anhydrous calcium sulfate. The ether was evaporated until the azido compound began to crystallize. It was then left to cool overnight. The crude compound was filtered off and recrystallized from methanol. Yield 8.2 g (82%) (Found: C, 32.10; H, 2.80; N, 65.70. Calc. for $C_8H_8N_{14}$: C, 32.00; H, 2.70; N, 65.30%); ν_{max}(KBr disc) 2950, 2090, 1392, 1270 and 1260 cm^{-1}. NMR: ^1H (CCl_4, 200 MHz), δ 4.51 (s); ^{13}C ($CDCl_3$) δ 52.29 (t) and 149.01 (s). UV_{max}(methanol) 290 nm (ε = 120 90 dm^3 mol^{-1} cm^{-1}).

2,3,5,6-*Tetrakis*(*aminomethyl*)*pyrazine* (*tampyz*) *and its hydrochloride*. 2,3,5,6-Tetrakis(azidomethyl)pyrazine **III** (10 mmol, 3 g) was completely dissolved in absolute methanol (280

g) in a hydrogenation flask. A suspension of 0.3 g of 10% palladium on charcoal catalyst in methanol (20 g) was added. The mixture was stirred under reduced pressure [5 bar (5×10^5 Pa) hydrogen] for 24 h at room temperature. The catalyst was filtered off over Celite or a porous membrane filter to give a pale yellow filtrate containing the free amine. Upon adding a 10% methanolic HCl solution to the filtrate a pale pink precipitate was formed. The crude hydrochloride was filtered off immediately, washed with ethanol, dried with absolute ether and then left under high vacuum overnight. Yield 3.2 g (94%) (Found: C, 27.55; H, 6.00; Cl, 39.95; N, 23.95. Calc. for $C_8H_{20}Cl_4N_6{\cdot}0.5H_2O$: C, 27.35; H, 6.05; Cl, 40.40; N, 23.95%); ν_{max}(CsBr disc) 3000, 2400, 1590, 1482, 1190, 1095, and 1000 cm^{-1}. NMR (D_2O): ^1H (200 MHz), δ 4.57 (s) and 4.72 (s); ^{13}C, δ 52.29 (t) and 149.01 (s). UV_{max}(water) 270 nm (ε = 6900 dm^3 mol^{-1} cm^{-1}).

Preparation of Complexes.—$[\{Mn(tampyz)Cl_2{\cdot}2H_2O\}_\infty]$. The salt $[H_4tampyz]Cl_4$ (345 g) was dissolved in water (10 cm^3) then deprotonated by addition of 4 equivalents of LiOH. The compound $MnCl_2{\cdot}3.78H_2O$ (194 mg) was dissolved in water (10 cm^3) and added, while stirring, to the ligand solution. The reaction mixture was heated to 50 °C, stirred for 30 min, then allowed to cool to room temperature. Yellow crystals were formed on cooling. Yield 150 mg (42%), m.p. >211 °C (decomp.) (Found: C, 26.35; H, 5.35; Cl, 19.65; N, 23.00. Calc. for $C_8H_{20}Cl_2MnN_6O_2$: C, 26.85; H, 5.65; Cl, 19.80; N, 23.45%); ν_{max}(CsBr disc) 3400, 3290, 3240, 2900, 1639, 1575, 1420, 1345, 1180, 1110, 1000 and 560 cm^{-1}.

$[Cu_2(tampyz)Cl_2]Cl_2{\cdot}2.25H_2O$. The compound $Cu(O_3SC_6H_4Me\text{-}p)_2{\cdot}5H_2O$ was first obtained by dissolving an excess of CuO in a warm solution of toluene-*p*-sulfonic acid. The excess of CuO was filtered off and the solution cooled. Blue crystals were obtained. A 0.5 g (1.101 mmol) amount was dissolved in methanol (10 cm^3). To this solution was added $[H_4tampyz]Cl_4$ (0.4 g, 1.17 mmol) in water (5 cm^3). The reaction mixture became dark blue. The complex was precipitated on adding methanol. The blue powder was recrystallized from methanol–water (1:2). Yield 140 mg (54%), m.p. >290 °C (decomp.) (Found: C, 19.25; H, 3.35; Cl, 29.00; N, 16.85. Calc. for $C_8H_{20}Cl_4CuN_6O_{2.5}$: C. 18.85; H, 4.15; Cl, 27.80; N, 16.45%); ν_{max}(KBr disc) 3600–3300, 3280, 3235, 2920, 1580, 1565, 1461, 1420, 1200, 1110, 1009 and 574 cm^{-1}.

$[Cl_2Zn(tampyz)ZnCl_2]$. An aqueous 0.5 mol dm^{-3} solution (20 cm^3) of $ZnCl_2$ (10 mmol) was added dropwise to an aqueous 0.1 mol dm^{-3} solution (50 cm^3) of free tampyz (5 mmol) while stirring at r.t. After the addition of two thirds of the $ZnCl_2$ solution the complex began to crystallize. The white crystals were filtered off, washed with methanol then dried with ether in a stream of air. Yield 1.43 g (61%), m.p. >320 °C (decomp.) (Found: C, 20.55; H, 3.25; Cl, 30.20; N, 17.85. Calc. for $C_8H_{16}Cl_4N_6Zn_2$: C, 20.50; H, 3.45; Cl, 30.25; N, 17.95%); ν_{max}(KBr disc) 3280, 3240, 2910, 1590, 1417, 1195, 1095 and 1010 cm^{-1}.

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