

**Structure of  $[\text{Mn}(m\text{-XBP})\text{Cl}_2]_n$  [Where  $m\text{-XBP} = N,N'\text{-}m\text{-Phenylenedimethylenebis(pyridin-2-one)}$ ]: A Novel Framework Polymer in Which Dinuclear, Chloride-Bridged  $[\text{MnCl}_2\text{O}_2]_2$  Units Are Linked by  $m\text{-XBP}$  Ligands To Form 52-Membered Rings**

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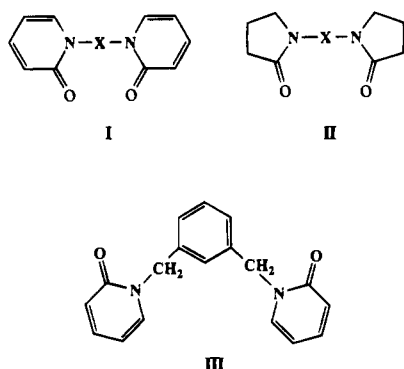
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**Introduction**

There is continuing interest in the development of new two- or three-dimensional framework complexes containing cavities or channels able to take up substrates, particularly if this can be achieved in a size- or shape-selective way. The ability to incorporate a range of metal ions as integral parts of such networks offers additional features, such as redox reactions between the metal centers and the occluded substrates, and also the potential for generating useful physical properties deriving from the assemblies of metal ions.

A number of fruitful directions have been followed for the construction of such networks.<sup>1</sup> Our own approach to the formation of framework complexes is the use of spacer-linked bis-pyridones (**I**) or bis-lactams (**II**),<sup>2</sup> or their thio analogues,<sup>3</sup>



to form complexes containing very large rings (up to 66-membered). These materials, which can form individual rings, chains of rings, sheets, or three-dimensional networks, have hitherto been based on the organic ligands linking sets of individual metal centers. We report here the synthesis and structural characterization of the complex  $[\text{Mn}_2(m\text{-XBP})_2\text{Cl}_4(\text{H}_2\text{O})]_n$  (**1**), where  $m\text{-XBP}$  is  $N,N'\text{-}m\text{-phenylenedimethylenebis(pyridin-2-one)}$  (**III**), which shows that this approach can be employed to link dinuclear units to form extended polymeric large-ring arrays.

- See, for example: Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1994**, *369*, 727; Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151; Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866; Soma, T.; Iwamoto, T. *Chem. Lett.* **1994**, 821; Efraty, A.; Feinstein, I.; Frolow, F. *Inorg. Chem.* **1982**, *21*, 485; and references therein.
- Doyle, G. A.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 207; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *Polyhedron* **1993**, *12*, 2933; Goodgame, D. M. L.; Hill, S. P. W.; Smith, A. M.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1994**, 859; Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1825.
- Atherton, Z.; Goodgame, D. M. L.; Katahira, D. A.; Menzer, S.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1423.

**Table 1.** Crystallographic Data for **1**

formula: $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{MnN}_2\text{O}_2 \cdot 0.5\text{H}_2\text{O}$	fw = 427.2
$a = 8.227(2) \text{ \AA}$	monoclinic
$b = 21.641(7) \text{ \AA}$	space group: $P2_1/a$ ,
$c = 10.180(3) \text{ \AA}$	$\lambda = 1.54178 \text{ \AA}$
$\beta = 104.08(2)^\circ$	$\mu(\text{Cu K}\alpha) = 9.060 \text{ mm}^{-1}$
$V = 1757.8(9) \text{ \AA}^3$	$F(000) = 872$
$Z = 4$	$T = 297 \text{ K}$
$\rho_{\text{calc}} = 1.614 \text{ g cm}^{-3}$	$R = 0.0434$ ( $R_w = 0.0448$ ) <sup>a</sup>

<sup>a</sup>  $R = \sum |F_o - F_c| / \sum |F_o|$ ;  $R_w = \sum [|F_o - F_c| w^{1/2}] / \sum [|F_o| w^{1/2}]$ , where  $w^{-1} = [\sigma^2(F_o) + g(F_o^2)]$  and  $g = 0.0005$ .

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for **1**

	x	y	z	$U(\text{eq})^a$
Mn(1)	1707(1)	9381(1)	90(1)	49(1)
Cl(1)	3605(2)	9512(1)	2280(1)	74(1)
Cl(2)	1201(2)	10576(1)	-409(1)	54(1)
O(1)	1743(4)	8382(1)	30(3)	47(1)
O(2)	1823(4)	9296(1)	-1936(3)	50(1)
C(10)	1380(5)	7962(2)	763(4)	39(1)
C(11)	770(6)	8059(2)	1931(4)	49(2)
C(12)	355(6)	7577(3)	2643(4)	57(2)
C(13)	537(6)	6975(2)	2255(4)	57(2)
C(14)	1147(5)	6873(2)	1152(4)	50(2)
N(15)	1573(4)	7353(2)	433(3)	35(1)
C(16)	2224(5)	7210(2)	-768(4)	42(2)
C(20)	828(6)	9276(2)	-3079(4)	40(2)
C(21)	-949(6)	9257(2)	-3335(5)	51(2)
C(22)	-1928(6)	9235(2)	-4615(5)	53(2)
C(23)	-1191(6)	9230(2)	-5728(5)	49(2)
C(24)	504(6)	9245(2)	-5486(4)	41(2)
N(25)	1485(4)	9254(1)	-4192(3)	36(1)
C(26)	3332(5)	9233(2)	-3970(4)	40(1)
C(27)	4002(5)	8593(2)	-3573(4)	34(1)
C(28)	3386(5)	8092(2)	-4389(4)	43(2)
C(29)	3955(5)	7500(2)	-4020(4)	45(2)
C(30)	5178(5)	7403(2)	-2854(4)	38(1)
C(31)	5864(5)	7895(2)	-2024(4)	35(1)
C(32)	5246(5)	8490(2)	-2392(4)	35(1)
O(3)	4634(8)	9630(3)	-83(7)	72(3) <sup>b</sup>

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup> sof  $[O(3)] = 0.5$ .

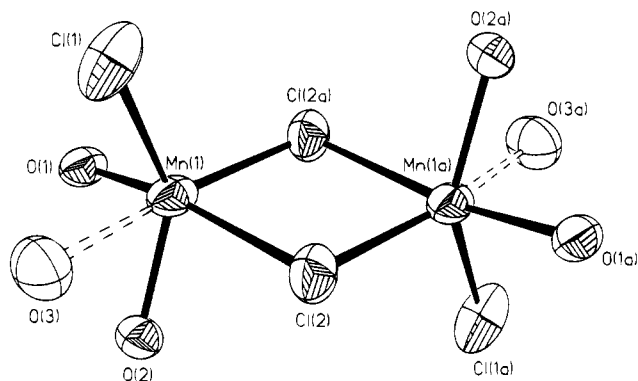
**Experimental Section**

**Preparation of  $[\text{Mn}_2(m\text{-XBP})_2\text{Cl}_4(\text{H}_2\text{O})]_n$  (**1**).** A solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.2 mmol) in a mixture of acetonitrile (2 mL) and methanol (1 mL) was added to a solution of  $m\text{-XBP}$  (0.2 mmol) in acetonitrile (3 mL). Within 30 min colorless crystals of **1** began to form, and these were collected, air-dried (69% yield), and characterized initially by elemental analysis and also by single crystal X-ray diffraction analysis. Anal. Calcd for  $\text{C}_{36}\text{H}_{34}\text{Cl}_4\text{Mn}_2\text{N}_4\text{O}_5$ : C, 50.6; H, 3.9; N, 6.7. Found: C, 50.8; H, 4.0; N, 6.6.

**Crystal Structure Determination of **1**.** Colorless thin plates were obtained from the mixed acetonitrile/methanol solvent system as described above and a crystal of approximate dimensions  $0.62 \times 0.14 \times 0.032 \text{ mm}$  was used for the diffraction study. Crystallographic data are summarized in Table 1. Intensity data were collected in the  $\omega$  scan mode on a Siemens P4RA/PC diffractometer using Cu K $\alpha$  radiation to a maximum  $2\theta$  value of  $116^\circ$ . The structure was solved by the heavy atom method and the non-hydrogen atoms refined anisotropically. H atoms for the organic ligand were included in calculated positions, assigned isotropic thermal parameters,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and allowed to ride on their parent carbons. The protons of the partial weight coordinated water molecule were not located. Computations (Siemens SHELXTL PLUS PC version) were by the full-matrix least squares method, using absorption corrected data (min. and max. transmission factors of 0.341 and 0.749), to  $R(R_w) = 0.0434$  (0.0448) for 1939 independent observed reflections [ $F > 4\sigma(F)$ ]. The final atomic coordinates are given in Table 2, and selected bond lengths and angles in Table 3.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **1**

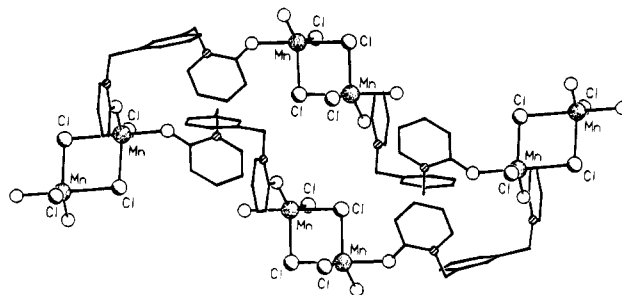
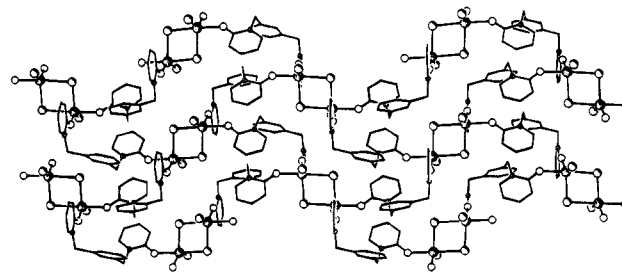
Mn(1)—Cl(1)	2.407 (2)	Mn(1)—Cl(2)	2.647 (2)
Mn(1)—O(1)	2.163 (3)	Mn(1)—O(2)	2.096 (3)
Mn(1)—O(3)	2.515 (7)	Mn(1)—Cl(2A)	2.493 (2)
Cl(2)—Mn(1A)	2.493 (2)		
Cl(1)—Mn(1)—Cl(2)	95.7(1)	Cl(1)—Mn(1)—O(1)	97.7(1)
Cl(2)—Mn(1)—O(1)	166.6(1)	Cl(1)—Mn(1)—O(2)	138.3(1)
Cl(2)—Mn(1)—O(2)	86.5(1)	O(1)—Mn(1)—O(2)	83.1(1)
Cl(1)—Mn(1)—O(3)	67.9(2)	Cl(2)—Mn(1)—O(3)	83.5(2)
O(1)—Mn(1)—O(3)	101.1(2)	O(2)—Mn(1)—O(3)	71.1(2)
Cl(1)—Mn(1)—Cl(2A)	107.6(1)	Cl(2)—Mn(1)—Cl(2A)	83.0(1)
O(1)—Mn(1)—Cl(2A)	93.5(1)	O(2)—Mn(1)—Cl(2A)	114.0(1)
O(3)—Mn(1)—Cl(2A)	165.1(2)	Mn(1)—Cl(2)—Mn(1A)	97.0(1)
Mn(1)—O(1)—C(10)	134.4(3)	Mn(1)—O(2)—C(20)	138.0(3)

**Figure 1.** The dinuclear Mn(II) unit present in the structure of **1** (with 50% probability thermal ellipsoids).

## Results and Discussion

The X-ray study shows that **1** is formulated as  $[\text{Mn}_2(m\text{-XBP})_2\text{Cl}_4(\text{H}_2\text{O})]_n$ . In **1** pairs of manganese atoms are linked by two Cl bridges (Figure 1). The geometry at each manganese center is best viewed as distorted trigonal bipyramidal with each Mn atom also being bonded to two oxygen atoms, one from each of two different *m*-XBP ligands, and a further chloride ion. The two non-bridging chloride ions in the dinuclear unit are *trans*-disposed, as in, for example,  $[\text{Mn}(2,2'\text{-biquinoline})\text{Cl}_2]_2$  (**2**).<sup>4</sup> The  $\text{Mn}_2\text{Cl}_2$  bridge unit in **1** is planar, with *trans*-annular Mn—Mn and Cl—Cl distances of 3.85 and 3.41 Å, respectively. It is, however, asymmetric with Mn—Cl bond lengths of 2.493(2) and 2.647(2) Å in contrast to the essentially symmetrical arrangement [2.539(1) and 2.543(1) Å] found<sup>4</sup> for **2**. The geometry about each Mn atom in **1** is distorted toward square pyramidal by an additional, weaker interaction with the oxygen atom of a half-weight occupancy included water molecule which approaches *trans*- to the bridging Mn(1)—Cl(2a) bond. The Mn—O(3) distance, 2.515(7) Å, is very much longer than the usual Mn—O bond length (2.15–2.25 Å) found for Mn(II)—aqua ligand bonds.

(4) Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 162.

**Figure 2.** The 52-membered ring which forms the repeat unit in the polymeric structure of **1**.**Figure 3.** Part of one of the sheets of contiguous 52-membered rings in the structure of **1**.

The novel feature in the structure of **1**, however, is the way the *m*-XBP ligands link sets of dinuclear Mn units to produce 52-membered rings, one of which is illustrated in Figure 2. Within the macrocycle the bridging *m*-XBP ligands all have the same conformation, but the connectivities at the manganese centers are of two types. Each ring contains six Mn atoms, four from two complete dinuclear units and one each from a further pair. The shortest transannular Mn···Mn contact is 6.1 Å. Each macrocyclic ring is self-filling, with one of the pyridone rings of each pair of adjacent *m*-XBP ligands aligned parallel and overlapping (the mean interplanar separation is 3.36 Å and the ring centroid—ring centroid distance is 4.12 Å).

The macrocycles are fused, forming continuous sheets that extend in the crystallographic *a* and *b* directions (Figure 3).

The structure reported here indicates what may form the basis for a more general strategy in which sets of preformed polynuclear units can be joined into large polymeric arrays by appropriately designed 'linking' molecules, thereby permitting exploration of features such as potential electron transport between the polynuclear units and magnetic cooperativity.

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**Supplementary Material Available:** Tables giving details of the crystallographic data collection, a full set of bond lengths and angles, anisotropic displacement coefficients, H-atom coordinates, and displacement coefficients for **1** (7 pages). Ordering information is given on any current masthead page.