Framework Coordination Chemistry; Generalised Entry into a New Class of Supramolecular Compounds exemplified by the Structures of $[Mn_2(ebpy)_3(NO_3)_4]_n$ [where ebpy = *N,N'*-ethylenebis(2-pyridone)] and $[Er_2(ebpyrr)_3(NO_3)_6]_n$ [where ebpyrr = *N,N'*-ethylenebis(2-pyrrolidone)]

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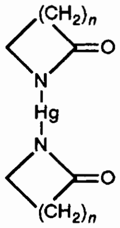
The ethylene-bridged bis(2-pyridone) ligand *N,N'*-ethylenebis(2-pyridone) and its bis(2-pyrrolidone) analogue react with manganese(II) nitrate and erbium(III) nitrate to form polymers containing 36-membered or 54-membered metallomacrocyclic rings, respectively; the 36-membered rings are linked to form a chain polymer and the 54-membered form contiguous two-dimensional sheets.

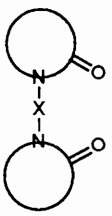
Some dramatic developments in the design of extended molecular systems incorporating metal centres have resulted from a constructive use of the conformational and bonding preferences of carefully selected organic ligands.[1] We have shown[2] that the mercury(II) complexes of stoichiometry HgL_2 (depicted schematically in **I**) formed by lactams and related ligands readily bind a wide range of other metal ions to the exocyclic oxygen atoms. Moreover, the resulting Hg/M complexes display a diversity of chain, sheet, or three-dimensional network arrays involving large metallomacrocycle rings. As well as the variety of ring sizes (8- to 80-membered) that have been obtained, the distinctive feature of this family of polymeric compounds is the incorporation of the metal ions *as integral parts of the ring framework*, as distinct from binding within an organic macrocycle as in *e.g.* crown ethers and cryptands.

Despite the diversity of this group of what might be termed 'framework coordination compounds', the involvement hitherto of the mercury atom as a key building block places chemical limitations on further synthetic developments and raises toxicological implications for their applications. Consequently, we have recently addressed the question as to whether the presence of the linear N–Hg–N bridge is a *requirement* for the generation of these extended frameworks, or whether a wider range of bridges X in ligands such as **II** may be equally effective. To this end we have prepared, *inter alia*, the ethylene-bridged bis(2-pyridone) **III**[3] (ebpy) and its bis(2-pyrrolidone) analogue **IV**[4] (ebpyrr) and investigated their potential as linking units in the formation of extended arrays.

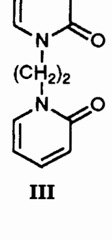
This approach has proved to be fully justified and we report here, as examples, the structures of: (*i*) the complex $[Mn_2(ebpy)_3(NO_3)_4]_n$ **1** formed by treating hydrated manganese(II) nitrate with **III**, and (*ii*) the complex $[Er_2(ebpyrr)_3(NO_3)_6]_n$ obtained from the reaction between hydrated erbium(III) nitrate and **IV**. Both complexes were readily obtained as crystalline materials by mixing the appropriate metal salts and the respective ligands in acetonitrile.†



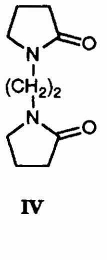
I



II



III



IV

X-Ray analysis of **1** reveals the stoichiometry to be $[Mn(ebpy)_{1.5}(NO_3)_2]$.‡ The manganese is six-coordinate,

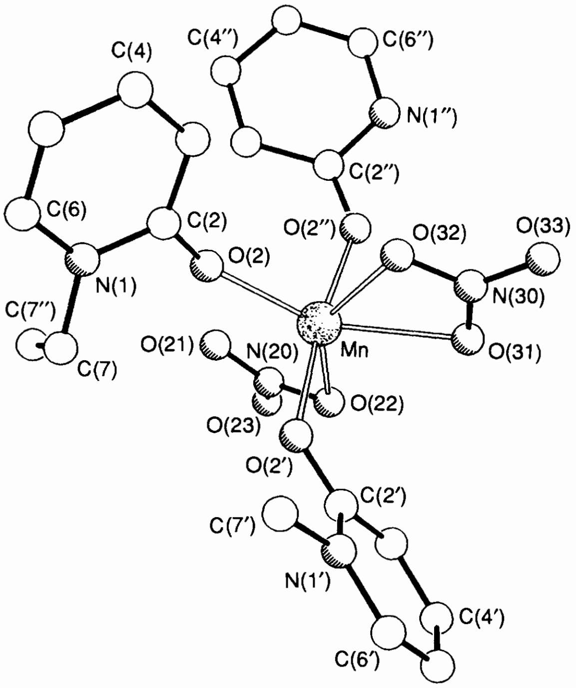


Fig. 1 Coordination environment about the manganese atom in **1** with selected bond lengths (Å): Mn–O(2) 2.076(3), Mn–O(2′) 2.145(4), Mn-O(2″) 2.130(4), Mn–O(22) 2.227(4), Mn–O(31) 2.351(3), Mn–O(32) 2.294(4)

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† Satisfactory microanalytical results were obtained for all the compounds reported here.

‡ *Crystal data* for **1**: $C_{18}H_{18}N_5O_9Mn$, triclinic, space group $P\bar{1}$, a = 8.027(2), b = 8.151(3), c = 16.483(6) Å, α = 96.78(2), β = 92.07(2), γ = 101.89(2)°, U = 1046 Å^3, Z = 2, M = 503.3, D_c = 1.60 g cm^{-3}, μ(Mo-Kα) = 6.9 cm^{-1}.

For **2**: $C_{15}H_{24}ErN_6O_{12}\cdot 1.5$ MeCN, monoclinic, space group $P2_1/c$, a = 7.911(2), b = 15.525(5), c = 23.135(9) Å, β = 92.38(3)°, U = 2839 Å^3, Z = 4, M = 709.1, D_c = 1.66 g cm^{-3}, μ(Cu-Kα) = 61 cm^{-1}.

Data for **1** were measured on a Siemens P4/PC diffractometer with graphite monochromated Mo-Kα radiation and those for **2** on a Siemens P3/PC diffractometer with graphite monochromated Cu-Kα radiation using, in both cases, ω-scans. Both structures were solved by the heavy-atom method. **1** was refined anisotropically to give R = 0.039, R_w = 0.039 for 2016 independent observed reflections [$|F_0|>4\sigma(|F_0|)$], $2\theta \leqslant 45°$. In **2** the major occupancy non-hydrogen atoms were refined anisotropically, the minor occupancy disordered solvent atoms isotropically to give R = 0.050, R_w = 0.055 for 2901 independent observed reflections [$|F_0|>4\sigma(|F_0|)$], $2\theta \leqslant 110°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

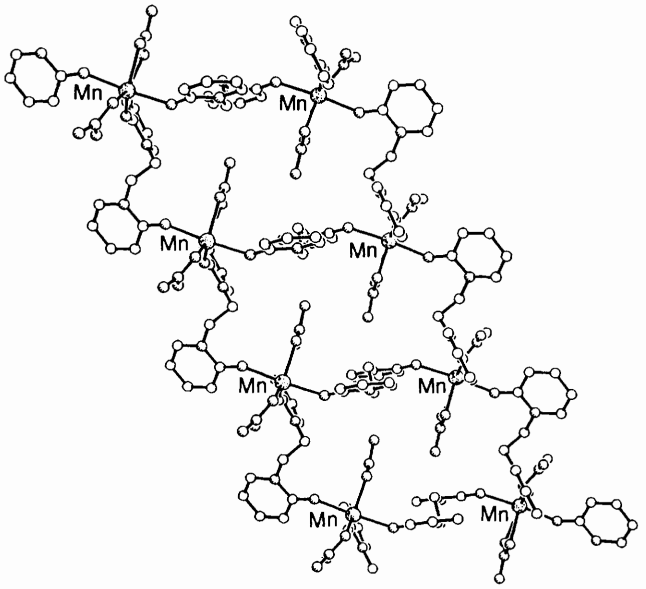

Fig. 2 Part of one of the chains of linked 36-membered macrocycles in the structure of **1**

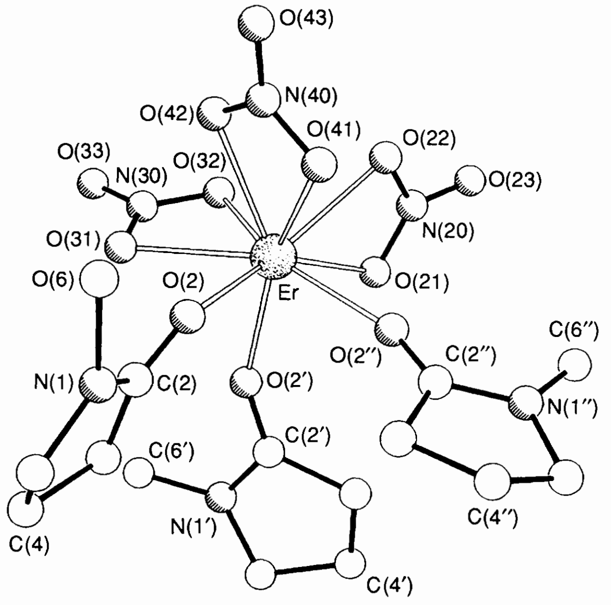

Fig. 3 Nine-coordinate arrangement about the erbium atom in **2**

being bonded to the oxygen atoms of three different ebpy ligands, two oxygen atoms from a bidentate nitrate and one from a monodentate nitrate (Fig. 1). If one considers the bidentate nitrate group as occupying a single coordination site the geometry can alternatively be described as trigonal bipyramidal. The axial oxygen atoms O(2′) and O(2″) subtend an angle of 172.7(1)°, and the equatorial oxygens O(2) and O(22) an angle of 126.7(1)°. The N(30)-Mn-O(2) and N(30)-Mn-O(22) angles are 115.3(1) and 118.0(1)°, respectively. The Mn-O distances are in the range 2.076(3) [for O(2)]-2.351(3) Å [for O(31)].

Adjacent manganese centres are linked *via* the ebpy ligands in two essentially orthogonal directions (Fig. 2). In one instance the $-CH_2-CH_2-$ bridge geometry is *anti-* whereas in the other it is *gauche-* [$N-CH_2-CH_2-N$ torsion angle 78.7(5)°]. The resulting structure comprises 36-membered macrocyclic rings, each containing four Mn atoms, linked by one edge to form a chain of macrocycles extending along the crystallographic *b* direction. There are marked face-to-face and edge-to-face π-π stacking interactions between the pyridyl rings of adjacent chains in both the *a* and *c* directions.

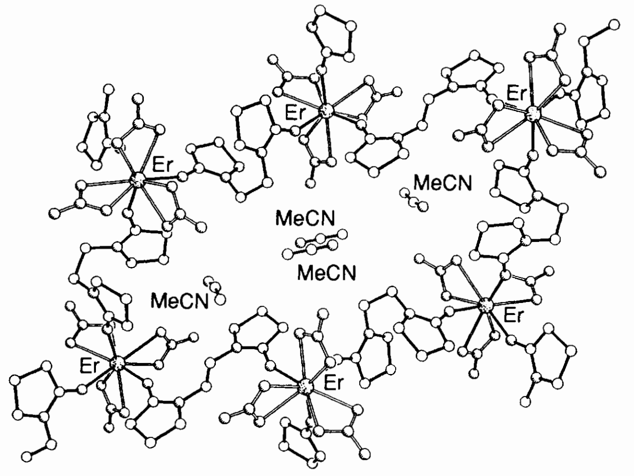

Fig. 4 The 54-membered macrocyclic ring in the structure of **2** showing the included acetonitrile molecules

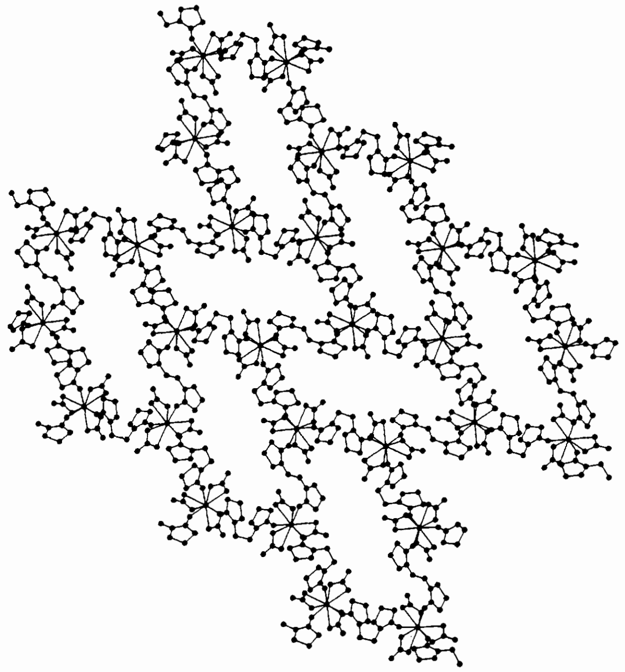

Fig. 5 The 'tyre-tread' pattern formed by edge-to-edge linking of the macrocycles in the sheet of **2**; (solvent molecules not shown)

The X-ray structure of **2**‡ shows the complex to have the stoichiometry (excluding trapped MeCN solvent molecules) $[Er(ebpyrr)_{1.5}(NO_3)_3]$ (Fig. 3). The erbium atom is nine-coordinate, being bonded to three different ebpyrr ligands and to three bidentate nitrate groups. The Er-O distances fall into two distinct groups, with those to the ebpyrr oxygen atoms in the range 2.246(6)-2.273(6) Å, and those to the nitrate groups in the range 2.398(7)-2.489(7) Å.

As in the case of **1**, the organic ligands link between adjacent metal centres to form a macrocyclic array. In **2**, however, both the macrocycle ring size and the nature of the three-dimensional array are very different. In this case 54-membered rings are formed, containing six erbium atoms (Fig. 4). Here again both *gauche-* and *anti-* $N-CH_2-CH_2-N$ bridging geometries are observed. However, whereas in **1** there are equal numbers of each type of bridge, in **2** they are in a ratio of two *gauche-* to one *anti-*.

The macrocyclic rings are not self-filling and they accommodate acetonitrile solvent molecules. Adjacent rings are fused in a 'parquet-like' pattern to form a two-dimensional sheet (Fig. 5) that extends in the crystallographic *b* and *c* directions. In the *a* direction the sheets stack in register so that continuous channels are formed, permitting solvent molecule diffusion through the lattice.

These two structural results illustrate both the versatility and potential of this general type of organic ligand, **II**, to form unusual framework coordination compounds. We are currently exploring the effects of altering such factors as: (*i*) the lengths and types of the bridging units X in **II**, (*ii*) the nature of the terminal ring systems (*e.g.* sizes of lactam rings and substitution on pyridone rings), (*iii*) replacement of exocyclic oxygen by sulfur and (*iv*) in each case, variation in metal type(s) and accompanying anions.

We thank the SERC for a studentship (to S.P.W.H) and for the diffractometer.

Received, 4th November 1992; Com. 2/05904E

References

1 *e.g.* J-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
2 L. H. Carrad, D. M. L. Goodgame and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 175, and references cited therein.
3 C. Alberti, *Gazz. Chim. Ital.*, 1956, **86**, 1181.
4 W. Reppe, *Liebigs Ann. Chem.*, 1955, **596**, 1.