Polynuclear Complexes of Macrocyclic Oxamide with Co-ligands: Syntheses, Crystal Structures and Magnetic Properties

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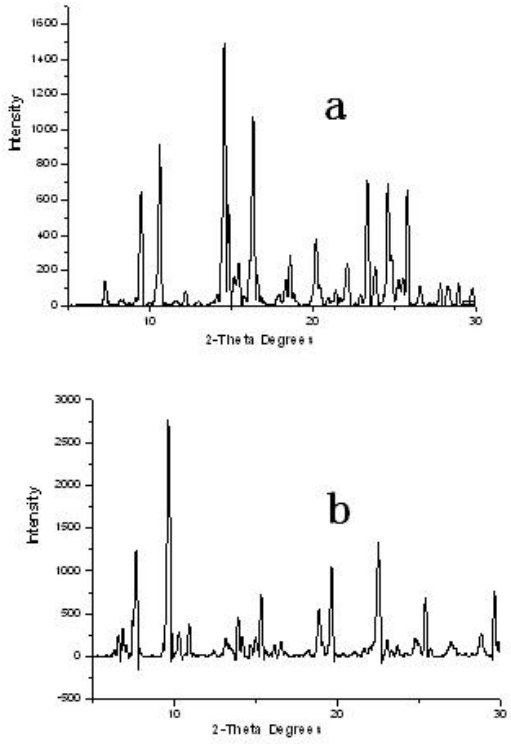

Fig.1 XRPD spectra of the title complex 1 (a) and complex 3 (b)

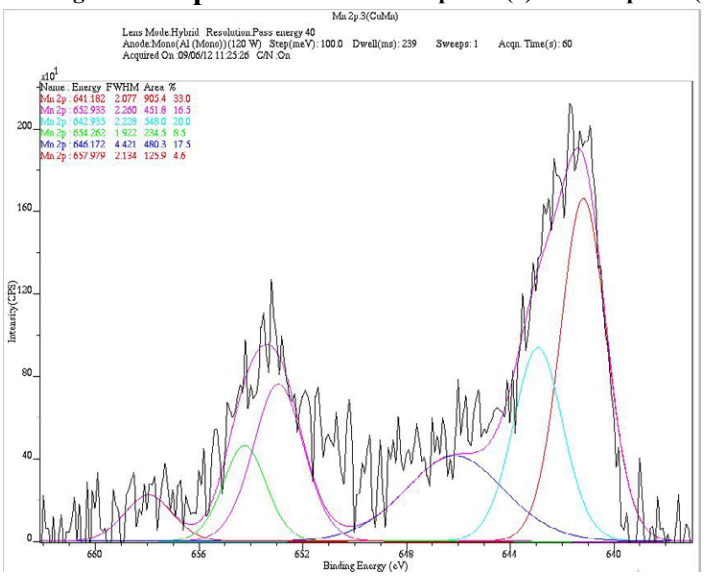

Fig.2 XPS spectrum of the title complex 1

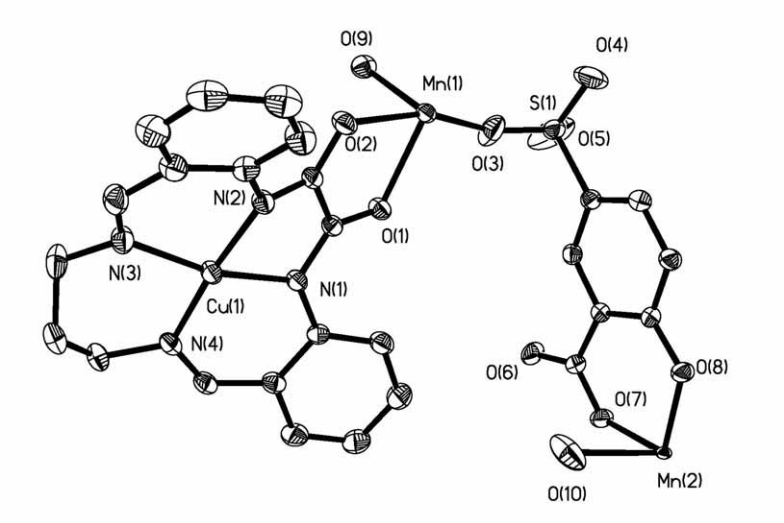

Fig. 3 ORTEP drawing of the complex 1(displacement ellipsoids are drawn at the 30% probability level)

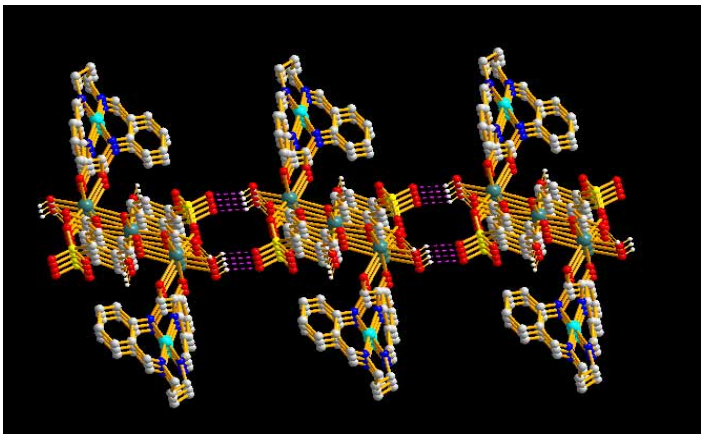

Fig.4 View of the self-assembly 2D porous superamolecular architecture through hydrogen bonding interactions for the complex 1

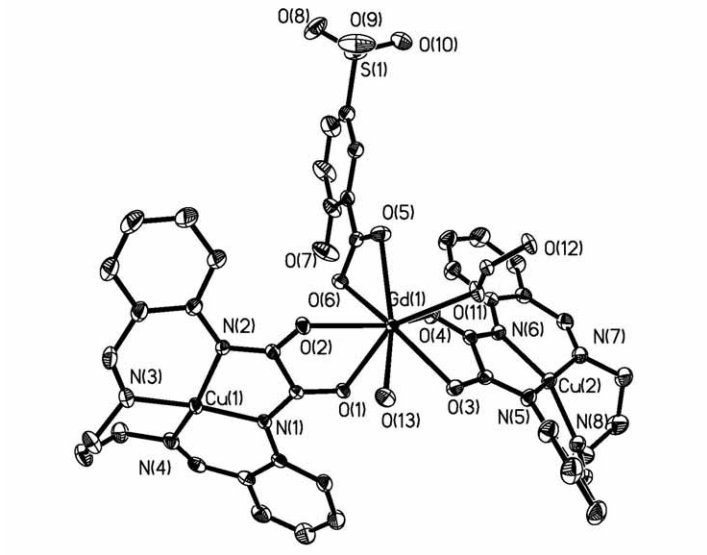

Fig. 5 ORTEP drawing of the complex 2(displacement ellipsoids are drawn at the 30% probability level)

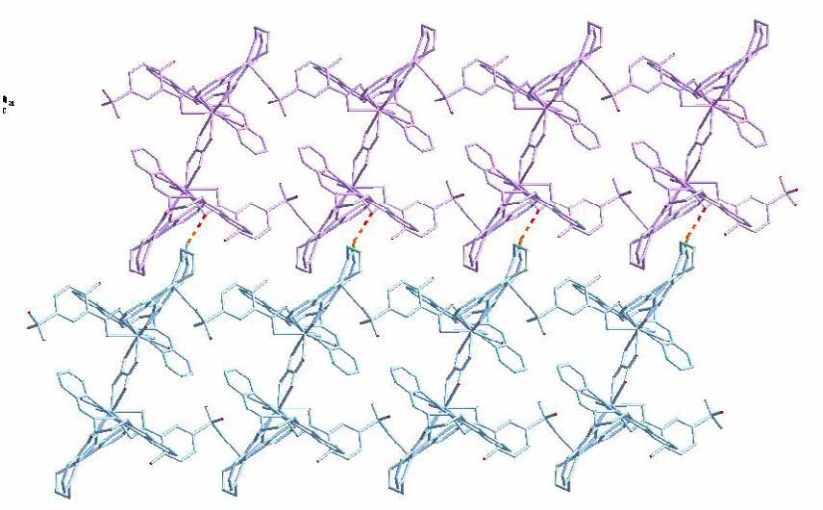

Fig.6 View of the self-assembly 2-D superamolecular architecture through hydrogen bonding interactions for the complex 2.

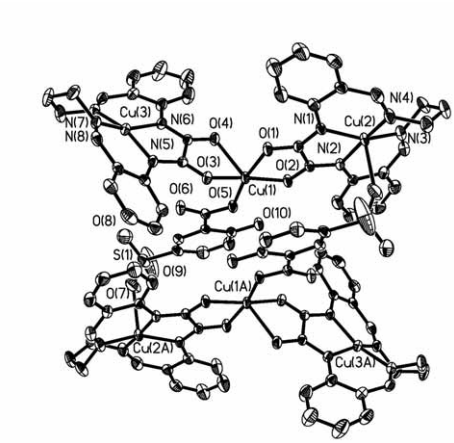

Fig. 7 ORTEP drawing of the complex 2(displacement ellipsoids are drawn at the 30% probability level)

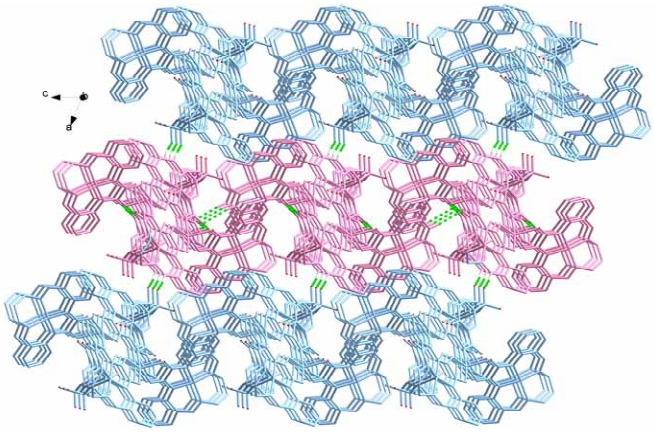

Fig. 8 View of the self-assembly 3-D superamolecular architecture through hydrogen bonding and π-π interactions for the complex 3.

Bond valence sum calculations of manganese atoms in complex1 is fellowing:

The oxidation state Z_j $\quad Z_j = \Sigma_j S_{ij}$

The valences of the individual bonds S_{ij}, $\quad S_{ij} = \exp[(R_o - R_{ij})/b]$

Table 1. Summary of distances and valences of the individual bonds

atom	Mni-Oj	distances Å	S_{ij}	Oxidation state Z_j
Mn1	Mn1-O3	2.087(4)	0.448	2.068
	Mn1-O9	2.169(3)	0.359	
	Mn1-O8#1	2.197(3)	0.333	
	Mn1-O2	2.201(3)	0.329	
	Mn1-O1	2.218(3)	0.315	
	Mn1-O7#2	2.256(3)	0.284	
Mn2	Mn2-O8#1	1.901(3)	0.741	3.304
	Mn2-O8#2	1.901(3)	0.741	
	Mn2-O7#1	1.920(3)	0.704	
	Mn2-O7#2	1.920(3)	0.704	
	Mn2-O10	2.372(8)	0.207	
	Mn2-O10#3	2.372(8)	0.207	

R_o = 1.79 for Mn-O; Symmetry transformations used to generate equivalent atoms: for **1**, #1 -x+1,-y+2,-z; #2 x-1,y,z; #3 -x,-y+2,-z

$$\chi_{Mn_3} = \frac{N\beta^2 g^2}{kT} \cdot \frac{A}{B} \quad (1)$$

$$A = 280 + 182\exp(-14J/kT) + 270\exp(-26J/kT) + 28\exp(-44J/kT) + 182\exp(-4J/kT)$$

$$+ 138\exp(-16J/kT) + 28\exp(-34J/kT) + 10\exp(-40J/kT) + 132\exp(2J/kT) + 120\exp(-18J/kT)$$
$$+ 10\exp(-32J/kT) + 2\exp(-36J/kT) + 38\exp(-20J/kT) + 2\exp(-30J/kT) + 10\exp(-22J/kT)$$

$$B = 15 + 13\exp(-14J/kT) + 44\exp(-26J/kT) + 7\exp(-44J/kT) + 13\exp(-4J/kT) + 18\exp(-16J/kT)$$
$$+ 7\exp(-34J/kT) + 5\exp(-40J/kT) + 11\exp(-2J/kT) + 3\exp(-30J/kT) + 18\exp(-18J/kT)$$

$$+ 6\exp(-32J/kT) + 3\exp(-36J/kT) + 12\exp(-20J/kT) + 5\exp(-22J/kT)$$

$$\chi_M = 2\chi_{Cu} + \chi_{Mn_3} \quad (2)$$