A self-assembled hexa-decanuclear 4 x [2x2] $Mn(II)_{16}$ square grid from a pyridazine bis–hydrazone ligand – synthesis, structure and magnetism

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Supplementary Material

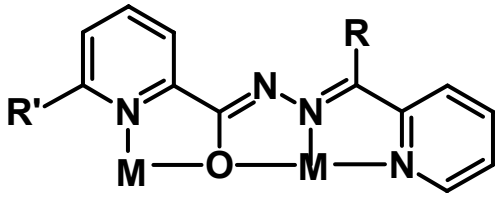
Synthesis of ligand L1.

Pyridine 2-carboxyldehyde (20.5 mmol) was added to a solution of pyradazine-dicarboxylic acid hydrazide (10 mmol) (prepared from the reaction of dimethyl 3,6-pyradazinedicarboxylate[S1,S2] with hydrazine (98%) in dry methanol), and the resulting mixture heated under reflux for 5 hours (at ~80°C). A white powder started to form while the reaction mixture was hot, which was filtered off after cooling, washed with dry methanol and Et_2O and dried under vacuum. Yield (>95%), m.pt. 275 °C, ^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.84 (s, 2H, H3, H3′), 8.76 (s, 2H, H4, H4′), 8.66 (d, 2H, H1, H2), 8.52 (d, 2H, H8, H8′), 8.04 (d, 2H, H5, H5′), 7.94 (dd, 2H, H7, H7′) and 7.46 ppm (dd, 2H, H6, H6′); IR/cm^{-1} (mull): 3313, 3286 (ν NH), 1700 (ν C=O), 1596 (ν C=N, imine), 1576 (ν C=N, arom), 1126, 917 (ν py); mass spectrum (M/z) (APCI): 375.35 $(M + H)^{+1}$; Elemental analysis calcd (%) for $C_{18}H_{14}N_8O_2$: C, 57.73; H, 3.74; N, 29.94; found: C, 57.31; H, 3.88; N, 30.05.

References

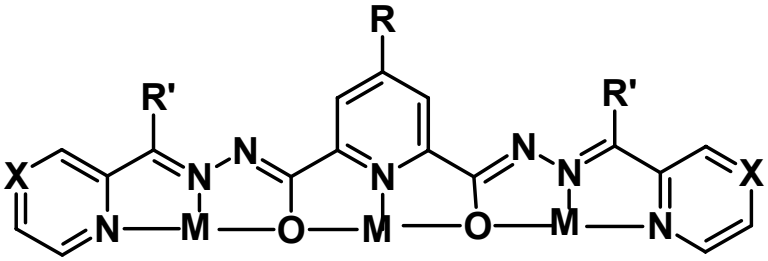
S1. G.H. Spencer, Jr., P.C. Cross, K.B. Wiberg, J. Chem. Phys., 1961, **35**, 1944.
S2. S. Sueur, M. Lagrenee, F. Abraham, J. Heterocyclic Chem., 1987, **24**, 1285.

[2x2]



poap (R=NH2,R'=H)
pomp (R=CH3,R'=H)
mpoap (R=NH_2, R'=CH_3)

[3x3]



[R'=NH2] 2poap (R=H,X=CH),2poapz (R=H,X=N)
Cl2poap (R=Cl,X=CH),S2poap (R=S^-,X=CH)
SEt2poap (R=SEt,X=CH), SMe2poap (R=SMe,X=CH);
[R'=CH3] 2pomp (R=H,X=CH),Cl2pomp(R=Cl,X=CH);
[R'=Ph] Cl2popp (R=Cl,X=CH)

[Cu_{36}]

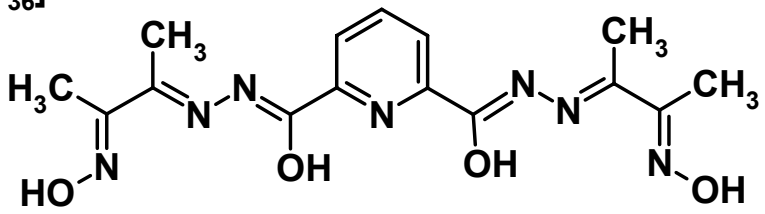


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Fig. S1. Ditopic and tritopic picolinic hydrazone ligands.