

Hexa-, hepta- and dodeca-nuclear nickel(II) complexes of three Schiff-base ligands derived from 1,4-diformyl-2,3-dihydroxybenzene

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Electronic Supporting Information

Crystallographic details:

$[\text{Ni}^{\text{II}}_7(\text{H}_2\text{L}^2)_4(\text{OAc})_6(\text{MeOH})_2] \cdot 7\text{MeOH} \cdot 4\text{H}_2\text{O}$

Half of this cluster is in the asymmetric unit; the other half is generated by 2-fold rotation (Ni4 is on this axis). All non-H atoms were refined anisotropically except the two disordered 0.5 occupancy MeOH molecules (C150, O150, C160 O160). All hydrogen atoms were placed at calculated positions and rode on the attached atom except for those on oxygen atoms. All of the O-H hydrogen atoms were found from difference maps, the O-H distances improved (HIMP) if needed, then their coordinates fixed (AFIX 01).

$[\text{Ni}^{\text{II}}_6(\text{H}_2\text{L}^2)_2(\text{OAc})_6(\mu\text{OME})_2(\text{MeOH})_2] \cdot 0.5\text{MeOH} \cdot 0.5\text{H}_2\text{O} \cdot \text{Et}_2\text{O}$

This neutral Ni₆ cluster has no internal symmetry. Solvents of crystallisation include: 1 Et₂O, 1 terminal atom of which is disordered over 2 sites 0.5/0.5 C154/C155 (an attempt to model C153 split over 2 sites gave no improvement); two 0.25 occupancy methanol molecules; a half occupancy water molecule. All non-H atoms were refined anisotropically except the 0.25 occupancy MeOH atoms. All hydrogen atoms were placed at calculated positions and rode on the attached atom except for the O-H hydrogen atoms on the propanolamine arms, the 0.25 occupancy MeOH molecules and the 0.5 occupancy H₂O: the hydrogen atoms on the propanolamine arms were located from difference maps and their coordinates fixed (AFIX 01); the hydrogen atoms on the MeOH and H₂O were either located from difference maps or inserted at positions suggested by SHELXL and their coordinates fixed (AFIX 01). One reflection, 0 0 1, was OMITed as it was behind the beamstop.

$[\text{Ni}_{12}(\text{L}^3)_6(\text{MeOH})_{6.5}(\text{H}_2\text{O})_{2.5}] \cdot \text{solvent}$

A very poor dataset, but better crystals were not obtained despite many attempts. The connectivity and identity of the complex is, however, clear. The neutral cluster has no internal symmetry so the asymmetric unit comprises the entire Ni₁₂ cluster, specifically, $[\text{Ni}_{12}(\text{L}^3)_6(\text{MeOH})_{6.5}(\text{H}_2\text{O})_{3.5}] \cdot \text{solvent}$. The data was cut back to 2θ(max) of 45° and three reflections behind the beamstop were OMITed (0 0 1; 1 1 0; 1 0 0). The 12 Ni atoms were refined anisotropically; all other atoms isotropically. The hydrogen atoms were inserted at calculated positions and rode on the attached atom, except for those on

the H₂O and MeOH molecules which were not inserted. The SQUEEZE³⁰ routine of the PLATON suite was applied: 2290 Å³ of potential solvent accessible void volume and 586 electrons/cell.

Magnetic properties:

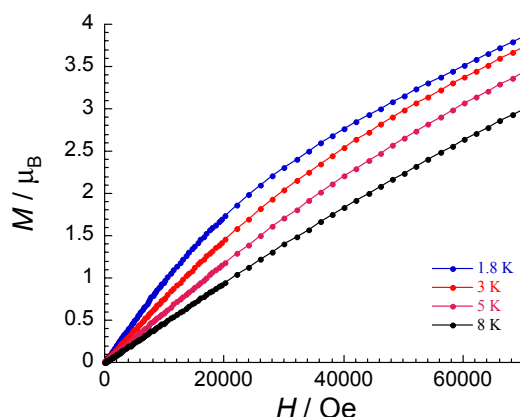


Figure S1: Field dependence of magnetization of 2·5H₂O at 1.8 K (blue line), 3 K (red line), 5 K (pink line) and 8 K (black line).

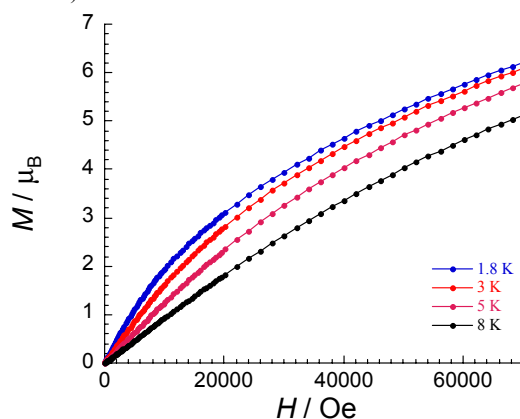


Figure S2: Field dependence of magnetization of 3·5H₂O at 1.8 K (blue line), 3 K (red line), 5 K (pink line) and 8 K (black line).

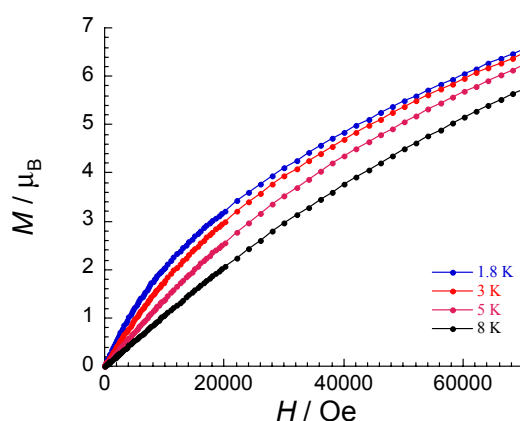


Figure S3: Field dependence of magnetization of 4·4H₂O at 1.8 K (blue line), 3 K (red line), 5 K (pink line) and 8 K (black line).