

A tetranickel(II) macrocyclic complex incorporating five different bridging groups†

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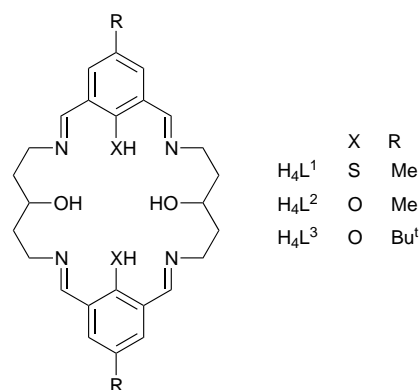
The synthesis and crystal structure of the tetranickel(II) complex $[\text{Ni}_4(\text{L}^1)(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})]$ is reported, where H_4L^1 is a macrocyclic ligand incorporating thiophenolate, alkoxo and imine donors; the faces of the tetranickel array are differentiated and two of the nickel ions share three monatomic bridges (S,O,O).

As part of a programme to synthesise and investigate polynuclear arrays, we have characterised tetranuclear macrocyclic complexes of ligands H_4L^2 and H_4L^3 containing phenoxo and alkoxo bridging groups.¹ The properties of these arrays can, in principle, be modified by varying the donor groups, size of the macrocycle, nature of the metal ions *etc.* In this way the assemblies can be tuned to give control over various aspects of metal–metal interactions, redox properties and exogenous ligand binding. Here, we report the synthesis and characterisation of a neutral tetranickel(II) complex of H_4L^1 , a new ligand in which the phenol donors are replaced by the larger and softer thiophenol group.

The tetranickel(II) complex was prepared by a template route. Solid $\text{Ni}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O}$ was added to 2,6-diformyl-4-methylthiophenol^{2,3} in refluxing isopropyl alcohol under an inert atmosphere, followed by dropwise addition of 1,5-diamino-3-hydroxypentane⁴ in methanol–isopropyl alcohol solution. After refluxing for 20 h, the volume of the solution was reduced, the brown powder filtered off, and recrystallised from chloroform–dichloromethane containing a small amount of methanol (yield *ca.* 30%). Microanalytical data were consistent with the formulation $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})] \cdot 1.5 \text{H}_2\text{O}$. The secondary ion mass spectrum confirms the presence of fragments containing the $[\text{Ni}_4\text{L}^1(\text{OH})]^{3+}$ core. Clusters centred at: m/z 924 (15), 888 (20), 829 (100, base peak) and 770 (35) are assigned to $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_2(\text{H}_2\text{O})_2]^+$, $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_2]^+$, $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)]^+$ and $[\text{Ni}_4\text{L}^1(\text{OH})]^+$, respectively. Dark brown crystals of the methanol solvate, $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})] \cdot \text{MeOH}$, suitable for X-ray diffraction studies[§] were obtained by slow diffusion of diethyl ether into a dmf–methanol solution of the complex. The asymmetric unit contains one $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})] \cdot \text{MeOH}$ complex (Fig. 1). The four coplanar nickel(II) ions

are each coordinated to one thiophenolate sulfur, one alkoxy oxygen and one imine from the macrocycle and to a central μ_4 -hydroxo group, O(3). Six-coordination is completed by three bridging acetate ligands and one acetic acid group. The macrocyclic donors are *fac* for Ni(1) and Ni(4) but *mer* for Ni(2) and Ni(3). The coordinated acetic acid molecule forms a one-atom bridge between Ni(2) and Ni(3) and is also quite strongly hydrogen-bonded to a macrocyclic alkoxy donor [O(62)⋯O(2) 2.516(7) Å]. The description of this bond as $\text{RCO}_2\text{H} \cdots \text{OR}'$ rather than $\text{RCO}_2 \cdots \text{HOR}'$ is made on the basis of an electron density peak 1.14 Å from O(62) and 1.46 Å from O(2) which is assigned to the carboxylic acid hydrogen. Similar coordinated acetic acid molecules are found in the related phenolate complex,⁵ $[\text{Ni}_4\text{L}^3(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$. The three acetate ligands act as conventional *syn-syn* three-atom bridges between pairs of nickel ions on the same side of the macrocyclic ring; one of the acetate ions is hydrogen-bonded to the solvent methanol [O(41)⋯O(71), 2.806(7) Å]. The oxygen atom of the central μ_4 -hydroxo group projects 0.581(4) Å from the plane of the four nickel ions into the cavity bounded by the three acetate ligands (Fig. 2) and is prevented from interacting with any other species. A sharp peak at 3598 cm^{-1} in the infrared spectrum is consistent with this environment and assigned to the ν_{OH} vibration.⁶ The hydroxo hydrogen atom was located unambiguously from difference Fourier maps.

Each nickel ion is linked to the next *via* three bridging groups. For Ni(1)⋯Ni(2) and Ni(3)⋯Ni(4) these are one alkoxy, one hydroxo, one 1,3-acetato group; for Ni(1)⋯Ni(4), thiophenolato, hydroxo and 1,3-acetato, while Ni(2) and Ni(3) are linked by three single-atom bridges [S(2), O(3) and O(61)], so that they share one octahedral face (Fig. 3). This geometry is not unusual where all three bridges are light atoms and there are several examples where all three are sulfur donors.⁷ However, the only other example containing three mixed sulfur/light atom bridges is at the active site of the [NiFe] hydrogenase from *Desulfovibrio gigas* where two cysteine thiolates and a putative oxo species form three monatomic bridges between the Ni and Fe centres.⁸ While the complex described in this paper is not



Scheme 1

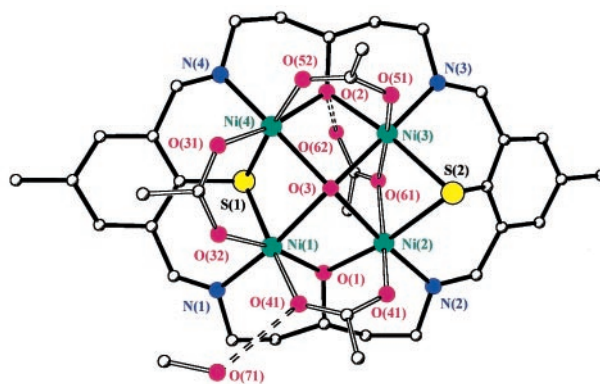


Fig. 1 Perspective view of $[\text{Ni}_4\text{L}^1(\text{OH})(\text{MeCO}_2)_3(\text{MeCO}_2\text{H})] \cdot \text{MeOH}$, hydrogen atoms are omitted. Selected interatomic distances (Å): Ni(1)–Ni(2) 2.998(1), Ni(2)–Ni(3) 2.910(1), Ni(3)–Ni(4) 3.061(1), Ni(4)–Ni(1) 3.170(1).

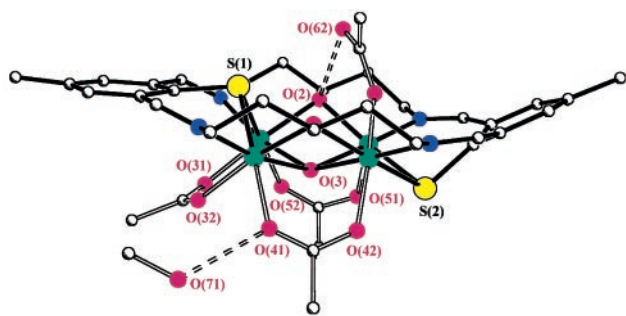


Fig. 2 View perpendicular to the Ni₄ plane showing the non-planar conformation of the macrocycle. Selected bond angles (°): Ni(1)–O(3)–Ni(2) 83.5(2), Ni(2)–O(3)–Ni(3) 82.1(2), Ni(3)–O(3)–Ni(4) 88.3(2), Ni(4)–O(3)–Ni(1) 90.4(2), Ni(4)–S(1)–Ni(1) 84.17(7), Ni(3)–S(2)–Ni(2) 76.29(6), Ni(2)–O(1)–Ni(1) 97.0(2), Ni(3)–O(2)–Ni(4) 93.1(2).

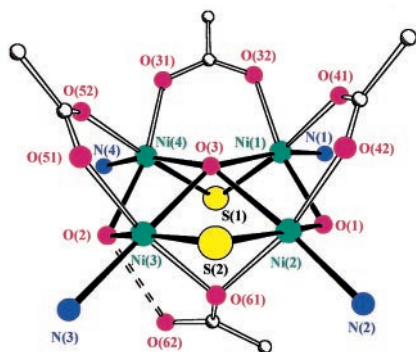


Fig. 3 The coordination spheres of the nickel ions. Selected bond distances (Å): Ni(1)–O(3) 2.237(4), Ni(2)–O(3) 2.263(5), Ni(3)–O(3) 2.165(4), Ni(4)–O(3) 2.231(5), Ni(1)–S(1) 2.366(2), Ni(4)–S(1) 2.363(2), Ni(2)–S(2) 2.365(2), Ni(3)–S(2) 2.347(2), Ni(1)–O(1), 2.029(5), Ni(2)–O(1) 1.973(4), Ni(3)–O(2) 2.094(5), Ni(4)–O(2) 2.124(5), Ni(1)–N(1), 2.057(6), Ni(2)–N(2) 2.062(6), Ni(3)–N(3) 2.066(5), Ni(4)–N(4) 2.072(6), Ni(1)–O(32) 2.059(5), Ni(1)–O(41) 2.111(5), Ni(2)–O(42) 2.048(5), Ni(2)–O(61) 2.166(4), Ni(3)–O(51) 2.025(5), Ni(3)–O(61) 2.120(5), Ni(4)–O(31) 2.002(5), Ni(4)–O(52) 2.074(5).

intended to model the biosite, it does provide some indications as to how accurate active site mimics could be achieved.

In Schiff-base ligands derived from 2,6-diformylthiophenols the large sulfur donor must be accommodated without appreciable expansion of the relatively inflexible thiophenol–diimine unit. This requirement generally causes the sulfur atom and the imine groups to lie on opposite sides of the plane of the phenyl ring with geometry similar to that at S(1).^{3,9–11} The deviations from the plane of the phenyl ring (Fig. 2) are much greater at S(2), presumably as a consequence of the face-sharing geometry of Ni(2) and Ni(3). Overall, the complex is markedly unsymmetric; the faces of the tetranickel array can be distinguished and two different Ni sites can be identified. One face is closed by the three acetato ligands; on the other side access to Ni(1) and Ni(4) is blocked by the apical thiolate donor S(1) but Ni(2) and Ni(3) have one site occupied only by the neutral acetic acid group. The solubility of the neutral complex in chloroform–dichloromethane suggests that the anionic ligands remain coordinated in solution, at least in these solvents.

Details of the magnetic properties of the present complex will be discussed along with those of related complexes⁵ but, in summary, the nickel ions are high-spin and the complex shows net antiferromagnetic coupling, very similar in magnitude to that observed in more symmetrical tetranickel(II) arrays.^{5,12,13} Murray and coworkers^{12,13} have modelled this behaviour in terms of isolated pairs of dimers each with a single J of ca. -30 cm^{-1} .

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Footnotes

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‡ This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: <http://chemistry.rsc.org/rsc/eccenaha.htm>

§ *Crystal data:* [Ni₄L¹(OH)(MeCO₂)₃(MeCO₂H)]·MeOH, C₃₇H₅₀N₄Ni₄O₁₂S₂, brown–green block, 0.60 × 0.53 × 0.32 mm, monoclinic, space group $P2_1/n$, $a = 11.105(2)$, $b = 18.297(3)$, $c = 20.027(3)$ Å, $\beta = 93.52(1)^\circ$, $U = 4061(1)$ Å³, $Z = 4$, $\mu = 1.996 \text{ mm}^{-1}$, $F(000) = 2160$. Using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 153(2) K, a total of 6009 reflections was collected in the range $4 < 2\theta < 50^\circ$. Data were corrected for Lorentz and polarisation effects and a semiempirical absorption correction, based on ψ -scans, was applied ($T_{\text{max}} = 0.980$, $T_{\text{min}} = 0.558$). The structure was solved by direct methods¹⁴ and refined by full-matrix least squares on F^2 , using all 5278 independent reflections ($R_{\text{int}} = 0.0583$). All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions, hydrogen atoms bonded to oxygen were located from difference Fourier maps and not further refined. Refinement converged with $wR_2 = 0.1351$, GOF = 1.124 (all data) and $R_1 = 0.0481$ (2σ data). All programs used in the structure refinement are contained in the SHELXL-93 package.¹⁵ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/507.

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