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Synthesis and structure of a heptanuclear nickel(II) complex uniquely exhibiting four distinct binding modes, two of which are novel, for a hydroxamate ligand

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The reaction of 2-(dimethylamino)phenylhydroxamic acid (2-dmAphaH) with $NiSO_4 \cdot 6H_2O$ gives the complex $[Ni_7(2\text{-dmAphaH}_{-1})_2(2\text{-dmApha})_8(H_2O)_2]SO_4 \cdot 15H_2O$ uniquely exhibiting four distinct hydroxamate binding modes, two of which are novel, and showing both antiferromagnetic and ferromagnetic interactions in contrast to $[Cu_5(2\text{-dmAphaH}_{-1})_4(HSO_4)_2(MeOH)_2] \cdot 2MeOH$, a strongly antiferromagnetic metallacrown formed with $CuSO_4 \cdot 5H_2O$.

Hydroxamic acids, RC(O)N(R′)OH, are important bioligands, acting as siderophores for iron(III),[1] as inhibitors of enzymes such as peroxidases,[2] ureases,[3] matrix metalloproteinases,[4] and as hypotensive,[5] anti-cancer, anti-tuberculous and anti-fungal agents.[6] Although the hydroxamate ligand in complexes is usually bidentate[1,7] there are also examples in which it is bridging[8] or even monodentate through the hydroxamate oxygen.[9] There is also a reported example of binding of the hydroxamate group of trifluoroacetohydroxamate to zinc(II) in human carbonic anhydrase II through the hydroxamate nitrogen only but this is stabilised by hydrogen bonding interactions and by the presence of a weak Zn–F bond.[10] The diversity of hydroxamate coordination modes/structures is further enriched by the presence of additional coordinating sites in the ligand *e.g.* in the copper(II) complexes of the isomeric aminophenylhydroxamic acids which we have previously described.[11] Herein we describe a nickel(II) complex which uniquely exhibits four distinct hydroxamate binding modes, two of which are novel for this important group of ligands, and which shows both antiferromagnetic and ferromagnetic interactions. This product contrasts with a strongly antiferromagnetic metallacrown formed with copper(II).

Reaction of 2-dmAphaH with $NiSO_4 \cdot 6H_2O$ in H_2O/MeOH at pH 5.7 afforded the green crystalline complex $[Ni_7(2\text{-dmAphaH}_{-1})_2(2\text{-dmApha})_8(H_2O)_2]SO_4 \cdot 15H_2O$ **1**, containing monodeprotonated 2-dmApha, and doubly deprotonated 2-dmAphaH$_{-1}$ hydroxamate ligands and a trigonal bipyramidal array of nickel(II) ions with a further two nickel ions annexed to the apical sites, Figs. 1 and 2.† Each metal ion is in an octahedral environment of donor atoms provided by hydroxamate and water ligands. The hydroxamate ligands may be categorised into three pairs and a set of four according to binding modes, Fig. 3. One of the doubly deprotonated hydroxamate ligands, C, using all of its donor atoms is doubly bidentate with respect to nickel ions, Ni1/Ni3 and, using the hydroxamate oxygen, is triply bridging to Ni2/Ni5/Ni3, Fig. 3. Ligand E is similarly bonded to Ni7/Ni5 and Ni6/Ni3/Ni5. The remaining eight hydroxamate ligands are singly deprotonated and are coordinated *via* the hydroxamate group only. Ligand D is bidentate with respect to Ni4 and triply bridging *via* the hydroxamate oxygen with respect to Ni4/Ni2/Ni5. Ligand K is similarly coordinated to Ni4 and Ni4/Ni6/Ni3. Ligand G bridges Ni4 and Ni6 *via* the hydroxamate oxygen while ligand J is similarly coordinated to Ni2 and Ni4. The four remaining hydroxamate ligands coordinate pairs of nickel ions in a bidentate bridging manner. Ligands A and B are bidentate with respect to Ni1 and Ni2, respectively, and both bridge these nickel ions through the hydroxamate oxygen. Ligands F and H exhibit the same coordination towards Ni6 and Ni7, respectively. The two binding modes observed for ligands D/K and G/J have not previously been reported for hydroxamate ligands, whilst a similar binding mode for ligands C/E, which involves an additional coordinating group, has only once previously been reported and this for a nickel(II)–metallacrown with salicylhydroxamic acid.[12] The double hydroxamate bridg-

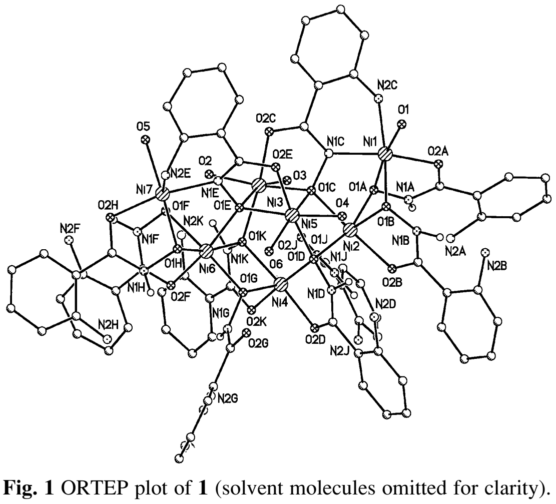

Fig. 1 ORTEP plot of **1** (solvent molecules omitted for clarity).

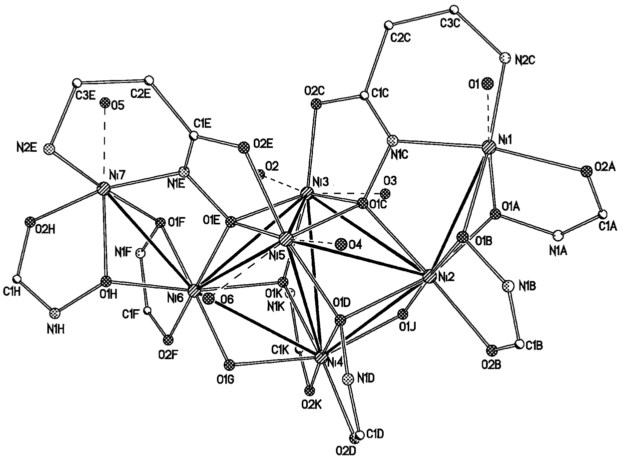

Fig. 2 ORTEP plot illustrating metal centres of **1** and showing the trigonal bipyramidal arrangement of the five central nickel(II) ions with one additional ion annexed to each apex.

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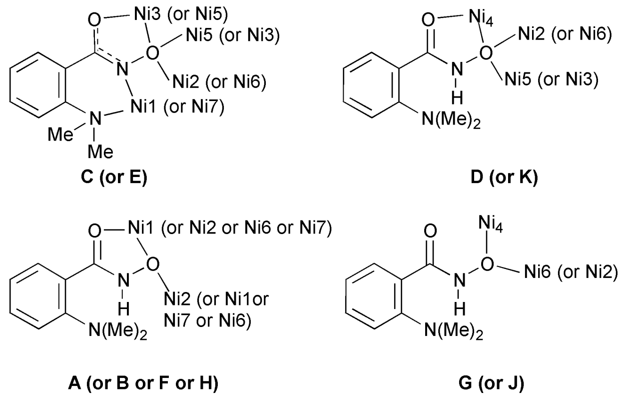

C (or E) **D (or K)**

A (or B or F or H) **G (or J)**

Fig. 3 Binding modes of hydroxamate ligands (2-dmApahaH$_{-1}$ and 2-dmApha) in structure **1**.

ing of Ni1–Ni2 and Ni6–Ni7 by ligands A and B and F and H, respectively, is similar to that observed in some dinickel model systems for urease inhibition[3] which also contain two hydroxamate bridges and for which inter-nickel distances of 3.016 and 3.005 Å have been reported, very similar to the values of 2.958(3) and 2.944(2) Å in the present case. Double hydroxamate bridging also exists between Ni2–Ni4, Ni2–Ni5, Ni3–Ni5, Ni3–Ni6 and Ni4–Ni6 whilst single hydroxamate bridging occurs between Ni2–Ni3, Ni3–Ni4, Ni4–Ni5 and Ni5–Ni6.

In contrast to the nickel product, reaction of 2-dmAphaH with $CuSO_4 \cdot 5H_2O$ resulted in the formation of the metallacrown[13] $[Cu_5(2\text{-dmAphaH}_{-1})_4(HSO_4)_2(MeOH)_2]\cdot 2MeOH$ **2**. The presence of the methyl groups in the ligand preclude formation of a dimeric metallacrown analogous to $[Cu_5(2\text{-AphaH}_{-1})_4(\mu\text{-SO}_4)(H_2O)_2]_2\cdot 10H_2O$, which we previously reported for 2-aminophenylhydroxamic acid, 2-AphaH.[11] Complex **2** contains a square of copper(II) ions coordinated by the doubly deprotonated 2-dmAphaH$_{-1}$ ligands forming a ring which binds the central copper(II) ion through four hydroxamate oxygens (O2, O2A, O4, O4A) (Fig. 4).

Despite the extensive internickel bridging, **1** was overall only weakly antiferromagnetic in the range 4–300 K.[14] The complex has a room temperature $\mu_{\text{eff}} = 7.93\ \mu_B$ (theoretical value 8.23 μ_B when $g = 2.2$) which falls to 5.62 μ_B at 4 K. Antiferromagnetic interactions occur between pairs of nickel ions in the trigonal bipyramidal array for which the Ni–O–Ni bond angles are *ca.* 96–103° whilst ferromagnetic interactions are observed between the apical and annexed nickels for which the Ni–O–Ni bond angles are *ca.* 88–92°.‡ On the other hand **2** is strongly antiferromagnetic having a room temperature magnetic moment of 3.1 μ_B, considerably lower than the calculated value of 4.12 μ_B for five independent $S = ½$ copper(II) ions. As in the case of $[Cu_5(2\text{-AphaH}_{-1})_4(\mu\text{-SO}_4)(H_2O)_2]_2\cdot 10H_2O$[11] a considerable decrease in μ_{eff} was observed below 12 K, due to intermolecular interactions.

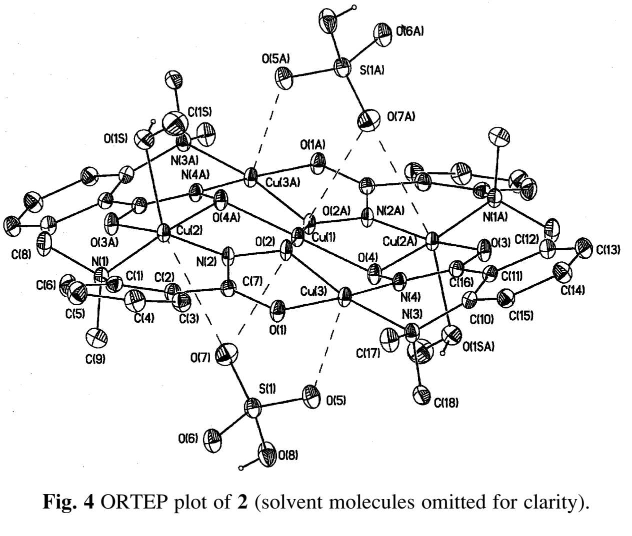

Fig. 4 ORTEP plot of **2** (solvent molecules omitted for clarity).

In summary, we report a structurally unusual nickel(II) complex which shows a rich variety of coordination modes, some novel, of a hydroxamate ligand, and which also shows both antiferromagnetic and ferromagnetic interactions between pairs of nickel ions.

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Notes and references

† *Crystal Data*: for **1**: $C_{90}H_{150}N_{20}O_{45}S_1Ni_7$, M_r = 2675.33, orthorhombic, space group $P2_12_12_1$, a = 16.398(9), b = 23.996(14), c = 30.666(12) Å, V = 12067(10) Å^3, $F(000)$ = 5608, Z = 4, μ(Mo-Kα) = 1.177 mm^{-1}, 41850 reflections collected, 20598 independent, R_{int} = 0.1354. Refinement converged at $wR2$ value of 0.1163, R 1 0.0605 [for reflections 6247 with $I > 2\sigma(I)$].

For **2**: $C_{40}H_{58}N_8O_{20}S_2Cu_5$, M_r = 1352.76, triclinic, space group $P\bar{1}$, a = 11.002(4), b = 11.393(4), c = 11.863(4) Å, α = 81.989(7), β = 64.844(6), γ = 68.106(6)°, V = 1248.6(7) Å^3, $F(000)$ = 691, Z =1, μ(Mo-Kα) = 2.264 mm^{-1}, 14707 reflections collected, 7140 independent, R_{int} = 0.0251. Refinement converged at $wR2$ value of 0.1107, R 1 0.0421 [for 5646 reflections with $I > 2\sigma(I)$].

CCDC reference numbers 175233 and 175234. See http://www.rsc.org/suppdata/cc/b1/b110799b/ for crystallographic data in CIF or other electronic format.

‡ The structure of complex **1** gives rise to three different independent exchange parameters which were used in the best fit procedure: $J_{12} = J_{67}$, $J_{24} = J_{25} = J_{35} = J_{36} = J_{46}$ and $J_{23} = J_{34} = J_{45} = J_{56}$ for Ni–Ni coupling between metal centres of corresponding number. The best fit parameters are J_{12} = 14.07 cm^{-1}, J_{24} = −8.17 cm^{-1}, J_{23} = −7.26 cm^{-1} and g = 2.2 with a relative error of 0.71% compared to experimental data indicating a ground state of S = 2 for the complex. J_{12} also agrees well with the exchange parameter quoted for ferromagnetic dinuclear complexes possessing a similar structure to the Ni1–Ni2 and Ni6–Ni7 cores.[3]

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