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Heterometallic complexes containing d- and f-block elements: synthesis and structural characterisation of novel Ni–Er and Co–Dy compounds

Euan K. Brechin, Steven G. Harris, Simon Parsons and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road,
Edinburgh EH9 3JJ, UK

The structures of new heterometallic tetranuclear complexes have been determined which each feature two 3d-metal centres, either Co or Ni, and two 4f-metal sites; preliminary magnetic data have also been reported.

A number of groups[1–8] have been investigating the magnetic interaction between copper(II) and gadolinium(III) which has been found to be directly ferromagnetic. Recent studies indicate that the magnitude of the ferromagnetic exchange integral can be related to the exponential of the distance between metal centres.[6] Nothing has been reported on the related interaction between other 3d–4f mixtures, and indeed very few structurally characterised complexes[9] are known which contain such combinations of metals. Even in the few known cases the oxidation state or co-ordination geometry of the 3d metal often renders the magnetic properties of the polymetallic complex uninteresting. For example, nickel(II) complexes are known where thiooxalate bridges between Ni(II) and a variety of 4f elements,[10] however in each case the nickel is in a square-planar environment and hence is diamagnetic. As we have had success in synthesising copper–lanthanoid complexes *via* preformed copper–pyridonate complexes[4] we have now examined a similar approach to both Ni–Ln and Co–Ln species.

Reaction of erbium nitrate (0.71 mmol) with $[Ni_4(OMe)_4(chp)_4(MeOH)_7]$[11] (0.18 mmol) (chp = 6-chloro-2-pyridonate) in acetonitrile (20 cm^3) leads to a green solution from which green cubes form in 10% yield after 2 weeks.† Structure solution‡ reveals a centrosymmetric complex of stoichiometry $[Ni_2Er_2(chp)_6(NO_3)_4(CH_3CN)_2]$ **1** which contains a central Er_2O_2 ring bridged to peripheral nickel atoms through six chp ligands (Fig. 1). The chp ligands show two distinct bonding modes. Four chelate to the Ni centre and bridge to the Er atom through the exocyclic oxygen which binds to both Ni and Er centres. The remaining chp groups bind to Ni through the N donor alone and provide the O atoms of the central Er_2O_2 ring and are therefore trinucleating. The metal atoms and these chp O donors therefore describe two interpenetrating rings; the Er_2O_2 unit and an eight-membered $Er_2Ni_2O_4$ metallacycle perpendicular to it.

The erbium sites are eight-co-ordinate, each bound to four chp O donors and two bidentate nitrate anions. The nickel sites have distorted octahedral geometry comprising three chp N donors, two chp O donors and the N atom of an CH_3CN molecule. The distortion is chiefly due to the two chelating chp groups which have bite angles considerably smaller than 90°.

A similar strategy to prepare mixed Co–Ln species involves the salt $[NEt_4]_2[Co(chp)_4]$ **2**, which can be prepared in 30% yield from the reaction of 4 equivalents of Na(chp) with $[NEt_4]_2[CoCl_4]$ in methanol, followed by extraction with CH_2Cl_2. Salt **2** has been structurally characterised and contains a Co^{II} centre bound to four O donors with a tetrahedral co-ordination geometry. Further reaction of **2** (0.60 mmol) with dysprosium nitrate (0.60 mmol) in a mixture of 1:1 CH_2Cl_2–methanol, gives a purple solution. Evaporation to dryness followed by extraction with dichloromethane gives a solution which produces a 24% yield of pink crystals after 4 d.

Structural analysis‡ reveals a salt of stoichiometry $[NEt_4]_2[Co_2Dy_2(OH)(chp)_6(NO_3)_5]$ **3** (Fig. 2). Like **1**, compound **3** contains a central Dy_2O_2 core, but whereas in **1** both of these oxygens are derived from pyridonates in **3** one is a μ_3-hydroxide which bridges not only the two dysprosium centres but also Co(1) leading to a much less symmetrical array of metal sites than in **1**. Again we find an eight-membered ring containing four chp oxygen atoms [O(61), O(62), O(65) and O(66)]. The two Dy atoms are both nine-co-ordinate and bound to three μ_2-O atoms

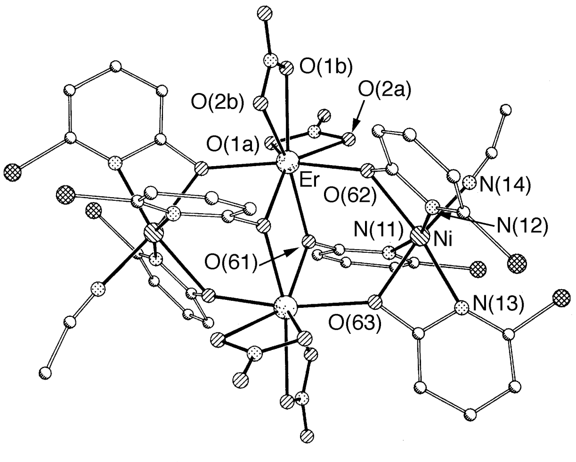

Fig. 1 The structure of compound **1** in the crystal. Bond length ranges (Å): Er–O 2.241 to 2.426, Ni–O 2.129 to 2.209, Ni–N 2.027 to 2.116 (average estimated standard deviation 0.006 Å)

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† Satisfactory elemental analyses were obtained for all compounds.

‡ Crystal data: $C_{34}H_{24}Cl_6Er_2N_{12}Ni_2O_{18}\cdot1.32C_2H_5O\cdot0.67C_2H_3N$ (**1**·1.32Et$_2$O·0.67MeCN): $M = 1679.7$, crystal size 0.39 × 0.31 × 0.27 mm, monoclinic, space group $P2_1/c$, green block, $a = 11.482(2)$, $b = 18.537(3)$, $c = 14.005(3)$ Å, $\beta = 97.41(2)°$, $U = 2956.0(9)$ Å^3, $Z = 2$, $D_c = 1.89$ g cm^{-3}, $F(000) = 1642$, $T = 150.0(2)$ K, $R1 = 0.0457$, $S = 1.013$. Crystal data: $C_{46}H_{59}Cl_6Co_2Dy_2N_{13}O_{22}\cdot3.46CH_2Cl_2$ (**3**·3.46CH_2Cl_2). $M = 2095.5$, crystal size 0.51 × 0.23 × 0.16 mm, triclinic, space group $P1$, pink block, $a = 14.099(4)$, $b = 14.957(3)$, $c = 18.941(5)$ Å, $\alpha = 83.59(2)$, $\beta = 87.91(2)$, $\gamma = 82.92(2)°$, $U = 3938(2)$ Å^3, $Z = 2$, $D_c = 1.77$ g cm^{-3}, $F(000) = 2071$, $T = 230.0(2)$ K, $R1 = 0.0765$, $S = 1.021$. Data collection, structure solution and refinement were performed as detailed in ref. 11 using programs SHELXS 86[12] and SHELXL 93.[13] Full details will be published later. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/493.

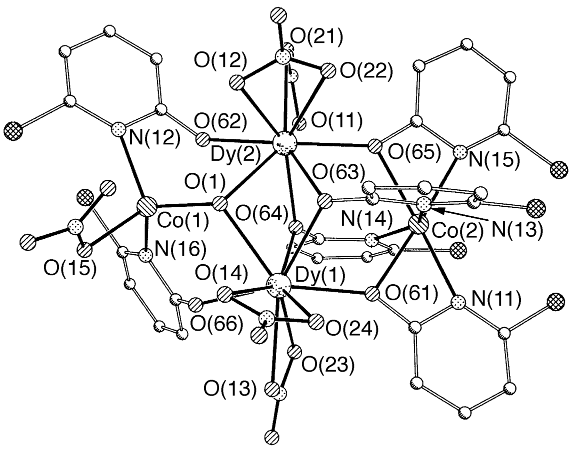

Fig. 2 The structure of the anion of compound **3** in the crystal. Bond length ranges (Å): Dy–O 2.264 to 2.538, Co–O 1.959 to 2.207, Co–N 2.060 to 2.200 (average estimated standard deviation 0.013 Å)

from chp groups, one μ_3-OH, two bidentate nitrates and an O-atom from a binucleating chp.

The two cobalt sites are quite distinct. The atom Co(1) has a tetrahedral geometry, bound to two chp N donors, the μ_3-hydroxide oxygen and a monodentate nitrate. It also has long contacts of 2.494, 2.655 and 2.697 Å to O(62), O(25) and O(66) respectively. The atom Co(2) is in a distorted octahedral arrangement, binding to both donors of two chelating chp groups, and two further N atoms from pyridonates which supply O donors exclusively to the Dy sites. Again the narrow bite angle of the chp groups is the chief cause of the distortion. It is somewhat unusual to find four- and six-co-ordinate Co atoms within the same structure. The pyridonates in **3** show three bonding modes: chelating to a Co site while bridging to a Dy atom through the exocyclic oxygen; bonding to a Co site through the ring N atom while bridging two Dy atoms through the exocyclic oxygen; binucleating, bound to Co(1) through the N donor and either Dy(1) or Dy(2) through an oxygen. The analogous Co–Gd and Co–Yb complexes can be made and crystallised by identical procedures, however we have found it more difficult to crystallise Ni–Ln complexes analogous to **1**.§

Preliminary magnetic studies have been performed on **1** and on $[Co_2Gd_2(OH)(chp)_6(NO_3)_5]$ **4**. In both cases the room-temperature value for χ_mT (where χ_m is the molar magnetic susceptibility) is consistent with the value expected if the metal centres are not interacting (for **1**: found 26.5 emu K mol^{-1}, calculated 25.5 emu K mol^{-1}, assuming $g_{Ni} = 2.2$, $g_{Er} = 1.2$; for **4**: found 21.9 emu K mol^{-1}, calculated 21.6 emu K mol^{-1}, assuming $g_{Co} = 2.5$, $g_{Gd} = 2.0$; where 1 emu is equivalent to 1 cm^3). For **1** this value declines gradually between 300 and 20 K, where the χ_mT value is 22 emu K mol^{-1}, below 20 K it falls sharply to 13 emu K mol^{-1} at 2 K. For **4** the value of χ_mT is almost constant until 50 K, but below this temperature the value falls, reaching 11.2 emu K mol^{-1} at 2 K. In both cases the room-temperature value of χ_mT indicates that all interactions are quite weak, and the fall in χ_mT at lower temperatures suggests that the strongest interaction present is antiferromagnetic. Unfortunately the presence of orbitally degenerate ions in both **1** and **4** prevents modelling of the data, and we have been unable to crystallise a Ni_2Gd_2 analogue of **1**.

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§ *Note added at proof*: A very recent paper[14] has reported an elegant Ni_6Sm cage bridged by L-prolinato ligands.