

Preparation, structure and preliminary magnetic studies of tri- and tetra-nuclear cobalt–lanthanide carboxylate complexes†

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Carboxylate-bridged cobalt–lanthanide complexes $[\text{Co}_2\text{Nd}(\text{O}_2\text{CCMe}_3)_6(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)]$ and $[\text{Co}_2\text{Er}_2(\text{O}_2\text{CCMe}_3)_8(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)_2]$ have been prepared and structurally characterised by X-ray diffraction; both of them are found to be antiferromagnetically coupled.

With the aim of clarifying the role of the exchange interactions between 4f and 3d metal ions modifying the properties of magnetic materials containing rare-earth metals, in the last few years, an increasing interest has been given to the magnetic properties of molecular complexes comprising simultaneously lanthanide and transition metal ions.^{1–8} This interest has been essentially focused on the $\text{Cu}^{\text{II}}\text{–Gd}^{\text{III}}$ couple^{1–6} which has been found to be directly ferromagnetic. Recent studies have revealed that the magnitude of the ferromagnetic exchange interaction between the different metal centres is exponentially dependent on the Cu–Gd distance.^{5,7} By comparison, the magnetic interactions between other 3d–4f mixtures have been poorly explored,^{8,9} and in fact only very few structurally characterised complexes are known which contain such combinations of metals.^{8–11} Herein we described the preparation, crystal structure and preliminary magnetic studies of $[\text{Co}_2\text{Nd}(\text{O}_2\text{CCMe}_3)_6(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)]$ **1** and $[\text{Co}_2\text{Er}_2(\text{O}_2\text{CCMe}_3)_8(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)_2]$ **2**. To the best of our knowledge, the present cases are the first two examples of carboxylate-bridged discrete heterometallic cobalt–lanthanide complexes^{9,10} and are new model complexes for magnetic investigation.

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.58 g, 2 mmol), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.44 g, 1 mmol) and pivalic acid (0.61 g, 6 mmol) was dissolved in EtOH (80 mmol), followed by addition of quinoline (0.24 mL). The resultant mixture was refluxed for 16 h, filtered while hot, and then concentrated to 25 mL. The filtrate was left at room temperature and red-brown prismatic crystals of **1** were deposited in 35% yield after two weeks.‡ X-Ray crystallography§ has established that complex **1** consists of a discrete trinuclear $[\text{Co}_2\text{Nd}(\text{O}_2\text{CCMe}_3)_6(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)]$ molecule as shown in Fig. 1. Two cobalt atoms are each co-ordinated by three carboxylate oxygen atoms and a quinoline molecule to form distorted tetrahedrons where the most distorted angles are 96.6(2) and 96.0(2)° for O(12)–Co(1)–N(1) and O(42)–Co(2)–N(2), respectively. Each terminal cobalt atom is connected to the central neodymium atom by three bridging pivalate ligands with $\text{Co} \cdots \text{Nd}$ separations of 4.0668(7) and 4.0700(7) Å. The arrangement of the three metals is quasi-linear with a Co(1)–Nd–Co(2) angle of 134.10(2)°. Besides the six carboxylate oxygen atoms, the eight-co-ordination sphere of the neodymium

atom is completed by a chelating nitrate anion. The co-ordination polyhedron around the neodymium atom is irregular, with the chief distortion being caused by the presence of a small bidentate nitrate anion, but it still can be described as a dodecahedron with the two trapezia defined by O(11), O(1), O(2), O(51) and O(31), O(21), O(61), O(41) intersecting at an angle of 86.3°.

The analogous reaction of hydrated cobalt nitrate with hydrated erbium nitrate leads to a quite different, crystallographically characterised product **2**. Here a centrosymmetric tetranuclear Co_2Er_2 complex is formed, the inversion center residing on the midpoint of the Er–Er vector, as shown in Fig. 2. Again two four-co-ordinated cobalt atoms, each having a terminal quinoline ligand, are each triply connected to the adjacent Er atom *via* three bridging pivalate groups. The structure of the dinuclear Co–Er subunits is very similar to the structure of Co–Nd moieties in **1**, but the $\text{Co} \cdots \text{Er}$ distance of 3.9127(9) Å is slightly shorter than the $\text{Co} \cdots \text{Nd}$ distance, as a consequence of the smaller size of the erbium atom. A pair of Er atoms in two centrosymmetrically related binuclear Co–Er subunits are linked together by two pivalate groups in a *syn–syn* bridging fashion with an Er \cdots Er distance of 5.2017(5) Å. As a result, the sequence of atoms Co–Er–Er–Co makes a broken line with a Co–Er–Er angle of 137.05(2)°. The Er atom is seven-co-ordinate, with five of the sites filled by five pivalate oxygen atoms and two sites by a chelating nitrate anion. The geometry of the Er atom is based on a pentagonal bipyramid, with the equatorial plane defined by O(1), O(2), O(21), O(11) and O(42A) and the axial positions occupied by O(31) and O(41) [O(31)–Er–O(41) = 176.6(2)°].

The change in structure from **1** to **2** probably results from the reduction in the ionic radius in going from Nd to Er, which is reflected in the lower co-ordination number of the lanthanide in **2**. Similar effects have been found previously.³ Elemental analysis and cell determination suggest that the Ce analogue has structure **1**, whilst the yttrium one has structure **2** (see SUP 57420). It should be noted that quinoline plays an important role in the formation of such 3d–4f mixed metal complexes, especially for those 3d metal ions having tetrahedral co-ordination sites. Detailed discussion will be given in subsequent reports.

The magnetic properties of **1** and **2** in the solid state have been investigated at 1.0 T, over the temperature range 5–280 K (see SUP 57420). For complex **1**, μ_{eff} per molecule decreases

§ Crystal data for **1** $\text{C}_{48}\text{H}_{68}\text{Co}_2\text{N}_3\text{NdO}_{15}$: $M = 1189.15$, triclinic, space group $P\bar{1}$, $a = 11.9406(2)$, $b = 12.6970(2)$, $c = 22.1401(1)$ Å, $\alpha = 98.209(1)$, $\beta = 98.083(1)$, $\gamma = 117.24(2)^\circ$, $U = 2871.74(7)$ Å³, $Z = 2$, $D_c = 1.375$ g cm^{−3}, $\mu = 1.522$ mm^{−1}, $F(000) = 1222$. Crystal data for **2** $\text{C}_{96}\text{H}_{136}\text{Co}_2\text{Er}_2\text{N}_4\text{O}_{32}$: $M = 1643.69$, triclinic, space group $P\bar{1}$, $a = 10.9792(3)$, $b = 12.4595(5)$, $c = 13.7959(2)$ Å, $\alpha = 85.5964(8)$, $\beta = 84.5640(7)$, $\gamma = 73.050(7)^\circ$, $U = 1794.72(5)$ Å³, $Z = 1$, $D_c = 1.521$ g cm^{−3}, $\mu = 2.838$ mm^{−1}, $F(000) = 828$. Data collection and processing: $T = 293$ K, $R = 0.038$ ($wR = 0.081$) for 6505 observed reflections [$2\theta \leq 45.5^\circ$, $F^2 > 2\sigma(F^2)$] and $S = 1.05$ for **1**, and $R = 0.050$ ($wR = 0.120$) for 5140 observed reflections [$2\theta \leq 50.0^\circ$, $F^2 > 2\sigma(F^2)$] and $S = 1.05$ for **2**. For complex **1** the *tert*-butyl groups of the pivalate ligands involving C(12) and C(52) were treated as having rotational disorder around the C(11)–C(12) or C(51)–C(52) bond with three methyl groups each occupying two half-weighted sites, while those *tert*-butyl groups involving C(32) and C(62) were wholly split into two parts each having site occupancy factor of 0.50. In the latter case the terminal C–C bonds in each pivalate ligand were restrained to be similar with a standard deviation of 0.03 Å. CCDC reference number 186/1115. See <http://www.rsc.org/suppdata/dt/1998/2955/> for crystallographic files in .cif format.

† Supplementary data available: cell parameters for $[\text{Co}_2\text{Ce}(\text{O}_2\text{CCMe}_3)_6(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)]$ and $[\text{Co}_2\text{Y}_2(\text{O}_2\text{CCMe}_3)_8(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)_2]$, Nd and Er co-ordination polyhedra in complexes **1** and **2**, and plots of μ_{eff} vs. T for complexes **1** and **2**. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/2955/>, otherwise available from BLDSC (No. SUP 57420, 5 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

‡ Satisfactory elemental analyses were obtained for both compounds. (**1**: Found C, 48.3; H, 5.9; N, 3.4. Calc. for $\text{C}_{48}\text{H}_{68}\text{Co}_2\text{N}_3\text{NdO}_{15}$: C, 48.5; H, 5.8; N, 3.5%. **2**: Found: C, 42.3; H, 5.3; N, 3.2. Calc. for $\text{C}_{96}\text{H}_{136}\text{Co}_2\text{Er}_2\text{N}_4\text{O}_{32}$: C, 42.4; H, 5.3; N, 3.4%.)

Non-SI unit employed: $\mu_{\text{B}} \approx 9.274 \times 10^{-24}$ J T^{−1}.

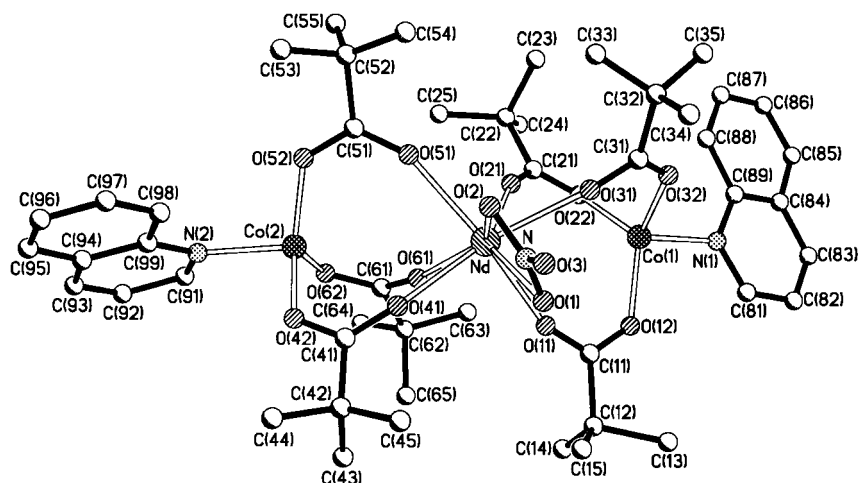


Fig. 1 Molecular structure of complex **1**. Only one part of the disordered *tert*-butyl groups is presented. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Nd–O(1) 2.565(5), Nd–O(2) 2.538(3), Nd–O(11) 2.358(3), Nd–O(21) 2.385(5), Nd–O(31) 2.385(4), Nd–O(41) 2.408(4), Nd–O(51) 2.385(3), Nd–O(61) 2.428(4), Co(1)–O(12) 1.943(4), Co(1)–O(22) 1.964(3), Co(1)–O(32) 1.940(3), Co(1)–N(1) 2.081(4), Co(2)–O(42) 1.948(4), Co(2)–O(52) 1.939(4), Co(2)–O(62) 1.948(4), Co(2)–N(2) 2.092(4)

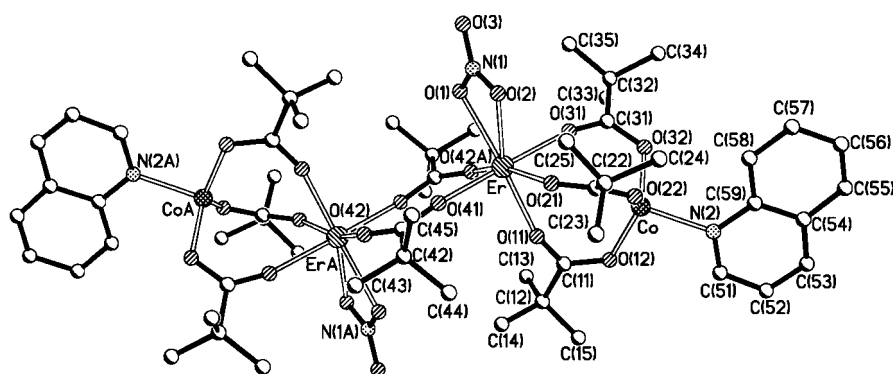


Fig. 2 Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Er–O(1) 2.412(5), Er–O(2) 2.404(6), Er–O(11) 2.229(6), Er–O(21) 2.287(5), Er–O(31) 2.231(5), Er–O(41) 2.174(5), Er–O(42A) 2.248(5), Co–O(12) 1.946(6), Co–O(22) 1.940(5), Co–O(32) 1.967(5), Co–N(2) 2.077(6). Symmetry code: $i = 2 - x, -y, 3 - z$

gradually from 6.82 at 280 K to 5.63 μ_B at 5 K. This behavior is clearly characteristic of intramolecular antiferromagnetic coupling. Complex **2** is also antiferromagnetically coupled: μ_{eff} per molecule is 14.19 μ_B at 274 K, which declines to 10.95 μ_B at 5 K. At room temperature, μ_{eff} per Co^{2+} ion is expected to be 3.83 μ_B ,¹² for Er^{3+} and Nd^{3+} ions, μ_{eff} is ≈ 9.6 and 3.5 μ_B ,¹² respectively. For $\text{Co}^{\text{II}}_2\text{Er}^{\text{III}}_2$ and $\text{Co}^{\text{II}}_2\text{Nd}^{\text{III}}$ complexes with non-interacting metal ions, μ_{eff} is expected to be ≈ 14.6 and 6.6 μ_B , respectively. The experimental values of μ_{eff} are thus close to the corresponding non-interacting values, indicating that all interactions are quite weak.

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