A rare earth alloy as a synthetic reagent: contrasting homometallic rare earth and heterobimetallic outcomes

Glen B. Deacon,* Craig M. Forsyth, Peter C. Junk and Stuart G. Leary

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Reaction of $LaNi_5$ with 2,2′-dipyridylamine ($HNpy_2$) at 170 °C under vacuum gave crystals of dimeric $[La(Npy_2)_3]_2$ as a previously unknown eight-coordinate isomer (**1a**) (two μ-η^2:η^2 and two terminal chelating (N_{amide},N_{py}) Npy_2 ligands), which reverts to the known ten coordinate isomer (**1b**) on recrystallisation from THF/PhMe, thereby establishing linkage isomerism of a $[Ln(Npy_2)_3]_2$ complex for the first time. Reaction of 8-hydroxyquinoline (HOQ) with excess $LaNi_5$ alloy at 190 °C resulted in extraction of both metals and the formation of heterobimetallic $[Ni_2La(OQ)_7]$ (**2**). The trinuclear complex has two terminal, *fac*-octahedral nickel(II) sites, each bound to three chelating 8-quinolinolate anions which bridge through the oxygen atoms to the lanthanum(III) centre. The eight-coordinate lanthanum environment is completed by a chelating OQ ligand.

Introduction

Direct reactions of rare earth (RE) elements with weakly acidic organic compounds (eqn (1)) are a simple yet highly effective route to a range of homoleptic RE compounds.[1–6]

$$RE + nHL \rightarrow [RE(L)_n] + n/2H_2 \qquad (1)$$

Recently, these reactions have been extended to syntheses of Group 2 metal complexes[7,8] as well as novel heterobimetallic RE–calcium complexes from a mixture of the two metals.[9] Rare earth alloys, *e.g.* $LaNi_5$, $SmCo_5$, have become increasingly more accessible due to their unique hydrogen storage and magnetic properties.[10,11] These materials have particular novelty as synthetic reagents through the potential to extract both metals yielding f^n/d^n bimetallic complexes. The properties of such compounds, as a consequence of the presence of disparate metal centres, have attracted increasing research interest in magnetochemistry, catalysis, luminescence and MOCVD applications.[12,13] We now report examples of the use of the RE alloy $LaNi_5$ as a synthetic reagent giving either a homometallic (La) or a heterobimetallic (La–Ni) homoleptic complex from reactions with 2,2′-dipyridylamine $HNpy_2$ or 8-hydroxyquinoline HOQ, respectively. From the former system, the first example of linkage isomers of a lanthanoid 2,2′-dipyridylamide has been demonstrated adding an unexpected feature to the extensive structural studies of such complexes.[4,6]

Results and discussion

The rare earth alloy $LaNi_5$ reacted with $HNpy_2$ at 170 °C under vacuum and gave crystalline yellow $[La(Npy_2)_3]_2$ (eqn (2)), as an eight coordinate complex **1a**, mixed with the residual metal. A ten coordinate isomer of this complex **1b** has recently been reported from an analogous reaction of pure lanthanum metal and $HNpy_2$.[6] Crystals of **1a** obtained from the cooled reaction flux were examined by single crystal X-ray structure determination. The structure (Fig. 1a, Table 1) consists of a di-lanthanum unit with two eight-coordinate La centres bridged through the amido nitrogen atoms of two Npy_2 ligands. Each of the py arms of both bridging ligands bind to one or other of the La atoms thus defining a μ-η^2:η^2 coordination (Fig. 1). Two terminal chelating Npy_2 ligands, bound through the amide and one of the py nitrogen atoms, complete each La coordination sphere. The structure matches those known for analogous complexes with smaller rare earths Gd and Yb,[6] and evidently for other members Ce → Yb,[4] but contrasts with the reported La structure *viz.* a ten-coordinate dimer $[La(\mu\text{-}Npy_2)_2(Npy_2)]_2$ (**1b**),[6] with four bridging (μ-η^2:η^2) and a single terminal (η^2) Npy_2 ligand for each La (Fig. 1b). Thus, the present structure establishes that the eight coordinate dimeric form extends to La, and thus covers the La → Yb series.

$$2LaNi_5 + 6HNpy_2 \rightarrow [La(Npy_2)_3]_2 + 3H_2 + 10Ni \qquad (2)$$

Complex **1a** was soluble in THF–PhMe and crystallisation of the bulk product from this medium gave the previously reported[6] ten coordinate **1b** in moderate yield, thereby establishing isomer interconversion in one direction. Despite the presence of THF, the complex crystallises as a solvent free homoleptic species (*i.e.* without incorporation of THF) attesting to the strength of the La–Npy_2 coordination (similarly, $[K(\mu\text{-}Npy_2)]_\infty$ crystallises from THF as a THF-free polymer[14]). Variable temperature (30–60 °C) ^1H NMR spectra of **1b** in $[D_8]$-THF, not previously reported, showed a set of four Npy_2 resonances corresponding to a symmetrically bound ligand (*i.e.* the μ-η^2:η^2-Npy_2 in **1b**), along with an 8-line pattern of an unsymmetrically bound Npy_2 (*i.e.* the terminal η^2-Npy_2 in **1b** which has one coordinated and one free py group). The relative integration indicated the two ligand types to be in a 2 : 1 ratio, consistent with the presence of the ten-

School of Chemistry, Monash University, Clayton, Australia. E-mail: glen.deacon@sci.monash.edu.au; Fax: +613 9905 4597; Tel: +613 9905 4568

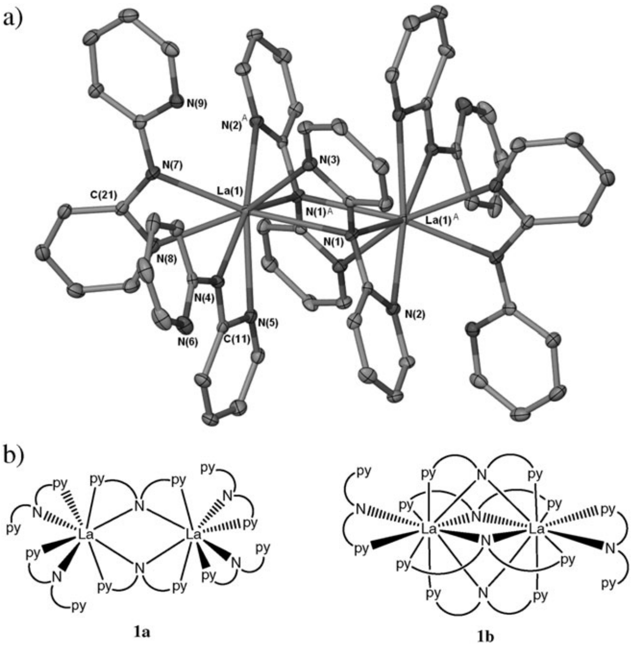

Fig. 1 (a) The molecular structure of eight-coordinate $[La(\mu\text{-}Npy_2)(Npy_2)_2]_2$ (**1a**) shown with 50% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Atoms N(1)A and N(2)A are generated by symmetry. (b) Schematic representation of the La–Npy_2 connectivity for eight-coordinate **1a** and ten-coordinate **1b**.[6]

coordinate **1b** in solution rather than the eight coordinate **1a** which would have two symmetrical (μ-η^2:η^2) and four unsymmetrical (η^2) Npy_2 ligands. The ready conversion of **1a** into **1b** suggests the latter is the thermodynamically favoured isomer at or near room temperature, the reaction being driven by the additional bonds formed. Only with the largest rare earth can the steric disadvantage of the higher coordination number be overcome.

Table 1 Bond distances (Å) and angles (°) in eight coordinate $[La(\mu\text{-}Npy_2)(Npy_2)_2]_2$ (**1a**)

La(1)–N(1)	2.758(2)	La(1)–N(5)	2.621(2)
La(1)–N(1)#1	2.668(2)	La(1)–N(7)	2.483(2)
La(1)–N(2)#1	2.636(2)	La(1)–N(8)	2.672(2)
La(1)–N(3)	2.633(2)	La(1)–C(11)	3.074(3)
La(1)–N(4)	2.532(2)	La(1)–C(21)	3.097(3)
		La(1)–La(1)#1	4.2015(8)
N(1)–La(1)–N(1)#1	78.53(7)	N(2)#1–La(1)–N(3)	86.23(7)
N(1)–La(1)–N(2)#1	102.89(6)	N(2)#1–La(1)–N(4)	164.54(7)
N(1)–La(1)–N(3)	50.24(6)	N(2)#1–La(1)–N(5)	141.60(7)
N(1)–La(1)–N(4)	86.80(7)	N(2)#1–La(1)–N(7)	79.69(7)
N(1)–La(1)–N(5)	76.75(6)	N(2)#1–La(1)–N(8)	97.51(7)
N(1)–La(1)–N(7)	158.09(7)	N(3)–La(1)–N(4)	91.01(7)
N(1)–La(1)–N(8)	147.13(6)	N(3)–La(1)–N(5)	118.09(7)
N(1)#1–La(1)–N(2)#1	51.15(6)	N(3)–La(1)–N(7)	108.96(7)
N(1)#1–La(1)–N(3)	103.89(7)	N(3)–La(1)–N(8)	158.00(7)
N(1)#1–La(1)–N(4)	143.91(7)	N(4)–La(1)–N(5)	51.98(7)
N(1)#1–La(1)–N(5)	92.35(7)	N(4)–La(1)–N(7)	86.87(7)
N(1)#1–La(1)–N(7)	117.61(7)	N(4)–La(1)–N(8)	79.61(7)
N(1)#1–La(1)–N(8)	95.14(7)	N(5)–La(1)–N(7)	114.91(7)
		N(5)–La(1)–N(8)	71.27(7)
		N(7)–La(1)–N(8)	51.15(7)

#1 symmetry operator: $-x + 1, -y + 1, -z$.

We have redetermined the structure of **1b** at a lower temperature (123 K) than that reported (170 K)[6] to provide comparability with the structure of **1a** at 123 K, and to improve the precision of the data (threefold reduction in esds) to assist the comparison. The eight coordinate La and analogous Gd[6] structures generally show the expected differential (*ca.* 0.11 Å based on ionic radii[15]) in comparable bond distances (Table 2). The $\langle La\text{–}N_{ter}\rangle$ bond length in eight coordinate **1a**, 2.507 Å, is marginally shorter than the analogous $\langle La\text{–}N_{ter}\rangle$ 2.552 Å in eight-coordinate $[La\{O(SiMe_2Ap)_2\}_2LaRh(cod)]$ (Ap = 2-amido-4-methylpyridine),[16] which also has a chelating La–amido-pyridine moiety. However, the amido La–N distances in the two isomeric La structures **1a** and **1b** show considerable variation, with only the terminal Npy_2 groups showing anywhere near the appropriate bond lengthening with increasing coordination number.[15] Surprisingly, the La–N(py) bond lengths are similar in both isomers **1a** and **1b** and both are significantly shorter than those of neutral py ligands in eight coordinate $[La(\mu\text{-}Cl)Cl_2(py)_4]_2$ (2.762 Å).[17] Furthermore, the La–N(py) bond lengths in **1b** are close to those of the La–N_{ter}(amide), suggesting some degree of delocalization of the negative charge over the NCN moiety (mimicking an amidinate ligand structure). Some of the *ipso* C of the py rings of the Npy_2 ligands are potentially within bonding distance of the La, *e.g.* 3.074(3) and 3.097(3) Å for **1a** (Table 1), (*cf.* $\langle La\text{–}\eta^6\text{-}Ph\rangle$ bond distance 3.186 Å in $La(Odpp)_3$ (Odpp = 2,6-diphenylphenolate)[18]). They are not considered to be bonded, but are brought close by the binding of two proximal nitrogen atoms.

We then examined the direct reaction of $LaNi_5$ with 8-hydroxyquinoline (HOQ) in an endeavour to extract both metals from the alloy, since this ligand system has previously been utilised for homoleptic RE–Ca bimetallics.[9] Thus, reaction of $LaNi_5$ with HOQ in the presence of mercury and an inert flux of 1,3,5-tri-*tert*-butylbenzene, gave yellow crystals of $[Ni_2La(OQ)_7]$ (**2**) (eqn (3)) along with a red glassy material.

$$LaNi_5 + 7HOQ \rightarrow [LaNi_2(OQ)_7] + 7/2H_2 + 3Ni \qquad (3)$$

Separation of the yellow crystals by hand enabled a single crystal structure determination of **2**, whilst a Ni : La ratio of 2 : 1 was confirmed for the remaining yellow crystals by Electron Dispersive X-ray spectroscopy (EDX). The composition of the bimetallic with a 2 : 1 Ni to La ratio contrasts with that of the analogous Nd–Ca complex $[CaNd_2(OQ)_8]$,[9] which has a higher RE content.

The structure of **2** (Fig. 2) shows a bent trimetallic Ni–La–Ni array (Ni–La–Ni 129.6°) located on a crystallographic twofold axis. The unique nickel atom is six-coordinate with a distorted *fac*-octahedral coordination geometry derived from three chelating (O,N) OQ ligands. The La is bound to the Ni subunits through the three *fac*-oxygen atoms, with the remaining OQ ligand (disordered about the twofold axis) located at the apex of the trimetallic and chelating to La. Thus the La is eight-coordinate with a distorted square antiprismatic geometry (defined by two parallel (2.3°) planes O1B, O1C, O1D, O1A* and O1A, N1D, O1B*, O1C*).

Bond distances (Table 3) around Ni are typical but with a slight elongation of the Ni–O bonds compared to, for example,

Table 2 Comparative bond distances (Å) in the two linkage isomers **1a** (CN = 8), and **1b** (CN = 10)[a] and $[Gd(\mu\text{-}Npy_2)(Npy_2)_2]_2$ (CN = 8)[6]

	1a	**1b**	Δ_1 (0.11)[b]
RE–N_{ter}(amide)	2.483(2), 2.532(2)	2.614(6), 2.652(6)	0.131, 0.120
RE–N_{br}(amide)	2.668(2), 2.758(2)	2.708(6)–3.002(6)	0.040, 0.244
RE–N(py)	2.621(2)–2.672(2)	2.598(7)–2.678(6)	−0.023, 0.006

	Gd	Δ_2 (0.11)[c]
RE–N_{ter}(amide)	2.415(5), 2.419(5)	0.068, 0.113
RE–N_{br}(amide)	2.550(6), 2.601(5)	0.118, 0.157
RE–N(py)	2.492(6)–2.524(6)	0.129, 0.148

[a] Current data used for **1b**. [b] Δ_1 = subtraction of **1a** from **1b** (calcd. ionic radii difference Å). [c] Δ_2 = subtraction of Gd from **1a** (calcd. ionic radii difference Å).

those (2.054 Å) of octahedral $[Ni(OQ)_2(HOQ)]$,[19] due to bridging to La. The average La–O_{br} (2.514 Å) is comparable with that (av. La–O_{br} 2.519 Å) of $[\{Ni(tam)\}_2La(ROH)(H_2O)][ClO_4]$ (**3**) (tam = (1,1,1-tris(((2-oxybenzyl)amino)-methyl)ethane; R = $Me_{0.5}Et_{0.5}$),[20] a bimetallic complex which possesses similar *fac*-octahedral $Ni(N_3,O_3)$ sites bridged through phenolate oxygen atoms to an eight-coordinate $La(O_7,N)$ environment. Both **2** and **3** also have a bent Ni–La–Ni (**2**: 129.6 *cf.* **3**: 142.6°) arrangement and similar La–Ni separations (**2**: 3.247(1) *cf.* **3**: 3.1533(7), 3.1900(7) Å). The Ni–La–Ni trimetallic array in **2** is also closely related to the homo-trinuclear complexes $[RE_3(OQ)_9]$ (RE = Ho,[21] Er[22]) and $[Yb_3(OQ)_8(O_2CCH_3)]$[23] in which the central rare earth atoms (M–M–M angles: Ho, 140.62(3); Er 133.48(1); Yb 139.0(1)°) are eight-coordinate, and bound to six OQ anions bridging through their oxygen atoms and one chelating ligand (either 8-quinolinolate or acetate). The M–O_{br} (av) values (Ho, 2.368; Er, 2.350; Yb, 2.319 Å) are consistent with those of **2**, 2.514 Å (av), after accounting for the variation in ionic radii.[15]

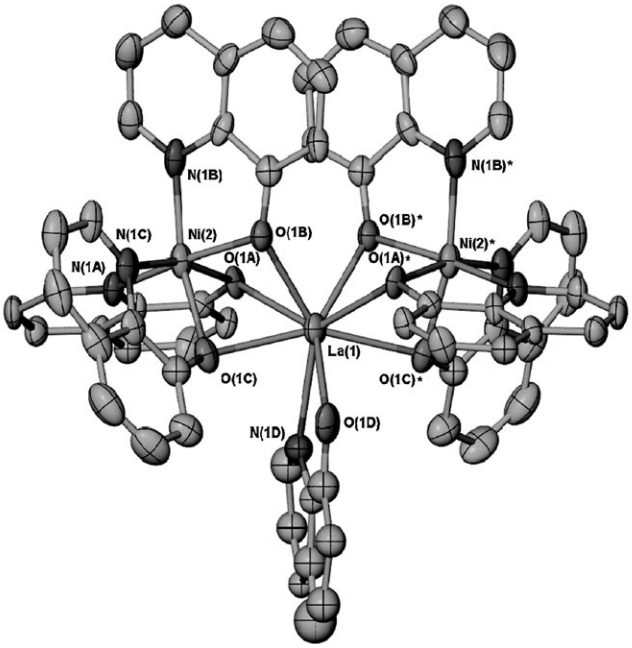

Fig. 2 The structure of the heterobimetallic $[(Ni(\mu\text{-}OQ)_3)_2La(OQ)]$ (**2**) as viewed perpendicular to the twofold axis (atoms denoted * are generated by symmetry) and shown with 50% thermal ellipsoids; hydrogens have been omitted for clarity. Ligand D is disordered over two positions about the twofold axis; only one component is shown.

We are attempting to develop a modified synthesis to provide a bulk amount of **2** to enable evaluation of its physicochemical properties.

Conclusions

We have established that the rare earth alloy $LaNi_5$ can participate in metal-based synthetic reactions. Furthermore, the current syntheses include an exciting new homoleptic lanthanum–nickel bimetallic complex as a result of the simultaneous extraction of both metals in a simple and one step reaction. The product $[LaNi_2(OQ)_7]$ has a higher proportion of the hetero-metal than in the analogous RE/Ca bimetallic $[Nd_2Ca(OQ)_8]$ prepared from a mixture of the two metals. Whilst this may simply reflect the relative ratios of the metals

Table 3 Bond distances (Å) and angles (°) in $[LaNi_2(OQ)_7]$ (**2**)

La environment		Ni environment	
La(1)–O(1A)	2.483(4)	O(1A)–Ni(2)	2.089(4)
La(1)–O(1B)	2.492(5)	O(1B)–Ni(2)	2.056(5)
La(1)–O(1C)	2.567(5)	O(1C)–Ni(2)	2.080(5)
La(1)–O(1D)	2.466(13)	N(1A)–Ni(2)	2.079(6)
La(1)–N(1D)	2.68(2)	N(1B)–Ni(2)	2.079(7)
La(1)–Ni(2)	3.2466(11)	N(1C)–Ni(2)	2.054(6)
O(1A)–La(1)–O(1A)#1	135.0(2)	O(1A)–Ni(2)–O(1B)	86.23(18)
O(1A)–La(1)–O(1B)	69.42(14)	O(1A)–Ni(2)–O(1C)	84.09(18)
O(1A)–La(1)–O(1B)#1	76.86(15)	O(1A)–Ni(2)–N(1A)	80.2(2)
O(1A)–La(1)–O(1C)	67.11(15)	O(1A)–Ni(2)–N(1B)	101.8(2)
O(1A)–La(1)–O(1C)#1	123.08(14)	O(1A)–Ni(2)–N(1C)	164.6(3)
O(1A)–La(1)–O(1D)	138.0(3)	O(1B)–Ni(2)–O(1C)	82.1(2)
O(1A)–La(1)–N(1D)	90.9(4)	O(1B)–Ni(2)–N(1A)	166.4(2)
O(1A)#1–La(1)–N(1D)	132.8(5)	O(1B)–Ni(2)–N(1B)	80.2(2)
O(1B)–La(1)–O(1B)#1	81.7(2)	O(1B)–Ni(2)–N(1C)	97.2(2)
O(1B)–La(1)–O(1C)	64.91(16)	O(1C)–Ni(2)–N(1A)	97.3(2)
O(1B)–La(1)–O(1C)#1	137.23(16)	O(1C)–Ni(2)–N(1B)	160.9(2)
O(1B)–La(1)–O(1D)	110.5(4)	O(1C)–Ni(2)–N(1C)	81.6(3)
O(1B)–La(1)–N(1D)	143.4(5)	N(1A)–Ni(2)–N(1B)	101.6(2)
O(1B)#1–La(1)–N(1D)	124.9(4)	N(1A)–Ni(2)–N(1C)	96.2(2)
O(1C)–La(1)–O(1C)#1	156.4(2)	N(1B)–Ni(2)–N(1C)	93.5(3)
O(1C)–La(1)–O(1D)	75.1(3)		
O(1C)–La(1)–N(1D)	79.2(4)	Ni(2)–La(1)–Ni(2)#1	129.58(4)
O(1D)–La(1)–N(1D)	64.0(6)		
O(1D)–La(1)–O(1A)#1	81.3(3)		
O(1D)–La(1)–O(1B)#1	145.0(3)		
O(1D)–La(1)–O(1C)#1	86.6(3)		
N(1D)–La(1)–O(1C)#1	79.4(5)		

#1 symmetry operator: $-x + 1, y, -z + 1/2$.

in the respective reaction, it is an interesting result given that Ca is significantly more electropositive than Ni.

Experimental

Manipulation of air-sensitive compounds, solvent handling and spectroscopic methods were as previously described.[2,3] Rare earth alloys were obtained from Santuko. 2,2′-Dipyridylamine (Aldrich) and 8-hydroxyquinoline (Merck) were used as received.

Syntheses

[La(Npy$_2$)$_3$]$_2$ (1). A thick walled Carius tube was loaded with LaNi$_5$ (2.59 g, 6.0 mmol of La), HNpy$_2$ (0.69 g, 4.0 mmol) and Hg (1 drop) and evacuated ($<10^{-3}$ mm Hg) and sealed, then heated to *ca.* 170 °C for 48 h. After cooling, several yellow crystals of **1a** were removed for X-ray characterisation (see below). The remaining yellow material mixed with unreacted alloy was extracted with 1 : 1 THF–PhMe (60 mL) and then the solution was concentrated and allowed to stand for several days. The resulting pale yellow crystals of **1b** were collected and dried under vacuum (yield 0.46 g, 53%). $C_{30}H_{24}LaN_9$ (649.48) Found: C 56.27, H 3.82, N 19.26%. Calcd.: C 55.48, H 3.72, N 19.41. IR(Nujol): 1598s, 1586s, 1547m, 1420vs, 1341vs, 1298m, 1150m, 1006w, 993m, 830w, 769m, 732m, cm^{-1}. ^{1}H NMR (300 MHz, 303 K, [D$_8$]-THF): δ 7.64, d J = 5.2 Hz, 1H; 6.59, dd ^3J = 5.2 Hz ^4J = 1.3Hz, 4H; 7.48, d J = 8.6 Hz, 1H; 7.37, t J = 8.5 Hz, 1H; 7.00, ddd ^3J = 8.6 Hz ^3J = 7.0 Hz ^4J = 2.0 Hz, 4H; 6.93, d J = 8.3 Hz, 1H; 6.77, d J = 8.4 Hz, 1H; 6.62, d J = 8.5 Hz, 4H; 6.38, t J = 6.7 Hz, 1H; 6.28, t, J = 6.3 Hz, 1H; 6.14, ddd ^3J = 7.0 Hz; ^3J = 5.3 Hz; ^4J = 1.0 Hz, 4H; 6.04, t J = 6.1 Hz, 1H; ppm.

[Ni$_2$La(OQ)$_7$] (2). LaNi$_5$ alloy (0.75 g, 1.74 mmol), HOQ (0.30 g, 2.07 mmol), Bu$^t{}_3$C$_6$H$_3$ (0.80 mmol) and 5 drops of Hg were heated to 190 °C for 4 d in a sealed and evacuated thick walled Carius tube giving yellow crystals and red glass. The Bu$^t{}_3$C$_6$H$_3$ was removed by sublimation and numerous small yellow crystals of **2** were separated by hand (yield $<10\%$) and identified by X-ray crystallography. $C_{63}H_{42}LaN_7Ni_2O_7$ (1265.35) Found: C 58.82, H 3.24, N 7.49%. Calcd.: C 59.80, H 3.35, N 7.75. Mp >360 °C, IR (Nujol): 1597s, 1566s, 1493s, 1425s, 1386s, 1278vs, 1227s, 1106vs, 822vs, 787vs, 744vs, 730vs cm^{-1}. EDX Ni : La = 2.0 : 0.9.

X-Ray crystallography

Representative crystals were covered in viscous oil and cut to a suitable size then mounted on a glass fibre and placed in the cold nitrogen stream of an Enraf-Nonius KAPPA CCD diffractometer. Spheres of data (MoK$_\alpha$ λ 0.71073 Å, 1.0° frames in ϕ and ω) were collected and, after correction for absorption (SORTAV), were merged to N unique data. Structures were solved by heavy atom methods and refined using full matrix least squares (SHELX 97) with anisotropic thermal parameter forms for all non-hydrogen atoms for **1a**. In **2**, ligand D was modelled as disordered over two positions, each component related by the twofold axis. The geometries of the six-membered rings were restrained and non-hydrogen atoms were refined with isotropic thermal parameters. Hydrogen atoms were not included in the disordered components. Otherwise, hydrogen atoms were placed in calculated positions for all structures and were not refined. For **1b**, initial data statistics suggested the centrosymmetric space group $C2/c$, which gave a solution having terminal Npy$_2$ ligands disordered about the twofold axis. The preferred solution in Cc has no disorder and marginally improved R values.

CCDC reference numbers 298866–298868. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600868b

[La(μ-Npy$_2$)(Npy$_2$)$_2$]$_2$ (1a). $C_{60}H_{48}La_2N_{18}$ FW 1298.98, monoclinic $P2_1/n$, yellow prism 0.30 × 0.30 × 0.38 mm^3, a = 10.5878(1), b = 15.3676(2), c = 17.7435(3) Å, β = 114.068(1)°, V = 2636.04(6) Å^3, $T \sim 123$ K, Z = 2, ρ_{calc} 1.637 g cm^{-3}, $\mu_{\text{MoK}\alpha}$ 1.660 mm^{-1}, $T_{\text{min,max}}$ 0.745, 0.815, $2\theta_{\text{max}}$ 55.0°, N_{total} 23117, N 6260 (R_{int} 0.073), GooF 1.051, $R1$ 0.0327, $wR2$ 0.0851 ($I > 2\sigma(I)$), $R1$ 0.0420, $wR2$ 0.0896 (all data).

[La(μ-Npy$_2$)(Npy$_2$)$_2$]$_2$ (1b). $C_{60}H_{48}La_2N_{18}$ FW 1298.98, monoclinic Cc, yellow prism 0.25 × 0.25 × 0.25 mm^3, a = 16.6833(2), b = 16.9265(2), c = 20.0193(2) Å, β = 106.219(1)°, V = 5428.3(19) Å^3, $T \sim 123$ K, Z = 4, ρ_{calc} 1.589 g cm^{-3}, $\mu_{\text{MoK}\alpha}$ 1.612 mm^{-1}, $2\theta_{\text{max}}$ 55.0°, N_{total} 29214, N 11588 (R_{int} 0.045), GooF 1.047, $R1$ 0.0293, $wR2$ 0.0648 ($I > 2\sigma(I)$), $R1$ 0.0446, $wR2$ 0.0719 (all data). x_{abs} = 0.023(14). Marginal differences with reported unit cell dimensions are attributed to the lower temperature of the current data collection.[6]

[{Ni(μ-OQ)$_3$}$_2$La(OQ)] (2). $C_{63}H_{36}LaN_7Ni_2O_7$ FW 1259.32, monoclinic $C2/c$, yellow rectangular 0.10 × 0.08 × 0.06 mm^3, a = 15.499(3), b = 19.150(4), c = 17.485(4) Å, β = 90.67(3)°, V = 5189.5(18) Å^3, $T \sim 123$ K, Z = 4, ρ_{calc} 1.612 g cm^{-3}, $\mu_{\text{MoK}\alpha}$ 1.660 mm^{-1}, $T_{\text{min,max}}$ 0.9105 and 0.8570, $2\theta_{\text{max}}$ 50.0°, N_{total} 21168, N 4543 (R_{int} 0.1419), GooF 1.020, $R1$ 0.0595, $wR2$ 0.0949 ($I > 2\sigma$ (I)), $R1$ 0.1692, $wR2$ 0.1279 (all data).

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