Solvent Control of Structural Type: Three Different Structures from the Reaction of a Dimeric Copper Complex with Lanthanum Nitrate in Three Different Solvents†

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The reaction of a dimeric copper complex, $[Cu_2L_4]$ **1** (L = $C_5H_3ClNO^-$, the anion of 6-chloro-2-hydroxypyridine), with hydrated lanthanum nitrate has been studied. The crystalline products are determined by the solvent used. If the reaction is carried out in a mixture of methanol–dichloromethane a compound of stoichiometry $[Cu_3LaL_5(NO_3)_3(OMe)(MeOH)_2]\cdot1.5MeOH\cdot0.5Et_2O$ **2** is isolated. If the reaction is carried out in ethanol–dichloromethane a compound of stoichiometry $[Cu_3LaL_8(NO_3)(EtOH)]\cdot0.5Et_2O$ **3** is found. If acetonitrile–dichloromethane is used the complex $[Cu_2La_2L_8(HL)_2(NO_3)_2]\cdot2HL\cdot2MeCN$ **4** can be crystallised. All of these compounds have been characterised by X-ray crystallography and the unusual structures are described.

Ligands based on 2-hydroxypyridine (2-pyridone, C_5H_5NO) have been used previously as bridges to form polynuclear arrays of d-block metals.[1–9] We have been attempting[10–12] to utilise such ligands to bridge between d- and f-block metals, giving complexes which will allow us to study the interaction between metals from different regions of the Periodic Table. The rationale behind the use of this ligand system is that the oxophilic f-block metal should bind preferentially to the exocyclic oxygen of the ligand, while the deprotonated ring nitrogen binds to the d-block metal.

In the initial stages of this investigation we have concentrated on copper–lanthanoid complexes, and have identified several factors which influence the structures of the compounds formed. We have shown that quite different compounds result if we vary the ligand from 2-hydroxypyridine[10] to 2-hydroxy-6-methylpyridine[11] to 6-chloro-2-hydroxypyridine HL;[12] we have also shown[10] that the nature of the anion present has a strong influence. Preliminary magnetic measurements on a Cu_4Gd_2 complex of the parent ligand[10] have shown that ferromagnetic coupling occurs between copper and gadolinium, confirming interesting results reported previously by Gatteschi,[13] Matsumato[14] and more recently Kahn[15] and their co-workers. In our earlier investigations, which were carried out either in methanol or in methanol–dichloromethane, we have found interference from the formation of methoxide bridges.[10,12] In the one reaction carried out in the absence of methanol, an unusual hydroxide-bridged La_8Cu_{12} complex resulted.[11] It therefore seemed worthwhile to investigate such reactions in different solvent mixtures. Here we report the results of this work. A brief account of part of this work has appeared in a preliminary communication.[12]

Experimental

Preparation of Compounds.—The compound $[Cu_2L_4]$ **1** was prepared as described previously.[12] All solvents were used as obtained. Hydrated lanthanum nitrate was obtained from Johnson Matthey. Satisfactory elemental analyses were obtained for all compounds (Found: C, 27.4; H, 2.8; N, 8.5. Calc. for **2**: C, 27.3; H, 2.6; N, 8.5. Found: C, 34.4; H, 2.9; N, 7.9. Calc. for **3**: C, 34.5; H, 2.3; N, 8.4. Found: C, 35.3; H, 2.0; N, 9.8. Calc. for **4**: C, 35.6; H, 2.2; N, 10.4%).

$[Cu_3LaL_5(NO_3)_3(OMe)(MeOH)_2]\cdot1.5MeOH\cdot0.5Et_2O$ **2**. Compound **1** (0.24 mmol) was dissolved in CH_2Cl_2 (20 cm^3) giving a deep red solution and to this was added $La(NO_3)_3\cdot5H_2O$ (0.5 mmol) dissolved in methanol (8 cm^3). The solution became green and was filtered then evaporated to give a green tar, which was redissolved in fresh methanol (5 cm^3) and filtered. Diethyl ether vapour was allowed to diffuse into the solution, leading to the formation of dark green crystals of **2** over a period of one week. Yield of crystalline material **2**: 17%.

$[Cu_3LaL_8(NO_3)(EtOH)]\cdot0.5Et_2O$ **3**. Compound **1** (0.24 mmol) was dissolved in CH_2Cl_2 (20 cm^3), giving a deep red solution and to this was added $La(NO_3)_3\cdot5H_2O$ (0.5 mmol) dissolved in ethanol (8 cm^3). The solution became green and was filtered. The volume was reduced to half by evaporation at reduced pressure and diethyl ether vapour was allowed to diffuse into the solution, leading to the formation of dark green crystals of **3** over a period of three months. Yield of crystalline material **3**: 9%.

$[Cu_2La_2L_8(HL)_2(NO_3)_2]\cdot2HL\cdot2MeCN$ **4**. Compound **1** (0.8 mmol) was dissolved in CH_2Cl_2 (50 cm^3), giving a deep red solution and to this was added $La(NO_3)_3\cdot5H_2O$ (1.6 mmol) dissolved in methanol (8 cm^3). The solution became green and was filtered to remove a small quantity of green precipitate. The solution was allowed to stand overnight, and a further cream precipitate formed which was again removed by filtration. The remaining solution was evaporated to dryness, then redissolved in fresh acetonitrile (5 cm^3) and again filtered. Diethyl ether vapour was allowed to diffuse into the solution. This led to the formation of crystals of **1**, which were removed by filtration. The filtrate was allowed to stand and green crystals of **4** grew after approximately thirteen months. Over this period unreacted **1** was also collected from the reaction vial. Yield of crystalline material **4**: 2%.

Crystallography.—Crystal data and data collection and refined parameters for compounds **2**–**4** are given in Table 1. Atomic coordinates are listed in Tables 2–4, and selected bond lengths and angles in Tables 5–7.

Data collection and processing. Stoë Stadi-4 diffractometer equipped with Oxford Cryostems low-temperature device[18] operating at 150 K, ω–2θ scans using the learnt-profile method[19] for **2** and **3**, ω–2θ scans for **4** (graphite-monochromated Mo-Kα radiation). Data were corrected for Lorentz and polarisation factors. For **2** an empirical absorption correction gave, based on azimuthal measurements, minimum

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Experimental data for the X-ray diffraction studies of compounds **2**–**4**[a]

Compound	**2**	**3**	**4**
Formula	$C_{31.5}H_{37}Cl_5Cu_3LaN_8O_{19}$	$C_{44}H_{35}Cl_8Cu_3LaN_9O_{12.5}$	$C_{64}H_{46}Cl_{12}Cu_2La_2N_{16}O_{18}$
M	1336	1502	2157
a/Å	11.2055(19)	10.850(15)	11.549(8)
b/Å	12.9050(28)	12.158(19)	13.785(10)
c/Å	17.059(4)	21.17(3)	14.144(12)
α/°	81.345(13)	79.41(8)	73.71(6)
β/°	85.310(11)	78.02(9)	66.63(6)
γ/°	76.025(13)	78.31(9)	82.37(6)
U/Å^3	2364(1)	2646(1)	1984(3)
Z	2	2	1[b]
D_c/g cm^{-3}	1.884	1.892	1.806
F(000)	1322	1480	1062
Crystal size/mm	0.66 × 0.39 × 0.08	0.19 × 0.19 × 0.10	0.50 × 0.25 × 0.25
Crystal colour and shape	Green plate	Green plate	Green column
θ range/°	2.5 to 22.5	2.5 to 22.5	2.5 to 22.5
μ/mm^{-1}	2.59	2.47	2.07
Absorption correction	Yes	No	No
No. of unique data	6337	6939	5161
Observed data [$I > 2\sigma(I)$]	5628	5102	5151
Refinement on	*F*	*F*	F^2
No. of parameters	607	687	514
Maximum Δ/σ ratio	0.038	0.038	0.01
R, *R*′[c]	0.0291, 0.0311	0.0473, 0.0481	
*R*1, *wR*[d]			0.0463, 0.1161
Weighting scheme,[e] w^{-1} =	$\sigma^2(F) + 0.000\,10F^2$	$\sigma^2(F) + 0.000\,63F^2$	$\sigma^2(F_o^2) + (0.0849p)^2 + 0.73p$
Goodness of fit	1.488	1.008	1.072
Largest difference peak and hole/e Å^{-3}	1.28, −0.63	1.09, −1.42	1.63, −1.57

[a] Details in common: T/K = 150.0(1), triclinic crystal system, space group $P\bar{1}$. [b] The molecule lies on an inversion centre. [c] Ref. 16. [d] Ref. 17. [e] $p = [\max.(F_o^2, 0) + 2F_c^2]/3$.

Table 2 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
La	10 615.5(2)	1 026.2(2)	2 980.5(1)	C(45)	5 567(4)	2 967(3)	3 233.3(24)
Cu(1)	7 086.5(4)	1 670.5(4)	2 022.8(3)	N(5)	6 971(3)	759.2(25)	3 069.1(20)
Cu(2)	7 902.5(4)	3 223.0(4)	3 297.8(3)	O(5)	8 349.2(23)	1 644.0(20)	3 399.7(16)
Cu(3)	6 921.9(4)	4 134.1(4)	1 713.4(3)	Cl(5)	5 442.6(11)	−169.3(10)	2 536.4(8)
N(1)	7 796(3)	526(3)	1 366.4(21)	C(51)	7 591(3)	1 010(3)	3 646.9(25)
O(1)	9 486(3)	379.8(23)	2 035.1(18)	C(52)	7 416(4)	618(3)	4 442(3)
Cl(1)	5 717.1(11)	943.2(11)	669.6(8)	C(53)	6 619(4)	−63(3)	4 644(3)
C(11)	8 995(4)	45(3)	1 498(3)	C(54)	6 003(4)	−339(3)	4 060(3)
C(12)	9 620(4)	−769(4)	1 039(3)	C(55)	6 205(4)	96(3)	3 294(3)
C(13)	9 002(5)	−1 061(4)	480(3)	N(1n)	12 266(3)	1 851(3)	1 553.4(23)
C(14)	7 771(5)	−550(4)	340(3)	O(11n)	12 958(3)	2 106(3)	1 010.9(19)
C(15)	7 235(4)	230(4)	796(3)	O(12n)	12 491.0(25)	1 794.6(23)	2 280.4(17)
N(2)	8 652(3)	4 428(3)	1 607.8(20)	O(13n)	11 251(3)	1 627.4(24)	1 421.8(18)
O(2)	9 364.3(24)	3 032.9(10)	2 577.5(16)	N(2n)	11 041(3)	1 763(3)	4 484.0(22)
Cl(2)	7 663.0(12)	5 960.9(10)	514.2(8)	O(21n)	11 460(3)	2 098.4(23)	3 813.5(18)
C(21)	9 574(3)	3 853(3)	2 071.7(25)	O(22n)	11 270(3)	2 063.4(24)	5 091.8(18)
C(22)	10 714(4)	4 139(3)	2 026(3)	O(23n)	10 364(3)	1 094.9(23)	4 514.5(18)
C(23)	10 904(4)	4 989(4)	1 482(3)	N(3n)	12 865(3)	−828(3)	3 165.2(25)
C(24)	9 966(4)	5 563(4)	996(3)	O(31n)	12 302(3)	−629.5(23)	2 514.0(19)
C(25)	8 870(4)	5 258(3)	1 092(3)	O(32n)	13 644(3)	−1 657(3)	3 323.2(24)
N(3)	7 764(3)	4 785(3)	3 319.8(20)	O(33n)	12 569(3)	−116.3(25)	3 627.5(19)
Cl(3)	9 499.3(11)	4 099.4(9)	4 328.1(8)	O(1m)	7 352.0(25)	2 835.8(21)	1 248.1(16)
O(3)	6 311.2(25)	5 232.6(22)	2 384.9(18)	C(1m)	8 159(5)	2 740(4)	556(3)
C(31)	6 926(4)	5 539(3)	2 878.6(25)	O(2m)	5 273.4(25)	4 690.2(23)	1 178.8(18)
C(32)	6 743(4)	6 635(3)	2 980(3)	C(2m)	4 635(4)	4 002(4)	862(3)
C(33)	7 434(4)	6 927(3)	3 494(3)	O(3m)	10 137(3)	−716.1(23)	3 687.5(20)
C(34)	8 321(4)	6 163(3)	3 924(3)	C(3m)	10 077(6)	−1 641(4)	3 343(4)
C(35)	8 431(4)	5 117(3)	3 809(3)	O(4m)	13 345(3)	5 905(3)	1 931(3)
N(4)	6 224(3)	3 235(3)	3 769.3(20)	C(4m)	13 238(7)	5 627(9)	2 784(5)
O(4)	6 105.4(24)	2 917.2(21)	2 518.2(16)	O(5m)	13 354(7)	7 890(6)	1 320(4)
Cl(4)	6 613.1(13)	3 711.0(11)	5 145.4(7)	C(5m)	14 532(10)	7 914(9)	1 267(7)
C(41)	5 718(4)	3 348(3)	4 499(3)	C(1e)	13 354(7)	7 890(6)	1 320(4)
C(42)	4 576(4)	3 184(4)	4 753(3)	C(5e)	12 114(13)	5 610(11)	3 198(9)
C(43)	3 932(4)	2 860(4)	4 198(3)	C(2e)	13 324(20)	6 868(18)	2 033(13)
C(44)	4 412(4)	2 748(4)	3 443(3)				

Table 3 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for compound **3**

Atom	*x*	*y*	*z*
La	1247.5(4)	3499.4(4)	2349.5(2)
Cu(1)	1405.9(9)	1702.3(8)	1013.8(5)
Cu(2)	2830.2(9)	461.7(8)	2496.1(5)
Cu(3)	2867.7(9)	1855.3(8)	3887.8(5)
N(1n)	−504(7)	5786(6)	2229(4)
O(11n)	−633(6)	5086(5)	2740(3)
O(21n)	430(5)	5529(5)	1780(3)
O(31n)	−1252(7)	6693(5)	2170(4)
N(1r)	4248(6)	−415(5)	2933(3)
O(1r)	2923(5)	289(4)	3788(3)
C(11r)	3980(8)	−375(6)	3577(4)
C(21r)	4777(8)	−1037(7)	3993(4)
C(31r)	5821(9)	−1781(8)	3734(5)
C(41r)	6087(8)	−1830(6)	3064(4)
C(51r)	5280(8)	−1129(6)	2696(4)
Cl(1r)	5557.7(20)	−1103.2(19)	1857.8(11)
N(2r)	2451(6)	−874(5)	2191(3)
O(2r)	2690(5)	419(4)	1285(3)
C(12r)	2397(7)	−574(6)	1551(4)
C(22r)	2013(7)	−1299(6)	1212(4)
C(32r)	1688(8)	−2316(7)	1549(5)
C(42r)	1795(8)	−2629(7)	2188(5)
C(52r)	2174(8)	−1881(6)	2492(4)
Cl(2r)	2310.7(23)	−2228.4(19)	3307.6(12)
N(3r)	80(6)	954(5)	1683(3)
O(3r)	1158(5)	1391(4)	2387(3)
C(13r)	250(7)	893(6)	2293(4)
C(23r)	−506(8)	318(7)	2813(4)
C(33r)	−1374(8)	−237(8)	2682(5)
C(43r)	−1532(8)	−214(8)	2054(5)
C(53r)	−778(8)	401(6)	1567(4)
Cl(3r)	−907.1(23)	488.9(20)	760.3(12)
N(4r)	73(6)	2990(5)	722(3)
O(4r)	−373(5)	3298(4)	1780(3)
C(14r)	−646(8)	3593(7)	1211(4)
C(24r)	−1612(8)	4506(7)	1052(5)
C(34r)	−1870(8)	4776(8)	441(5)
C(44r)	−1168(8)	4168(7)	−52(5)
C(54r)	−221(8)	3298(7)	126(4)
Cl(4r)	702.5(23)	2505.1(19)	−4605(12)
N(5r)	1147(6)	1834(5)	4407(3)
O(5r)	582(5)	2832(5)	3478(3)
C(15r)	219(8)	2354(7)	4052(4)
C(25r)	−1059(8)	2327(8)	4348(4)
C(35r)	−1370(9)	1789(8)	4972(5)
C(45r)	−410(8)	1238(7)	5325(25)
C(55r)	816(8)	1305(7)	5016(4)
Cl(5r)	2090.8(24)	692.0(23)	5411.3(12)
N(6r)	4488(6)	1965(5)	3241(3)
O(6r)	3247(5)	1960(4)	2509(3)
C(16r)	4371(7)	2073(6)	2619(4)
C(26r)	5369(8)	2333(7)	2108(4)
C(36r)	6482(8)	3475(7)	2269(5)
C(46r)	6644(8)	2320(7)	2913(5)
C(56r)	5634(8)	2049(7)	3378(4)
Cl(6r)	5722.3(22)	1789.6(21)	4197.2(12)
N(7r)	2944(6)	2332(5)	487(3)
O(7r)	2406(5)	3495(4)	1251(3)
C(17r)	3205(8)	3158(7)	769(4)
C(27r)	4352(8)	3613(7)	506(5)
C(37r)	5175(8)	3164(8)	−7(5)
C(47r)	4909(9)	2289(8)	−260(5)
C(57r)	3816(8)	1893(7)	9(4)
Cl(7r)	3444.6(23)	757.6(19)	−2618(12)
N(8r)	4212(9)	4694(7)	3128(6)
O(8r)	2687(6)	4482(5)	2617(3)
C(18r)	3694(9)	4858(7)	2561(5)
C(28r)	4336(10)	5419(8)	2023(8)
C(38r)	5434(13)	5833(9)	1980(9)
C(48r)	5914(13)	5668(11)	2533(10)
C(58r)	5291(13)	5106(10)	3082(10)
Cl(8r)	5865(5)	4854(3)	3820(3)
O(1e)	2950(6)	3328(5)	4107(4)
C(1e)	2053(22)	4141(19)	4386(12)
C(2e)	2550(21)	5016(18)	4627(11)
C(1s)	312(24)	4637(20)	3919(13)
C(2s)	923(23)	5503(20)	4507(13)
O(1s)	921(14)	4538(12)	4923(8)
C(3s)	144(3)	4452(22)	5519(14)
C(4s)	988(22)	3456(19)	5992(12)

and maximum transmission factors of 0.2295 and 0.3714 respectively.

Structure analysis and refinement. All three structures were solved by the heavy-atom method, which revealed the position of the lanthanum atom. All remaining non-hydrogen atoms were located from subsequent ΔF maps and were refined anisotropically. The hydrogen atoms were included in the refinement at idealised positions [C–H 1.08 Å], and with fixed isotropic thermal parameters [U = 0.06 Å^2]. Structure solution of **2**, **3** and **4**, and refinement of **2** and **3** were carried out using SHELX 76[16] and published scattering factors;[20] refinement of **4** used SHELXL 92.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Reaction in Methanol.—The dimeric copper compound **1** is deep red both as a solid and in CH_2Cl_2 solutions. Upon addition of MeOH the colour changes immediately to light green, but repeated attempts to isolate a green solid from these solutions merely led to red crystals of **1** reforming. If extremely dilute solutions were prepared a new purple tetranuclear copper complex, $[Cu_4(OMe)_4L_4]$ could be isolated.[21] Addition of hydrated lanthanum nitrate in MeOH also leads to a green solution, but here diffusion of diethyl ether vapour into the solution gives dark green crystals of $[Cu_3LaL_5(NO_3)_3(OMe)(MeOH)_2]\cdot 1.5MeOH\cdot 0.5Et_2O$ **2**.

The structure of compound **2** is shown in Fig. 1. It is a highly asymmetric complex, with each of the three copper atoms in chemically distinct sites. Cu(1) is four-co-ordinate, bound to two nitrogens from L rings, one μ-oxygen from a third L, and one μ-oxygen from a deprotonated methanol. These two μ-O atoms are shared with Cu(3). Cu(1) therefore has a *cis* 2N,2O array of donor atoms. Atom Cu(2) also has a *cis*-2N,2O set of donor atoms, with all the donors coming from L units. The oxygens are again μ-bridging, this time between Cu(2) and La. Atom Cu(3) has a quite different co-ordination sphere, consisting of one N and four O atoms. Two of the oxygens are the pair shared with Cu(1), one is from a L unit, and the final oxygen comes from a terminal molecule of MeOH. The nitrogen bound to Cu(3) comes from a L unit.

The co-ordination geometries of these three coppers are all distorted. For Cu(1) and Cu(2) the distortion is from square planar. For Cu(1) the chief distortions are a reduction of the angle between the two O atoms to 79.3°, and an angle between the O–Cu–O and the N–Cu–N planes of 17.3°. For Cu(2) the chief distortions are a reduction of the angle between the two μ-oxygens to 80.9°, and a 19.2° angle between the O–Cu–O and N–Cu–N planes. Atom Cu(3) shows even greater distortion from a geometry based on a trigonal bipyramid, with O(3) and O(1m) in the axial positions. The O(3)–Cu(3)–O(1m) angle is 166.0°, and the angles within the triangular plane all deviate from 120°, being 89.1, 132.0 and 138.8°. The Cu–O bond lengths vary greatly, from a minimum of 1.899 Å [between Cu(3) and the bridging methoxide] to a maximum of 2.246 Å [Cu(3) to O(4), an oxygen from a binucleating L]. The Cu–N bond

Table 4 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for compound **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
La	387(1)	866(1)	10 881(1)	Cl(3r)	803(3)	5 145(2)	8 282(2)
Cu	2 428(1)	968(1)	7 905(1)	N(4r)	3 561(6)	−144(6)	8 364(6)
N(1n)	1 102(9)	2 011(6)	12 124(7)	O(4r)	2 423(6)	270(5)	9 932(5)
O(11n)	1 908(6)	1 521(6)	11 534(6)	C(14r)	3 361(8)	−245(7)	9 412(8)
O(21n)	−15(6)	1 998(6)	12 185(6)	C(24r)	4 156(8)	−875(7)	9 861(8)
O(31n)	1 368(8)	2 476(6)	12 626(6)	C(34r)	5 095(9)	−1 419(8)	9 286(9)
N(1r)	3 273(6)	2 058(6)	8 077(6)	C(44r)	5 275(9)	−1 350(8)	8 230(9)
O(1r)	1 494(5)	2 326(4)	9 470(5)	C(54r)	4 486(9)	−711(7)	7 827(8)
C(11r)	2 664(8)	2 569(7)	8 838(7)	Cl(4r)	4 640(2)	−625(2)	6 527(2)
C(21r)	3 279(10)	3 322(8)	8 953(8)	N(5r)	51(7)	−337(6)	12 893(6)
C(31r)	4 480(10)	3 566(8)	8 271(9)	O(5r)	−1 671(5)	36(5)	12 442(5)
C(41r)	5 105(9)	3 083(8)	7 467(9)	C(15r)	−1 236(9)	−325(7)	13 205(7)
C(51r)	4 482(8)	2 258(7)	7 396(8)	C(25r)	−2 028(10)	−670(8)	14 303(8)
Cl(1r)	5 161(2)	1 754(2)	6 367(2)	C(35r)	−1 484(13)	−1 019(8)	15 031(9)
N(2r)	1 050(6)	1 963(6)	7 697(6)	C(45r)	−159(12)	−1 061(8)	14 688(8)
O(2r)	−43(5)	871(4)	9 257(4)	C(55r)	532(10)	−703(8)	13 634(9)
C(12r)	−75(8)	1 645(7)	8 489(7)	Cl(5r)	2 165(3)	−735(3)	13 167(3)
C(22r)	−1 208(8)	2 173(7)	8 467(7)	N(6r)	6 257(7)	4 210(6)	4 540(6)
C(32r)	−1 162(9)	3 015(7)	7 645(8)	O(6r)	4 499(6)	4 525(5)	4 125(5)
C(42r)	12(9)	3 345(8)	6 840(8)	C(16r)	5 583(9)	4 015(7)	4 032(7)
C(52r)	1 048(8)	2 785(7)	6 921(7)	C(26r)	5 982(9)	3 312(7)	3 419(8)
Cl(2r)	2 524(2)	3 151(2)	5 948(2)	C(36r)	7 109(9)	2 784(8)	3 327(8)
N(3r)	−504(7)	3 613(6)	9 684(6)	C(46r)	7 839(9)	2 996(7)	3 834(8)
O(3r)	−1 339(5)	2 128(5)	10 812(5)	C(56r)	7 357(9)	3 680(8)	4 422(7)
C(13r)	−1 529(9)	3 027(8)	10 364(8)	Cl(6r)	8 221(2)	3 960(2)	5 086(2)
C(23r)	−2 720(9)	3 524(8)	10 484(8)	N(1s)	4 092(10)	4 077(8)	1 775(10)
C(33r)	−2 819(10)	4 488(8)	9 941(8)	C(1s)	3 219(12)	4 062(9)	2 499(10)
C(43r)	−1 737(9)	5 043(8)	9 220(7)	C(2s)	2 080(12)	4 059(9)	3 419(10)
C(53r)	−610(9)	4 566(7)	9 112(7)				

Table 5 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **2**

La–O(1)	2.366(3)	La–O(23n)	2.774(3)	Cu(1)–N(5)	2.001(3)	Cu(2)–O(5)	1.962(3)
La–O(2)	2.630(3)	La–O(31n)	2.608(3)	Cu(1)–O(1m)	1.914(3)	Cu(3)–N(2)	2.053(3)
La–O(5)	2.589(3)	La–O(33n)	2.625(3)	Cu(2) ··· Cu(3)	2.9699(7)	Cu(3)–O(3)	1.916(3)
La–O(12n)	2.613(3)	La–O(3m)	2.599(3)	Cu(2)–O(2)	1.954(3)	Cu(3)–O(4)	2.246(3)
La–O(13n)	2.605(3)	Cu(1) ··· Cu(3)	3.1080(7)	Cu(2)–N(3)	1.990(3)	Cu(3)–O(1m)	1.899(3)
La–O(21n)	2.609(3)	Cu(1)–N(1)	1.960(4)	Cu(2)–N(4)	1.982(3)	Cu(3)–O(2m)	2.050(3)
		Cu(1)–O(4)	1.976(3)				
O(1)–La–O(2)	93.53(9)	O(5)–La–O(3m)	76.44(9)	Cu(3)–Cu(1)–N(1)	131.07(10)	Cu(1)–Cu(3)–O(4)	39.33(7)
O(1)–La–O(5)	75.96(9)	O(12n)–La–O(13n)	49.05(9)	Cu(3)–Cu(1)–O(4)	46.07(8)	Cu(1)–Cu(3)–O(1m)	35.57(8)
O(1)–La–O(12n)	118.22(10)	O(12n)–La–O(21n)	65.21(9)	Cu(3)–Cu(1)–N(5)	127.66(10)	Cu(1)–Cu(3)–O(2m)	101.45(9)
O(1)–La–O(13n)	70.67(10)	O(12n)–La–O(23n)	110.33(9)	Cu(3)–Cu(1)–O(1m)	35.26(8)	Cu(2)–Cu(3)–N(3)	77.29(10)
O(1)–La–O(21n)	167.64(10)	O(12n)–La–O(31n)	74.24(9)	N(1)–Cu(1)–O(4)	168.02(13)	Cu(2)–Cu(3)–O(3)	74.04(9)
O(1)–La–O(23n)	131.43(9)	O(12n)–La–O(33n)	72.65(9)	N(1)–Cu(1)–N(5)	98.95(14)	Cu(2)–Cu(3)–O(4)	58.81(7)
O(1)–La–O(31n)	80.88(10)	O(12n)–La–O(3m)	140.22(9)	N(1)–Cu(1)–O(1m)	96.06(13)	Cu(2)–Cu(3)–O(1m)	97.33(9)
O(1)–La–O(33n)	125.36(10)	O(13n)–La–O(21n)	109.01(9)	O(4)–Cu(1)–N(5)	88.16(12)	Cu(2)–Cu(3)–O(2m)	140.10(9)
O(1)–La–O(3m)	74.87(10)	O(13n)–La–O(23n)	156.09(9)	O(4)–Cu(1)–O(1m)	79.25(12)	N(2)–Cu(3)–O(3)	92.57(13)
O(2)–La–O(5)	58.26(8)	O(13n)–La–O(31n)	76.62(9)	N(5)–Cu(1)–O(1m)	160.78(13)	N(2)–Cu(3)–O(4)	132.04(12)
O(2)–La–O(12n)	84.08(9)	O(13n)–La–O(33n)	109.34(10)	Cu(3)–Cu(2)–O(2)	76.08(8)	N(2)–Cu(3)–O(1m)	96.36(13)
O(2)–La–O(13n)	75.02(9)	O(13n)–La–O(3m)	135.70(10)	Cu(3)–Cu(2)–N(3)	79.31(10)	N(2)–Cu(3)–O(2m)	138.79(13)
O(2)–La–O(21n)	74.72(9)	O(21n)–La–O(23n)	47.31(9)	Cu(3)–Cu(2)–N(4)	91.46(10)	O(3)–Cu(3)–O(4)	92.96(11)
O(2)–La–O(23n)	92.50(9)	O(21n)–La–O(31n)	111.27(9)	Cu(3)–Cu(2)–O(5)	110.27(8)	O(3)–Cu(3)–O(1m)	165.95(12)
O(2)–La–O(31n)	151.33(9)	O(21n)–La–O(33n)	66.79(10)	O(2)–Cu(2)–N(3)	94.91(13)	O(3)–Cu(3)–O(2m)	85.69(12)
O(2)–La–O(33n)	140.59(9)	O(21n)–La–O(3m)	110.54(10)	O(2)–Cu(2)–N(4)	162.38(13)	O(4)–Cu(3)–O(1m)	73.00(11)
O(2)–La–O(3m)	134.70(9)	O(23n)–La–O(31n)	112.34(9)	O(2)–Cu(2)–O(5)	80.92(11)	O(4)–Cu(3)–O(2m)	89.13(11)
O(5)–La–O(12n)	141.35(9)	O(23n)–La–O(33n)	67.68(9)	N(3)–Cu(2)–N(4)	94.94(14)	O(1m)–Cu(3)–O(2m)	94.61(12)
O(5)–La–O(13n)	119.57(9)	O(23n)–La–O(3m)	67.08(9)	N(3)–Cu(2)–O(5)	168.00(13)	La–O(2)–Cu(2)	107.52(11)
O(5)–La–O(21n)	94.22(9)	O(31n)–La–O(33n)	48.91(10)	N(4)–Cu(2)–O(5)	92.08(13)	Cu(1)–O(4)–Cu(3)	94.61(11)
O(5)–La–O(23n)	66.85(9)	O(31n)–La–O(3m)	71.14(10)	Cu(1)–Cu(3)–Cu(2)	69.685(17)	La–O(5)–Cu(2)	108.82(11)
O(5)–La–O(31n)	144.04(9)	O(33n)–La–O(3m)	70.04(10)	Cu(1)–Cu(3)–N(2)	110.37(10)	Cu(1)–O(1m)–Cu(3)	109.18(14)
O(5)–La–O(33n)	131.05(9)			Cu(1)–Cu(3)–O(3)	130.64(9)		

lengths are more consistent, with the range being from 1.960 to 2.053 Å (average e.s.d.s, 0.003 Å and 0.12°).

The lanthanum atom is ten-co-ordinate, bound to six oxygens from bidentate nitrate ions, two μ-oxygen atoms from L units shared with Cu(2), one further oxygen from an L ligand, and finally a molecule of MeOH. The co-ordination geometry is difficult to describe, but it can be envisaged as based on a distorted pentagonal bipyramid with each bidentate nitrate ion occupying one co-ordination site. One of these nitrates [that involving N(2n)] and O(1) occupy the axial positions of the co-ordination sphere. The La–O bond lengths fall into three regions: that to the oxygen of the bidentate L ligand is 2.366 Å; the bonds to the μ-oxygens of the trinucleating L ligand are 2.589 and 2.630 Å; the bonds involving nitrate or

Table 6 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **3**

La–O(11n)	2.619(7)	Cu(1)–N(4r)	2.006(7)
La–O(21n)	2.606(6)	Cu(1)–N(7r)	2.012(7)
La–O(3r)	2.570(5)	Cu(2)–N(1r)	1.981(7)
La–O(4r)	2.402(5)	Cu(2)–N(2r)	1.998(7)
La–O(5r)	2.386(6)	Cu(2)–O(3r)	1.967(5)
La–O(6r)	2.598(5)	Cu(2)–O(6r)	1.970(6)
La–O(7r)	2.403(6)	Cu(3)–O(1r)	1.942(6)
La–O(8r)	2.358(7)	Cu(3)–N(5r)	1.963(7)
Cu(1)–O(2r)	1.956(5)	Cu(3)–N(6r)	2.003(7)
Cu(1)–N(3r)	2.029(7)	Cu(3)–O(1e)	1.954(7)
O(11n)–La–O(21n)	48.61(19)	O(5r)–La–O(8r)	90.50(21)
O(11n)–La–O(3r)	127.21(19)	O(6r)–La–O(7r)	77.83(18)
O(11n)–La–O(4r)	78.30(19)	O(6r)–La–O(8r)	75.63(20)
O(11n)–La–O(5r)	75.90(20)	O(7r)–La–O(8r)	91.74(21)
O(11n)–La–O(6r)	153.18(19)	O(2r)–Cu(1)–N(3r)	87.67(24)
O(11n)–La–O(7r)	125.21(20)	O(2r)–Cu(1)–N(4r)	178.4(3)
O(11n)–La–O(8r)	88.95(22)	O(2r)–Cu(1)–N(7r)	83.34(25)
O(21n)–La–O(3r)	142.39(17)	N(3r)–Cu(1)–N(4r)	91.9(3)
O(21n)–La–O(4r)	73.82(18)	N(3r)–Cu(1)–N(7r)	168.5(3)
O(21n)–La–O(5r)	123.73(19)	N(4r)–Cu(1)–N(7r)	97.3(3)
O(21n)–La–O(6r)	145.28(18)	N(1r)–Cu(2)–N(2r)	95.1(3)
O(21n)–La–O(7r)	77.42(19)	N(1r)–Cu(2)–O(3r)	159.55(25)
O(21n)–La–O(8r)	81.17(21)	N(1r)–Cu(2)–O(6r)	95.15(25)
O(3r)–La–O(4r)	69.32(17)	N(2r)–Cu(2)–O(3r)	93.49(25)
O(3r)–La–O(5r)	75.52(18)	N(2r)–Cu(2)–O(6r)	162.3(3)
O(3r)–La–O(6r)	59.74(17)	O(3r)–Cu(2)–O(6r)	81.65(22)
O(3r)–La–O(7r)	87.99(18)	O(1r)–Cu(3)–N(5r)	87.9(3)
O(3r)–La–O(8r)	134.38(20)	O(1r)–Cu(3)–N(6r)	92.3(3)
O(4r)–La–O(5r)	107.32(19)	O(1r)–Cu(3)–O(1e)	170.8(3)
O(4r)–La–O(6r)	123.79(18)	N(5r)–Cu(3)–N(6r)	171.2(3)
O(4r)–La–O(7r)	78.26(19)	N(5r)–Cu(3)–O(1e)	92.7(3)
O(4r)–La–O(8r)	154.51(21)	N(6r)–Cu(3)–O(1e)	88.5(3)
O(5r)–La–O(6r)	82.33(19)	La–O(3r)–Cu(2)	109.88(22)
O(5r)–La–O(7r)	158.81(20)	La–O(6r)–Cu(2)	108.71(23)

Table 7 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **4***

La–O(4r)	2.368(6)	La–O(1r)	2.464(6)
La–O(3r)	2.480(6)	La–O(2r)	2.534(6)
La–O(21n)	2.606(7)	La–O(11n)	2.632(7)
La–O(5r)	2.641(6)	La–N(5r)	2.765(8)
La–O(2r′)	2.551(6)	Cu–N(2r)	2.016(7)
Cu–N(1r)	2.014(8)	Cu–N(4r)	2.017(8)
Cu–O(5r)	1.991(6)		
O(4r)–La–O(1r)	73.3(2)	O(4r)–La–O(3r)	146.3(2)
O(1r)–La–O(3r)	76.6(2)	O(1r)–La–O(2r)	73.6(2)
O(3r)–La–O(2r)	73.1(2)	O(4r)–La–O(21n)	122.9(2)
O(1r)–La–O(21n)	85.8(2)	O(3r)–La–O(21n)	68.6(2)
O(2r)–La–O(21n)	139.7(2)	O(4r)–La–O(11n)	75.0(2)
O(1r)–La–O(11n)	72.7(2)	O(3r)–La–O(11n)	110.0(2)
O(2r)–La–O(11n)	144.2(2)	O(21n)–La–O(11n)	48.0(2)
O(4r)–La–O(5r)	135.5(2)	O(1r)–La–O(5r)	150.9(2)
O(3r)–La–O(5r)	74.6(2)	O(2r)–La–O(5r)	101.7(2)
O(21n)–La–O(5r)	80.0(2)	O(11n)–La–O(5r)	113.7(2)
O(4r)–La–N(5r)	98.9(2)	O(1r)–La–N(5r)	145.5(2)
O(3r)–La–N(5r)	114.5(2)	O(2r)–La–N(5r)	140.1(2)
O(21n)–La–N(5r)	70.2(3)	O(11n)–La–N(5r)	72.9(2)
O(5r)–La–N(5r)	49.7(2)	O(2r′)–La–O(4r)	75.0(2)
O(2r′)–La–O(1r)	129.6(2)	O(2r′)–La–O(3r)	115.0(2)
O(2r′)–La–O(2r)	65.0(2)	O(2r′)–La–O(21n)	144.7(2)
O(2r′)–La–O(11n)	133.2(2)	O(2r′)–La–N(5r)	77.3(2)
O(2r′)–La–O(5r)	68.3(2)	N(2r)–Cu–N(1r)	90.0(3)
N(2r)–Cu–N(4r)	169.6(3)	N(1r)–Cu–N(4r)	93.6(3)
O(5r)–Cu–N(1r)	173.5(3)	O(5r)–Cu–N(2r)	88.5(3)
O(5r)–Cu–N(4r)	88.9(3)	La–O(2r)–La′	115.0(2)
La–O(5r)–Cu′	114.1(3)		

* Primed atoms are related to their unprimed equivalents by the symmetry operation $-x$, $-y$, $2-z$.

methanol oxygens fall between 2.599 and 2.744 Å (average e.s.d.s 0.003 Å).

The molecule contains five L ligands. Two of these are trinucleating, with the exocyclic oxygen shared by Cu(2) and La and the ring nitrogens bound to either Cu(1) and Cu(3). This is a bonding mode displayed by the unsubstituted ligand in Cu_4Ln_2 complexes reported previously.[10,22] A third L ligand is also trinucleating, but here the oxygen bridges Cu(1) and Cu(3) while the nitrogens binds to Cu(2). The remaining two ligands are binucleating, with one ligand bound *via* the nitrogen to Cu(1) and *via* the oxygen to La, and the other bridging Cu(2) and Cu(3). These various bridging modes lead to several short metal–metal contacts with Cu(1)···Cu(3) 3.108, Cu(2)···Cu(3) 2.970 and Cu(2)···La(1) 3.719 Å (average e.s.d.s 0.001 Å).

Methanol has become involved in the final compound in three ways. First, and most importantly, it has been deprotonated to provide a μ-oxygen bridge between Cu(1) and Cu(3). Methoxide bridges were also found in a Yb_2Cu_2 complex of L.[12] Secondly, a MeOH molecule is attached in the fifth co-ordination site of Cu(3). Finally the co-ordination sphere of La contains one molecule of solvent. The lattice also contains two solvent fragments the first of which was modelled as a full-occupancy methanol molecule, and the second of which was modelled as 50:50 methanol/diethyl ether with three atoms common to both the methanol and ether. The formula of the asymmetric unit is therefore $[Cu_3LaL_5(NO_3)_3(OMe)(MeOH)_2]\cdot 1.5MeOH\cdot 0.5Et_2O$.

Reaction in Ethanol.—Addition of ethanol to a dichloromethane solution of **1** leads to a rapid colour change to green, but on isolating a solid the compound returns to the red colour characteristic of **1**. The addition of $La(NO_3)_3\cdot 5H_2O$ to the solution of **1** dissolved in ethanol–dichloromethane allows isolation, by slow diffusion of ether vapour, of a dark green crystalline product.

An X-ray structural analysis reveals a compound of stoichiometry $[Cu_3LaL_8(NO_3)_3(EtOH)]\cdot 0.5Et_2O$ **3** (Fig. 2). As in **2** all three copper sites are chemically distinct, although this time all are four-co-ordinate. Atom Cu(1) is bound to three nitrogens and one oxygen from L units. Atom Cu(2) has a *cis* arrangement of 2N and 2O atoms from L units, the two oxygens being μ-bridging to La. Atom Cu(3) is bound to 2N and 2O with a *trans* geometry, with the two nitrogens and one of the oxygens coming from L units, and the final oxygen from a molecule of EtOH. All three coppers have geometries close to square planar. The largest distortions observed are a reduction of the angle O(3r)–Cu(2)–O(6r) to 81.7(2)°, and a twist between the O(3r)–Cu(2)–O(6r) and N(2r)–Cu(2)–N(1r) planes of 14.7(2)°.

The lanthanum atom is eight-co-ordinate, bound to two μ-oxygens shared with Cu(2), four mononucleating oxygens from L units, and a bidentate nitrate ion. The co-ordination geometry can be described as bicapped trigonal prismatic, with the upper face described by O(3r), O(4r) and O(7r) and the lower face by O(5r), O(8r) and O(11n), with the two caps being O(6r) and O(21n). The chief distortion is caused by the small bite angle of the bidentate nitrate. Lanthanum–oxygen bond lengths fall into three groups. Those involving oxygens from binucleating and mononucleating L vary between 2.358 and 2.403 Å; those involving μ-oxygens from trinucleating L are 2.570 and 2.598 Å; those to nitrate oxygens are 2.606 and 2.619 Å (average e.s.d. 0.006 Å).

In compound **3**, as in **2**, both binucleating and trinucleating L ligands are found. In **3** there are two trinucleating ligands, both bridge La and Cu(2) *via* the exocyclic oxygen and bind to either Cu(1) or Cu(3) *via* the ring nitrogen. Five more L ligands act in a binucleating fashion, three of them bridging between La and

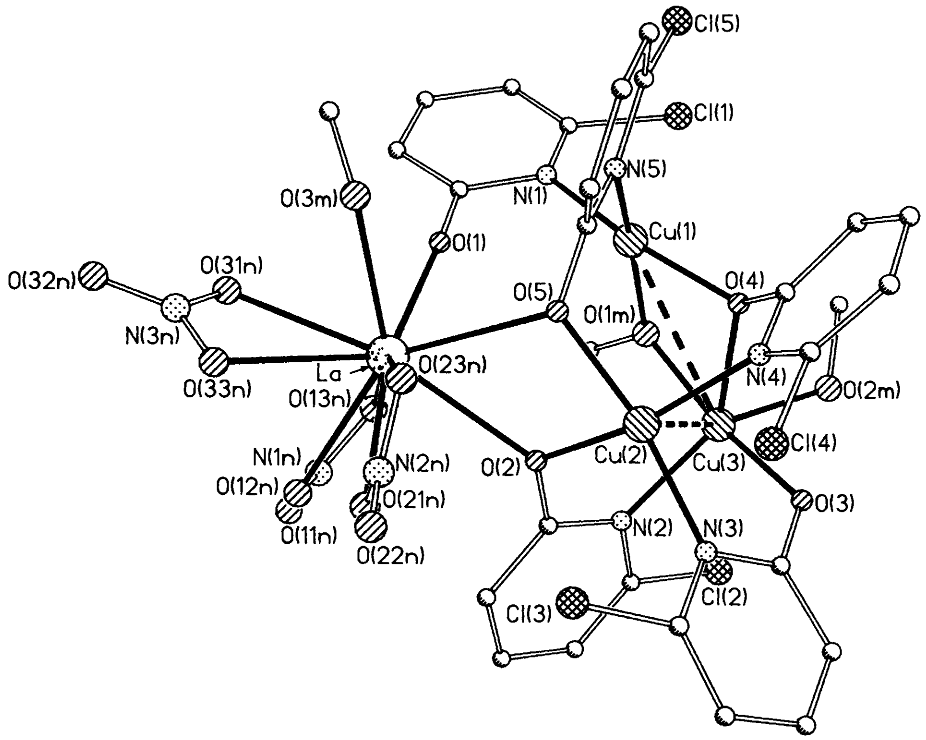

Fig. 1 The structure of compound **2** in the crystal showing the crystallographic numbering scheme

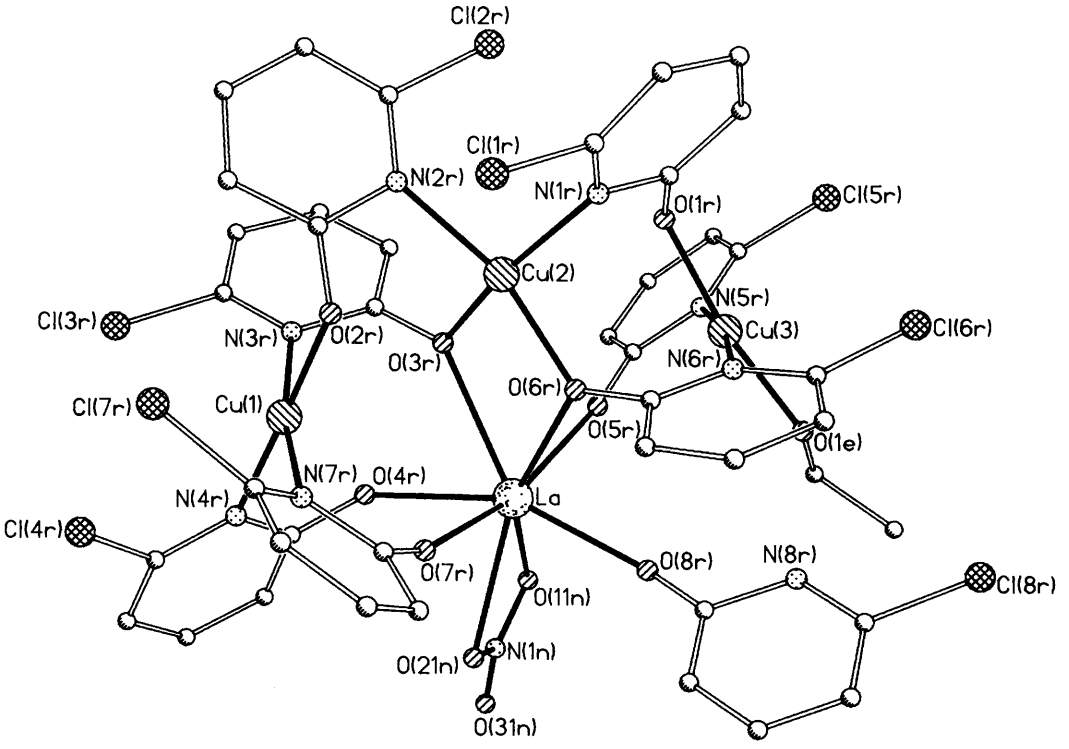

Fig. 2 The structure of compound **3** in the crystal showing the crystallographic numbering scheme

Cu(1), with in each case the oxygen bound to La and the nitrogen bound to Cu(1). Two bridge La and Cu(3) in a similar fashion. The eighth ligand is slightly different. It is mononucleating, bound only *via* the oxygen to La(1). Atom N(8r) is involved in hydrogen bonding to the EtOH molecule bound to Cu(3). It is unclear whether the hydrogen is attached to the oxygen of the EtOH or to N(8r). If N(8r) were bound directly to Cu(3), then the molecule would have a two-fold rotation axis running through Cu(2) and La. We have reported a Cu_3Mg complex of the 2-hydroxy-6-methylpyridine ligand where this is the case.[23]

The closest metal–metal contacts in **3** are La $\cdots$ Cu(2) 3.730, Cu(2) $\cdots$ Cu(1) 3.720 and Cu(2) $\cdots$ Cu(3) 3.699 Å (average e.s.d.s 0.001 Å).

Ethanol therefore takes a small part in the structure of **3**, binding to one of the copper atoms, and hydrogen bonding to an L unit. This involvement is much less than that of MeOH in the structure of **2**. The lattice contains one disordered solvent fragment which was modelled as a half-occupancy diethyl ether, hence the formula of the asymmetric unit is $[Cu_3LaL_8(NO_3)(EtOH)]\cdot 0.5Et_2O$.

Reaction in Acetonitrile.—Unlike the reactions in alcohols, there is no immediate colour change when acetonitrile is added to a solution of compound **1** in dichloromethane. In the presence of hydrated lanthanum nitrate a very slow colour change is observed, and after a period of over a year crystals of $[Cu_2La_2L_8(HL)_2(NO_3)_2]\cdot 2HL\cdot 2MeCN$ **4** formed in 2% yield. During this period crystals of **1** are also formed in the reaction vial. This observation combined with the low yield of **4** suggests that the presence of a protic solvent, as in the reactions which result in **2** and **3**, is important in disrupting the structure of **1**.

The structure of compound **4** is shown in Fig. 3. As it lies across a crystallographic inversion centre the asymmetric unit of **4** contains only one unique Cu and one unique La site. The copper is four-co-ordinate, bound to one O and three N atoms from L units, with a square-planar geometry. The La atom is nine-co-ordinate, bound to eight oxygens and one nitrogen. The eight oxygens come from two trinucleating L units [O(2r) and O(2r′)], related by an inversion centre, three binucleating L ligands, one monodentate HL, and one bidentate nitrate. The nitrogen [N(5r)] comes from a L unit and is the first example of the ring nitrogen from a pyridone ligand binding to an f-block element. The co-ordination geometry about the lanthanum is completely irregular. Again the La–O bond lengths show a variation dependent on the source and connectivity of the oxygen atom. For terminal oxygens from L, the bonds vary from 2.368 to 2.480 Å; for μ-oxygens from L, the bond lengths are 2.534 and 2.551 Å; for La–O(nitrate) the bond lengths are 2.606 and 2.632 Å. The bonds between La and the chelating L ligand are still longer, La–O(5r) is 2.641, and La–N(5r) is 2.765 Å (average e.s.d.s, 0.007 Å).

The four crystallographically unique L units show three different bonding modes. Two of the ligands are binucleating and bidentate, bound *via* N(1r) and N(4r) to Cu and *via* O(1r) and O(4r) to the La. The third L is trinucleating, bridging the symmetry related lanthanums (La and La′) *via* O(2r) and binding to the Cu through N(2r). This type of bonding was observed in a La_4Cu_4 complex of the unsubstituted ligand.[10] The fourth ligand shows a quite new bonding interaction for these mixed-metal compounds: O(5r) forms a μ-bridge between La and Cu′, while N(5r) binds to the same lanthanum. The ligand is thus tridentate, but only binucleating. It is unusual for pyridone ligands to be chelating, although examples have been seen before, *e.g* in a dodecanuclear cobalt complex of the 2-hydroxy-6-methylpyridine ligand.[2] In **4** the close metal–metal contacts are La ··· La′ 4.289, La ··· Cu 3.896 and La ··· Cu′ 3.904 Å (average e.s.d.s 0.001 Å).

Although a molecule of acetonitrile was located in the lattice, acetonitrile plays no part in the structure of the complex. A hydrogen bonded pair of HL molecules is also present. The overall formula is therefore $[Cu_2La_2L_8(HL)_2(NO_3)_2]\cdot 2HL\cdot 2MeCN$.

Discussion

Carrying out essentially the same reaction in three different mixed solvents has led to three different, crystallographically characterised compounds. It is worth considering the similarities and differences between these three structures.

All three structures contain at their centre a $MM'O_2$ ring. In **2** this features La, Cu(2), O(2) and O(5); in **3** it includes La, Cu(2), O(3r) and O(6r); in **4** it includes La, La′, O(2r) and O(2r′). In all cases the oxygens of this ring are part of a L ligand which bridges to the remaining coppers *via* the nitrogen of the L, *e.g.* in **2** N(5) binds to Cu(1) and N(2) binds to Cu(3); in **3** N(3r) binds to Cu(1) and N(6r) binds to Cu(3); in **4** N(2r) binds to Cu and N(2r′) binds to Cu′. Compound **4** differs from **2** and **3** in that the $MM'O_2$ ring contains two La atoms, rather than an La and a Cu; compound **2** differs from **3** and **4** in that the two coppers not in the $MM'O_2$ ring are on the same side of this metallocycle, rather than separated by it. In **2** the two further coppers are

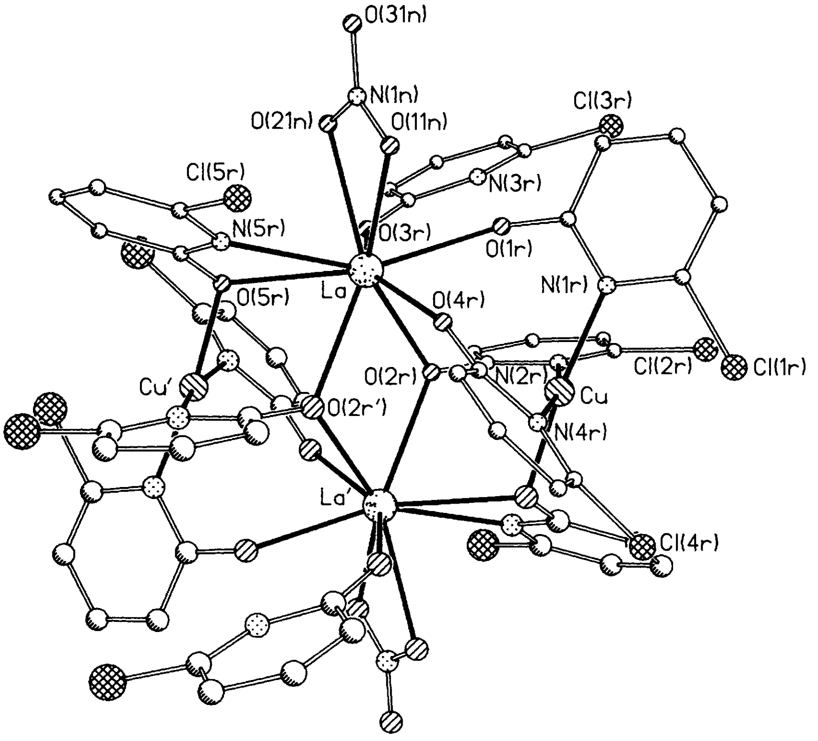

Fig. 3 The structure of compound **4** in the crystal showing the crystallographic numbering scheme. Primed atoms are related to their unprimed equivalents by the symmetry operation $-x, -y, 2-z$

themselves part of a metallocycle, bridged by two μ-oxygens from a L ligand [O(4)] and a methoxide [O(1m)]. It is possibly the readiness of MeOH to form methoxide bridges that leads to this alteration in the structural type of **2** compared with that of **3** and **4**. It is less clear why the metal stoichiometry in **4** is different to that in **2** and **3**.

The difference in structures leads to the metal–metal distances varying between the three different compounds. In **2** there are two Cu ··· Cu contacts of 2.970 and 3.108 Å; in **3** the closest contacts are La ··· Cu(2) 3.730, Cu(2) ··· Cu(1) 3.720 and Cu(2) ··· Cu(3) 3.669 Å; in **4** the close metal–metal contacts are La ··· La′ 4.289, La ··· Cu 3.896 and La ··· Cu′ 3.904 Å. Thus in **2** we expect the properties to be dominated by Cu ··· Cu interactions. In **3** the three short metal–metal contacts are all similar, but the La ··· Cu(2) interaction is directly bridged by two μ-oxygens, therefore we expect magnetic properties to involve a significant Cu ··· Ln interaction if La were replaced by a paramagnetic lanthanoid, *e.g.* Gd^{III}, and if any super-exchange were involved in the magnetic interaction. Variable-temperature magnetic measurements on a series of Cu_3Ln complexes structurally related to **3** (Ln = Gd, Dy and Er) are being carried out and will be the subject of a future report.[24] For compound **4** the closest contacts are between unlike metals, but as yet we have no crystallographically characterised materials related to structure **4** which contain a paramagnetic lanthanoid.

Conclusion

The results reported show the flexibility of 6-chloro-2-hydroxypyridine as a means of bridging dissimilar metals. Different structural types result simply from changing solvent, and thus we can envisage a wide range of compounds which should be accessible using this ligand system. Although we cannot predict or control the likely product of any individual reaction, we can produce a series of compounds with differing Cu : Ln ratios, with different bridging modes of the ligand and with different spatial arrangements of the metals. This should allow systematic investigation of the interactions of d- and f-block elements, and the dependence of the interaction on factors such as metal–metal distance and possible ligand-mediated super-exchange pathways. Current explanations[15] of the magnetic exchange interactions between d- and f-block metals suggest that a charge-transfer type process is involved: by synthesising and studying a range of different compounds we should be able to confirm or possibly refute this model.

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