From Compounds to Materials: Heterodinuclear Complexes as Precursors in the Synthesis of Mixed Oxides; Crystal Structures of [Cu(H₂L$_A$)] and [{CuY(L$_A$)(NO₃)(dmso)}₂]·2dmso [H₄L$_A$ = N,N'-ethylenebis(3-hydroxysalicylideneimine), dmso = dimethyl sulphoxide] *
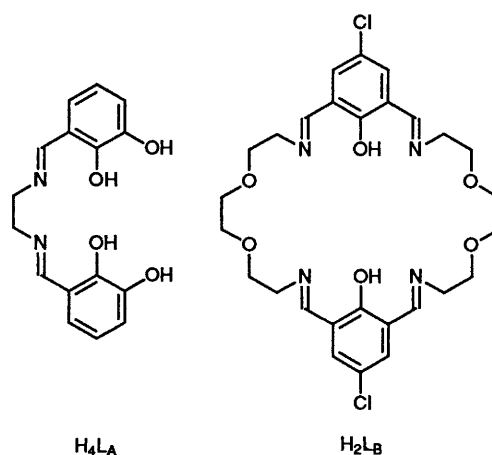
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Mononuclear copper(II) and nickel(II) complexes [M(H₂L$_A$)] have been obtained by reaction of the appropriate metal acetate with the potentially hexadentate compartmental ligand H₄L$_A$, prepared by condensation of 2,3-dihydroxybenzaldehyde with ethylenediamine. Physicochemical data suggest the metal ion is in the inner N₂O₂ compartment. An X-ray investigation on [Cu(H₂L$_A$)] showed that the crystals are orthorhombic, space group *Pnca*, with a = 19.381(5), b = 15.327(4), c = 10.158(4) Å for Z = 8 and confirms the inner occupancy of copper(II) which exhibits an almost square-planar configuration. The bond lengths to Cu^{II} [Cu–N 1.93(1), Cu–O 1.89(1) Å (mean)] are within the usual range. The complexes [M(H₂L$_A$)] act as ligands in the formation of heterodinuclear [M¹M²L$_A$(X)(solv)$_n$] (M¹ = Cu or Ni, M² = La or Y, X = NO₃ or Cl) or [M¹M²L$_A$(solv)$_n$] (M = Cu or Ni, M² = UO₂ or Ba) species [solv = H₂O, methanol or dimethyl sulphoxide (dmso)]. Crystals of [{CuY(L$_A$)(NO₃)(dmso)}₂]·2dmso, grown from dmso–MeOH are triclinic, space group P1̄, with a = 9.919(5), b = 11.357(5), c = 13.789(6) Å for Z = 1 (the asymmetric unit is half of the molecule). The X-ray structure shows that the copper(II) is four-co-ordinated in the inner N₂O₂ compartment while the yttrium(III) is eight-co-ordinated in the outer O₂O₂. The complex is a tetranuclear asymmetric unit, two yttrium(III) ions being held together by phenolic oxygen bridges. The Y–O(ligand) bonds are in the range 2.28–2.40 Å, Y–O(dmso) is 2.31(1) Å and Y–O(nitrate) are 2.48 Å(mean). The Cu···Y and Y···Y distances are 3.397(3) and 3.781(2) Å respectively. The co-ordination of each yttrium(III) ion is completed by the oxygens of a bidentate nitrate ion and a dmso molecule. The geometry around the metal ion can be described as pentagonal bipyramidal. Two dmso molecules are present in the cell as clathrate solvent. The thermal decomposition of copper(II)–yttrium(III) and –lanthanum(III) complexes and the consequent formation of mixed oxides have also been studied and the preliminary results are reported.

It was recently shown that co-ordination and/or organo-metallic compounds can offer interesting advantages in the synthesis of solid-state compounds.[1,2] They have been successfully used as precursors in the preparation of ceramic materials, favouring an intimate mixing of the elements which can enable reactions at lower temperatures than for the traditional preparative route or the preparation of purer or inaccessible solid-state phases.[3–5] Preparation routes to high-temperature superconductors based on soluble precursors have received considerable attention owing to the low cost, the possibility to coat large unusually shaped objects and high homogeneity and purity.[6] In the preparation of these materials it is important to characterize as completely as possible the reactions of the starting material to give the solid-state products. Much effort is currently devoted to the isolation and characterization of intermediate products in order to give insight into both the chemistry of formation of a bulk solid and the evolution of the size-dependent physical properties.[3–5,7]

The ability of compartmental or polynucleating ligands to hold two or more metal ions in close proximity is quite well known and very sophisticated systems are now available.[8–15] Some of these complexes have already been considered as useful precursors in the preparation of new materials, particularly

H₄L$_A$ H₂L$_B$

mixed oxides.[1,6] As an example, by thermal decomposition of homo- or hetero-dinuclear complexes of the type [Ln₂L$_B$-(NO₃)₄]·xH₂O and [Ln¹Ln²L$_B$(NO₃)₄]·xH₂O, where H₂L$_B$ is the macrocycle obtained by condensation of 4-chloro-2,6-di-formylphenol and 1,8-diamino-3,6-dioxaoctane,[14] almost the whole series of Ln₂O₃ and several Ln¹Ln²O₃ oxides have been obtained in two, well characterized and crystallographically pure forms (monoclinic and cubic).[1]

We have prepared the new, potentially hexadentate, compartmental ligand H_4L_A by condensation, in alcoholic solution, of 2,3-dihydroxybenzaldehyde and ethylenediamine. This ligand easily produces mononuclear and homo- and hetero-dinuclear complexes. In the present paper we report the preparation and properties of the mononuclear copper(II) and nickel(II) and heterodinuclear copper(II)–lanthanum(III), –yttrium(III), –barium(II) and –uranyl(VI) complexes with the ligand H_4L_A. The X-ray crystal structures of $[Cu(H_2L_A)]$ and $[\{CuY(L_A)(NO_3)(dmso)\}_2]\cdot2dmso$ (dmso = dimethyl sulphoxide) are also reported. The obtaining of crystals for some heterodinuclear complexes shows that the preparation of these species in a quite pure form is feasible. It is thus possible to propose the use of these compounds as precursors in the synthesis of mixed oxides containing d and f metal ions. Consequently, the thermal behaviour of the prepared complexes has been studied and the formation and characterization of mixed oxides investigated. The first results obtained are described here.

Experimental

2,3-Dihydroxybenzaldehyde, ethylenediamine, the inorganic salts and the solvents were commercial products used without further purification.

Preparations.—The ligand H_4L_A. To a warm methanolic solution (150 cm³) of 2,3-dihydroxybenzaldehyde (1105 mg, 8 mmol) was added dropwise ethylenediamine (240.4 mg, 4 mmol) in methanol (100 cm³). The yellow solution turned to orange and was refluxed for 1 h. By evaporation to a small volume under reduced pressure an orange precipitate was obtained. It was filtered off, washed with methanol and dried *in vacuo* (Found: C, 63.00; H, 5.75; N, 9.10. Calc. for $C_{16}H_{16}N_2O_4\cdot0.5CH_3OH$: C, 62.65; H, 5.75; N, 8.85%).

Mononuclear complexes $[M(H_2L_A)]$ (M = Cu or Ni).To a warm methanolic solution (150 cm³) of 2,3-dihydroxybenzal-dehyde (1105 mg, 8 mmol) was added dropwise ethylenediamine (240.4 mg, 4 mmol) in methanol (100 cm³). After the addition of the appropriate amount (4 mmol) of $M(CH_3CO_2)_2\cdot xH_2O$ in methanol, the resulting solution was refluxed for 1 h. The microcrystalline precipitate [brown for copper(II), brick red for nickel(III)] was filtered off, washed with methanol and dried *in vacuo* (Found: C, 52.45; H, 4.05; N, 7.40. Calc. for $C_{16}H_{14}CuN_2O_4$: C, 53.10; H, 3.90; N, 7.75. Found: C, 54.25; H, 4.30; N, 7.50. Calc. for $C_{16}H_{14}N_2NiO_4$: C, 53.85; H, 3.95; N, 7.85%).

$[CuUO_2L_A]\cdot dmso\cdot2H_2O$. To a warm dmso solution (20 cm³) of $[Cu(H_2L_A)]$ (180 mg, 0.5 mmol) was added $[UO_2(CH_3-CO_2)_2]\cdot2H_2O$ (212 mg, 0.5 mmol) in methanol (30 cm³). The brown solution obtained was refluxed for 2 h, then reduced in volume. After cooling, the brown precipitate obtained by addition of methanol was filtered off, washed with methanol and dried *in vacuo* (Found: C, 30.10; H, 2.20; N, 3.70. Calc. for $C_{16}H_{12}CuN_2O_6U\cdot C_2H_6SO\cdot2H_2O$: C, 30.20; H, 2.25; N, 3.75%).

$[CuLn(L_A)(NO_3)]\cdot solv$ (Ln = La or Y; solv = CH_3OH or H_2O). To a methanolic solution (100 cm³) of $[Cu(H_2L_A)]$ (180 mg, 0.5 mmol) was added LiOH (24 mg, 1 mmol). The suspension was refluxed for 2 h. To the solution obtained, the appropriate amount of nitrate salt (0.5 mmol) was added. The brown-green precipitate obtained was refluxed for 3 h and after the solution had been reduced in volume was filtered off and washed with methanol and diethyl ether (Found: C, 33.15; H, 2.30; N, 6.95. Calc. for $C_{16}H_{12}CuLaN_3O_7\cdot H_2O$: C, 33.20; H, 2.45; N, 7.25. Found: C, 36.35; H, 3.15; N, 7.40. Calc. for $C_{16}H_{12}CuN_3O_7Y\cdot CH_3OH$: C, 36.40; H, 3.25; N, 7.50%).

$[CuY(L_A)Cl]\cdot2CH_3OH$. The procedure employed for the synthesis of copper(II)–lanthanide nitrate complexes was used, but with $YCl_3\cdot5H_2O$ instead of the corresponding nitrate salt (Found: C, 39.40; H, 3.40; N, 5.35. Calc. for $C_{16}H_{12}Cl-CuN_2O_4Y\cdot2CH_3OH$: C, 39.45; H, 3.65; N, 5.10%).

$[CuBaL_A]\cdot2H_2O$. The reaction procedure was the same as that used for copper–rare-earth metal complexes, but with $BaCl_2\cdot2H_2O$ (0.5 mmol, 122 mg) instead of the rare-earth salts (Found: C, 36.05; H, 2.90; N, 5.00. Calc. for $C_{16}H_{12}-BuCuN_2O_4\cdot2H_2O$: C, 36.05; H, 3.00; N, 5.25%).

*X-Ray Structure Determination.—*Crystals of $[Cu(H_2L_A)]$ (brown) and $[\{CuY(L_A)(NO_3)(dmso)\}_2]\cdot2dmso$ (yellow-brown) suitable for an X-ray investigation were obtained by dissolving the respective crude products in the minimum amount of dmso containing some drops of methanol and maintaining the solution in an atmosphere of diethyl ether for 2 d. Those of maximum dimensions 0.2 mm were selected. Data were collected on a Philips PW1100 four-circle diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle reflections and are given in Table 1 together with other crystal and experimental data.

Both crystals were stable under irradiation. The structures were solved by standard Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. The full-matrix refinement was obtained by mini-mizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift of the non-hydrogen atoms was less than 0.4σ for the copper compound and 0.2σ for the copper–yttrium compound. A Fourier difference map for the bimetallic complex showed that the asymmetric unit of the cell also contained one molecule of dmso as clathrate solvent. Owing to the paucity of diffraction data, all the phenyl rings were treated as rigid bodies with an individual isotropic thermal parameter assigned to each carbon atom; the clathrate molecule was also isotropically refined. The H atoms were generated in trigonal or tetrahedral positions and introduced with a fixed isotropic thermal parameter of 0.07 Å^2. Hydrogens bonded to atoms O(3) and O(4) of the copper(II) complex as well as those present in the dmso molecule were not calculated.

No significant residual electron density was observed in the final Fourier-difference maps apart from some ripples around the metal position in the copper complex due to series termination effects.

Scattering factors for neutral atoms were taken from ref. 17 and those for Cu and Y were corrected for anomalous dispersion.[18] The programs used were SHELX 76[19] for structure solution and refinement, ORTEP[20] for drawing and PARST[21] for geometrical calculations. Final atomic parameters are listed in Tables 2 and 4, selected bond distances and angles in Tables 3 and 5.

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

*Physicochemical Measurements.—*IR spectra were recorded as KBr pellets on a Perkin-Elmer 580B spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Bruker AM 200 spectrometer equipped with an Aspect 3000 computer (solvent [2]H$_6$]dmso, concentration 1 mg sample per 1 ml solvent). Mass spectro-metric measurements were performed on a VG ZAB-ZF instrument operating in electron impact (EI) mode [70 eV (ca. 1.12×10^{-17} J), 200 µA, ion-source temperature 200 °C]. Magnetic susceptibilities were determined by the Faraday method (Oxford Instruments) at room temperature, the apparatus being calibrated with $HgCo(NCS)_4$.[22] Diamagnetic corrections were carried out.[23]

Thermogravimetric and differential thermoanalysis curves were obtained using NETZSCH STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 cm³ min⁻¹, heating rate 5 °C min⁻¹) and in air under the same conditions. Neutral alumina (C. Erba) was used as reference material.

Metal ratios were determined by the integral counting of X-ray fluorescence radiation from a Philips SEM model 515 scanning electron microscope equipped with an energy-

Table 1 Crystal and experimental data[a]

Compound	$C_{16}H_{14}CuN_2O_4$	$C_{40}H_{48}Cu_2N_6O_{18}S_4Y_2$[b]
M	361.8	1334.0
System	Orthorhombic	Triclinic
Space group	*Pnca*	$P\bar{1}$
General positions	$\pm(x, y, z; \frac{1}{2} + x,$	$\pm(x, y, z)$
	$\frac{1}{2} - y, \frac{1}{2} - z; x,$	
	$\frac{1}{2} - y, \frac{1}{2} + z;$	
	$\frac{1}{2} - x, y, z)$	
Z	8	1[b]
$a/\text{Å}$	19.381(5)	9.919(5)
$b/\text{Å}$	15.327(4)	11.357(5)
$c/\text{Å}$	10.158(4)	13.789(6)
$\alpha/°$		76.44(3)
$\beta/°$		100.25(4)
$\gamma/°$		111.68(4)
$U/\text{Å}^3$	3017(1)	1396(1)
$D_c/\text{g cm}^{-3}$	1.60	1.62
μ/cm^{-1}	14.0	29.5
$F(000)$	1480	666
No. of independent reflections	4405	5961
No. observed $[I > 3\sigma(I)]$	1161	1602
No. reflections per parameter refined	9	8
Final R factor	0.075	0.075

[a] Details in common: Mo-$K\alpha$ radiation ($\lambda = 0.7107$ Å); θ-2θ scan mode; scan rate $2°$ min^{-1}; Lorentz polarization and absorption corrections.[16] [b] The asymmetric unit is half of the molecule.
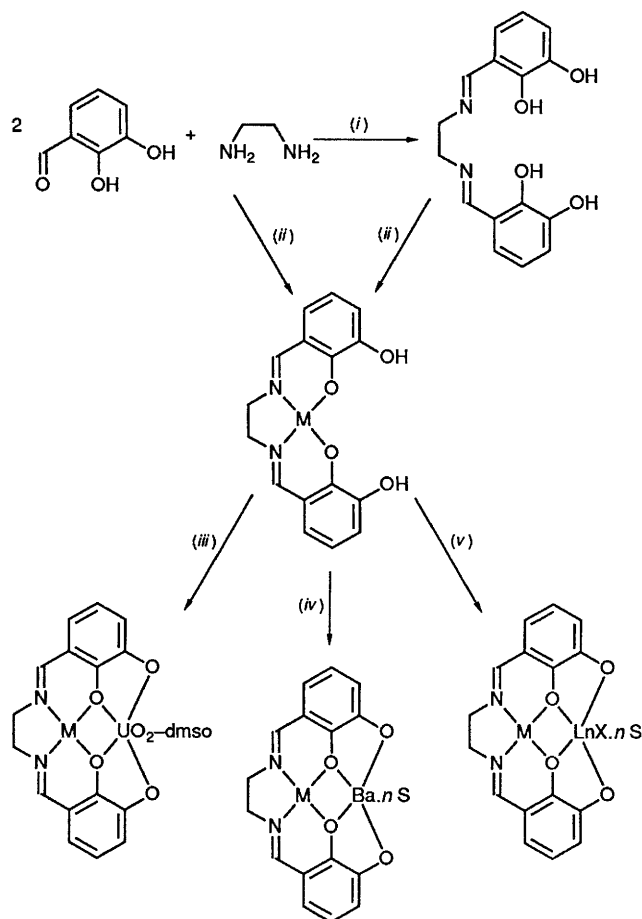
Table 2 Fractional coordinates for $[Cu(H_2L_A)]$

Atom	x	y	z
Cu	0.242 79(8)	0.309 92(8)	0.664 1(2)
O(1)	0.190 9(5)	0.400 6(5)	0.584 8(11)
O(2)	0.298 5(5)	0.397 2(5)	0.742 0(11)
N(1)	0.190 0(7)	0.218 8(7)	0.580 5(14)
N(2)	0.291 2(7)	0.215 2(6)	0.749 9(13)
O(3)	0.131 3(6)	0.545 3(5)	0.502 8(13)
O(4)	0.355 2(6)	0.540 6(5)	0.845 7(12)
C(1)	0.140 0(5)	0.391 6(5)	0.499 1(10)
C(2)	0.109 4(5)	0.468 8(5)	0.455 8(10)
C(3)	0.056 5(5)	0.466 0(5)	0.362 9(10)
C(4)	0.034 1(5)	0.386 0(5)	0.313 3(10)
C(5)	0.064 7(5)	0.308 8(5)	0.356 6(10)
C(6)	0.117 6(5)	0.311 5(5)	0.449 5(10)
C(7)	0.142 1(8)	0.228 1(7)	0.496 3(17)
C(8)	0.208 2(9)	0.131 3(9)	0.627 3(22)
C(9)	0.268 2(10)	0.128 4(8)	0.707 0(20)
C(10)	0.338 5(8)	0.223 1(8)	0.837 1(17)
C(11)	0.365 0(5)	0.303 8(4)	0.887 2(9)
C(12)	0.412 8(5)	0.298 8(4)	0.989 5(9)
C(13)	0.440 5(5)	0.375 0(4)	1.043 1(9)
C(14)	0.420 4(5)	0.456 1(4)	0.994 3(9)
C(15)	0.372 6(5)	0.461 2(4)	0.891 9(9)
C(16)	0.344 9(5)	0.385 0(4)	0.838 4(9)

dispersive X-ray analysis system. Samples suitable for scanning electron microscopy (SEM) analysis were prepared by suspension of the microcrystalline powders in light petroleum (b.p. 30–40 °C). Some drops of the resulting suspension were placed on a graphite disc and, after evaporation of the solvent, the samples were metallized (to take photographs) with graphite or gold by means of an Edward's S150B sputter coater.

X-Ray diffraction patterns were recorded by the transmission technique using a GD 2000 Ital Structures diffractometer operating in the Seemann–Bohlin geometry with a quartz monochromator on the primary beam and a NaI(Tl) scintillation counter; Cu-$K\alpha_1$ radiation was employed. The step-scanning recording was performed in the range 5–60° (2θ) at 0.02° steps and with a counting time of 15 s per step.

Results and Discussion

The preparation of the ligand and of the copper(II), nickel(II), copper(II)–rare earth(III), –barium(II) and –uranyl(VI) complexes follows the reaction sequence in Scheme 1. As can be seen, it is quite easy to obtain heterodinuclear complexes owing to the compartmental nature of the binucleating ligand and to the marked differences in the two co-ordination compartments.

Scheme 1 Preparation of the ligand H_2L_A and related mono- and heterodi-nuclear complexes. solv $= H_2O$, MeOH or dmso. (*i*) MeOH; (*ii*) M^{2+} (M $=$ Cu or Ni); (*iii*) $[UO_2(CH_3CO_2)_2]\cdot2H_2O$, dmso–MeOH; (*iv*) $BaCl_2\cdot2H_2O$; (*v*) LnX_3 (X $=$ NO$_3$ or Cl) $+$ 2LiOH

The potentially hexadentate ligand H_4L_A has been obtained by condensation, in alcoholic solution, of 2,3-dihydroxy-benzaldehyde with ethylenediamine in a 2:1 molar ratio. It is an orange solid which has in its IR spectrum a strong $\nu(C=N)$ peak at 1640 cm^{-1} and two $\nu(OH)$ at 3400 (sharp) and 3270–3259 (br) cm^{-1}. Proton NMR data are reported in Table 6. In addition in the EI mass spectrum the parent peak ($M^{+\bullet}$) at the expected m/z value of 300 is present.

By reaction of the preformed ligand with copper(II) acetate or by template procedure in methanol, the mononuclear complex can be prepared as brown microcrystals. A similar reaction can be employed for the preparation of the nickel(II) mononuclear complex. For these complexes $\nu(C=N)$ lies at 1631 (Cu) and 1626 cm^{-1} (Ni) with a shift toward lower frequencies of about 10–15 cm^{-1} with respect to the free ligand. For the copper(II) and nickel(II) complexes a single sharp and strong band due to $\nu(OH)$ occurs at 3387 and 3399 cm^{-1} respectively; in addition a band, not very intense, due to $\nu(C-O)$ (phenolate) acquiring partial double-bond character lies at 1561 (Cu) and 1564 (Ni) cm^{-1}.

The inner N_2O_2 compartment of the ligand is particularly designed for a d-transition-metal ion while the outer O_2O_2 is too large for such an ion. On the other hand, it was recently

Table 3 Selected bond distances (Å) and angles (°) for [Cu(H₂Lₐ)]

Cu–O(1)	1.896(9)	Cu–O(2)	1.892(9)
Cu–N(1)	1.93(1)	Cu–N(2)	1.94(1)
O(1)–C(1)	1.32(1)	O(2)–C(16)	1.34(1)
N(1)–C(7)	1.27(2)	N(2)–C(10)	1.28(2)
N(2)–C(9)	1.47(2)	N(1)–C(8)	1.47(2)
O(3)–C(2)	1.33(1)	O(4)–C(15)	1.35(1)
C(6)–C(7)	1.44(1)	C(10)–C(11)	1.43(2)
C(8)–C(9)	1.42(3)		

Contact distances

O(1)⋯O(2)	2.63(1)	N(1)⋯N(2)	2.60(2)
O(1)⋯N(1)	2.79(1)	O(2)⋯N(2)	2.79(1)
O(1)⋯O(3)	2.62(1)	O(2)⋯O(4)	2.67(1)
O(1)⋯O(4ᴵ)	2.93(1)	O(2)⋯O(3ᴵ)	2.92(2)

N(1)–Cu–N(2)	85.0(5)	O(2)–Cu–N(2)	93.8(5)
O(1)–Cu–N(1)	93.6(5)	O(1)–Cu–O(2)	87.8(4)
C(7)–N(1)–C(8)	120(1)	C(9)–N(2)–C(10)	121(1)
C(1)–C(6)–C(7)	124(1)	C(5)–C(6)–C(7)	115.9(9)
O(1)–C(1)–C(6)	124.2(8)	O(1)–C(1)–C(2)	115.8(8)
O(3)–C(2)–C(1)	119.9(9)	O(3)–C(2)–C(3)	120.1(8)
N(1)–C(7)–C(6)	124(1)	N(1)–C(8)–C(9)	114(1)
N(2)–C(9)–C(8)	113(1)	N(2)–C(10)–C(11)	126(1)
O(4)–C(15)–C(14)	118.4(7)	O(4)–C(15)–C(16)	121.6(8)
O(2)–C(16)–C(15)	115.2(7)	O(2)–C(16)–C(11)	124.8(8)
C(10)–C(11)–C(16)	122.9(9)	C(10)–C(11)–C(12)	117.1(8)

Symmetry code: I, $\frac{1}{2} - x, 1 - y, z$.

Table 4 Fractional coordinates for [{CuYLₐ(NO₃)(dmso)}₂]·2dmso

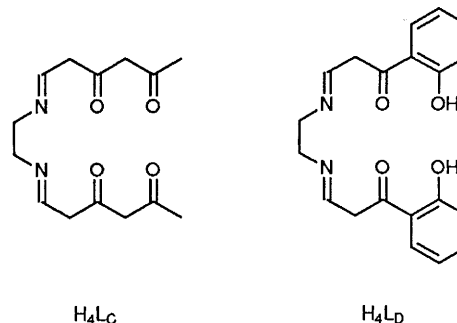| Atom	x	y	z
Y(1)	0.4260(2)	0.8984(2)	0.6213(2)
Cu(1)	0.0886(2)	0.8041(2)	0.6979(2)
O(1)	0.1826(11)	0.8823(12)	0.5810(10)
O(2)	0.2816(11)	0.8303(11)	0.7567(10)
O(3)	0.3609(11)	0.9709(10)	0.4476(9)
O(4)	0.5369(11)	0.8201(12)	0.7698(10)
N(1)	−0.1068(14)	0.7697(14)	0.6285(16)
N(2)	0.0084(15)	0.7254(14)	0.8256(15)
C(3)	0.1602(10)	0.9725(11)	0.3136(7)
C(4)	0.0104(10)	0.9425(11)	0.2878(7)
C(5)	−0.0848(10)	0.8886(11)	0.3624(7)
C(6)	−0.0301(10)	0.8648(11)	0.4627(7)
C(1)	0.1197(10)	0.8948(11)	0.4884(7)
C(2)	0.2149(10)	0.9487(11)	0.4139(7)
C(7)	−0.1386(20)	0.7991(18)	0.5336(18)
C(8)	−0.2151(20)	0.6957(22)	0.7044(20)
C(9)	−0.1510(19)	0.7132(20)	0.8095(19)
C(10)	0.0736(22)	0.6838(19)	0.9096(19)
C(12)	0.2792(12)	0.6278(11)	1.0020(8)
C(13)	0.4191(12)	0.6220(11)	1.0114(8)
C(14)	0.5089(12)	0.6873(11)	0.9345(8)
C(15)	0.4588(12)	0.7582(11)	0.8483(8)
C(16)	0.3189(12)	0.7640(11)	0.8389(8)
C(11)	0.2291(12)	0.6988(11)	0.9158(8)
O(6)	0.4967(13)	0.7481(13)	0.5516(11)
O(7)	0.2891(15)	0.6706(13)	0.6087(13)
O(8)	0.3682(18)	0.5496(16)	0.5566(15)
N(3)	0.3875(20)	0.6545(15)	0.5746(16)
O(5)	0.4475(12)	1.0912(11)	0.6625(10)
S(1)	0.5798(6)	1.1970(6)	0.6926(6)
C(17)	0.5224(30)	1.3255(22)	0.6969(25)
C(18)	0.6138(38)	1.1475(33)	0.8250(30)
S(2)	1.0356(7)	0.4789(7)	0.7426(5)
O(9)	0.9089(19)	0.4151(18)	0.8026(14)
C(19)	1.1818(29)	0.4136(28)	0.7949(22)
C(20)	0.9807(26)	0.4039(24)	0.6338(18)
O(10)*	0.000	0.000	0.000
C(21)*	0.1590(66)	0.0197(62)	−0.0054(47)

* Population parameter = 0.5.

observed that the inner compartment must be considerably enlarged to accommodate an f ion whereas the outer O_2O_2 co-

ordination site is suitable for a 4f- or 5f-metal ion and too large for a d-metal ion. Consequently all the steps of the reaction scheme produce well defined compounds without positional isomers or undesired species. We have observed that it is possible to fill the outer co-ordination compartment with a transiton-metal ion but always after the co-ordination of the first metal ion in the inner compartment. It must be noted that, with the similar compartmental ligands H_4L_C and H_4L_D, copper(II), for instance, produces two positional isomers [24–26] one having the metal in the O_2O_2 site and the other with it in the N_2O_2 site. Physicochemical data on mononuclear copper(II) and nickel(II) complexes confirm the existence of a single N_2O_2 isomer. In [Ni(H₂Lₐ)] the metal ion is diamagnetic in a square-planar configuration as already found for nickel(II) complexes with tetradentate Schiff bases,[27] while for [Cu(H₂Lₐ)] the magnetic moment (μ_{eff} = 1.89) is normal and not diagnostic of any particular co-ordination.

The very low solubility in non-co-ordinating solvents (*i.e.* chlorinated hydrocarbons) does not allow electronic spectral measurements and the correct assignment of the structural configuration of these complexes in such solvents. Electronic spectra in co-ordinating solvents (*i.e* dimethyl sulphoxide or dimethylformamide) show bands at 558 or 557 nm for the copper complex and at 550 or 557 nm for the nickel complex in line with a N_2O_2 co-ordination.[27] In addition, an X-ray investigation on crystals of [Cu(H₂Lₐ)] is fully consistent with the physicochemical data. The molecular structure of this complex is shown in Fig. 1 together with the atom numbering.

The Schiff base $H_2L_A{}^{2-}$ behaves as a tetradentate dianionic ligand; it is almost planar and the copper(II) ion is located in its N_2O_2 site. The four atoms of the co-ordination square [O(1),O(2),N(1),N(2)] are almost coplanar being alternately

H₄L_C   H₄L_D

displaced from the mean plane [*i.e.* O(1) −0.03, O(2) +0.03, N(2) −0.05, N(1) +0.05 Å]. The bond lengths to Cuⁱⁱ [Cu–N 1.93(1) and Cu–O 1.89(1) Å (mean)] are within the usual range [28] and the metal ion is displaced less than 0.01 Å from the N_2O_2 mean plane and does not present any other relevant contact in the 'fifth' or 'sixth' axial positions normal to the co-ordination plane. The bond lengths and angles (Table 3) show that the corresponding values for the two halves of the Schiff-base ligand are perfectly comparable, in particular N(1)–C(7) and N(2)–C(10) (mean 1.27 Å) are essentially double bonds whereas C(1)–O(1) and C(16)–O(2) are only partially double bonded (mean 1.33 Å).

The quasi-planar ligand molecule has a slightly stepped conformation (see terminology used in ref. 29). The angles (φ) between the donor-atom plane N_2O_2 and the two NCCCO chelate planes are 2.8° for the O(1),C(1),C(6),C(7),N(1) and 1.9° for the O(2),C(16),C(11),C(10),N(2) plane. The half-step distances (σ) of the metal ion from the above NCCCO planes are 0.16 and 0.10 Å respectively. The displacements of the ethylene carbon atoms C(8) and C(9) above and below the co-ordination plane are −0.6 and +0.3 Å respectively and the torsion angle N(1)–C(8)–C(9)–N(2) is 12°, the ethylene bridge being present in a *gauche* conformation.

As shown in Fig. 2 and reported in Table 3, the four oxygen atoms of the molecule are involved in hydrogen bonds. The free

Table 5 Selected bond distances (Å) and angles (°) for [{CuYL$_A$(NO$_3$)(dmso)}$_2$]·2dmso

Y(1)–O(3)	2.40(1)	O(3)–Y(1^I)	2.30(1)
Y(1)–O(1)	2.33(1)	Y(1)–O(2)	2.36(1)
Y(1)–O(4)	2.29(1)	Y(1)–O(6)	2.50(2)
Y(1)–O(7)	2.47(1)	Y(1)–N(3)	2.86(2)
Y(1)–O(5)	2.31(1)	Cu(1)–O(1)	1.87(1)
Cu(1)–O(2)	1.88(1)	Cu(1)–N(1)	1.94(1)
Cu(1)–N(2)	1.94(2)	O(3)–C(2)	1.39(1)
O(1)–C(1)	1.32(2)	O(2)–C(16)	1.28(2)
O(4)–C(15)	1.34(2)	N(1)–C(7)	1.28(3)
N(1)–C(8)	1.51(3)	N(2)–C(9)	1.52(2)
N(2)–C(10)	1.30(3)	C(6)–C(7)	1.45(2)
C(8)–C(9)	1.50(4)	C(10)–C(11)	1.48(3)
O(6)–N(3)	1.23(2)	O(7)–N(3)	1.24(3)
O(8)–N(3)	1.21(3)	O(5)–S(1)	1.49(1)
S(1)–C(17)	1.77(3)	S(1)–C(18)	1.79(4)
S(2)–O(9)	1.48(1)	S(2)–C(19)	1.83(1)
S(2)–C(20)	1.80(1)		
O(10)–C(21)	1.52(7)		

Contacts

Y(1)···Cu(1)	3.397(3)	Y(1)···Y(1^I)	3.781(2)
O(3)···O(3^I)	2.80(1)	O(1)···O(3)	2.55(2)
O(4)···O(3^I)	3.41(2)	O(2)···O(4)	2.55(2)
O(1)···O(2)	2.47(2)	O(1)···N(1)	2.80(2)
O(2)···N(2)	2.77(2)	N(1)···N(2)	2.76(3)
O(6)···O(7)	2.13(2)		

O(3)–Y(1)–O(3^I)	73.0(4)	O(3^I)–Y(1)–O(4)	95.7(4)
O(6)–Y(1)–O(7)	50.9(5)	O(2)–Y(1)–O(4)	66.4(5)
O(1)–Y(1)–O(2)	63.5(4)	O(3)–Y(1)–O(1)	65.3(4)
O(3)–Y(1)–O(3^I)	73.0(4)	O(3^I)–Y(1)–O(4)	95.7(4)
N(1)–Cu(1)–N(2)	90.6(8)	O(2)–Cu(1)–N(2)	92.7(7)
O(1)–Cu(1)–N(1)	94.6(7)	O(1)–Cu(1)–O(2)	82.2(6)
Cu(1)–O(1)–C(1)	127(1)	Y(1)–O(1)–C(1)	123.7(9)
Y(1)–O(1)–Cu(1)	107.5(6)	Y(1)–O(2)–Cu(1)	105.6(6)
Cu(1)–O(1)–C(1)	126.6(7)	Cu(1)–O(2)–C(16)	125(1)
Y(1)–O(1)–C(1)	123.7(7)	Y(1)–O(2)–C(16)	120(1)
Y(1)–O(3)–C(2)	118.8(7)	Y(1)–O(4)–C(15)	119.7(9)
Cu(1)–N(1)–C(8)	108(1)	Cu(1)–N(1)–C(7)	126(1)
Cu(1)–N(2)–C(9)	107(1)	Cu(1)–N(2)–C(10)	128(1)
C(7)–N(1)–C(8)	126(1)	C(9)–N(2)–C(10)	125(1)
C(5)–C(6)–C(7)	116(1)	C(10)–C(11)–C(12)	115(1)
C(1)–C(6)–C(7)	124(1)	C(10)–C(11)–C(16)	125(1)
O(1)–C(1)–C(6)	125(1)	O(2)–C(16)–C(11)	124(1)
O(1)–C(1)–C(2)	115(1)	O(2)–C(16)–C(15)	116(1)
O(3)–C(2)–C(1)	115(1)	O(4)–C(15)–C(16)	116(1)
O(3)–C(2)–C(3)	125(1)	O(4)–C(15)–C(14)	123(1)
N(1)–C(7)–C(6)	124(1)	N(2)–C(10)–C(11)	120(2)
N(1)–C(8)–C(9)	112(1)	N(2)–C(9)–C(8)	111(1)
Y(1)–O(5)–S(1)	130.1(8)		
O(6)–N(3)–O(7)	119(1)	O(6)–N(3)–O(8)	121(2)
O(7)–N(3)–O(8)	119(2)		

dmso molecules

O(5)–S(1)–C(18)	104(1)	O(5)–S(1)–C(17)	107(1)
C(17)–S(1)–C(18)	97(1)		
O(9)–S(2)–C(19)	111(1)	O(9)–S(2)–C(20)	104(1)
C(19)–S(2)–C(20)	96(1)		

Symmetry code: I 1 − x, 2 − y, 1 − z.

Table 6 Proton and ^{13}C NMR data (δ) for the ligand H$_4$L$_A$ in [^{2}H$_6$]dmso solution

	^{13}C-{^{1}H}	^{1}H
NCH$_2$	57.96	3.91 (s, 4)
arom. o- and p-CH	117.61	6.82 (m, 4)
arom. m-CH	121.8	6.63 (t, 2)
arom. =CCN	118.05	—
arom. o=COH	145.11	8.9 (br, 2)
arom. m=COH	151.13	13.3 (br, 2)
CH=N	167.11	8.53 (s, 2)

hydroxyl groups [O(3) and O(4)] of each complex are connected respectively to co-ordinated O(1) and O(2) atoms of the molecule correlated by the symmetry operation $\frac{1}{2}$ − x, 1 − y, z (two-fold axis) so that the cell contents, as a whole, can be represented as four cross-linked pairs of complex molecules. This structure agrees well, in the common part, with that reported in the literature for a chloroform solvate complex of N,N'-ethylenebis(salicylideneiminato)copper(II).[30]

Heterodinuclear d–f complexes can be obtained by reaction of the mononuclear d complex with uranyl(VI) in co-ordinating solvents and with lanthanide(III) and barium(II) ions in methanol and in the presence of a base (i.e. LiOH). In the infrared spectrum of the copper(II)–uranyl(VI) complex the sharp bands due to phenolic OH groups disappear and a very broad band, due to water molecules, is present. The v(C=N) band at 1660 cm^{-1} is practically unaffected by the co-ordination of the second metal ion. Two bands due to v(C=O) (phenolate) at 1597 and 1548 cm^{-1} are present. The strong bands at 914 and 904 cm^{-1} are easily attributable to v$_3$(O–U–O). The presence of two asymmetric v$_3$(O–U–O) bands is not unusual and has been observed several times for uranyl(VI) Schiff-base complexes. Moreover, a strong band due to co-ordinated dmso, is present.

By reaction of the mononuclear copper(II) complex [Cu(H$_2$L$_A$)] with LnX$_3$·6H$_2$O (Ln = Y or La, X = NO$_3$ or Cl), heterodinuclear complexes [CuLn(L$_A$)X] have been obtained. The IR spectra of these species show a strong band in the range 1640–1630 cm^{-1} {only [CuY(L$_A$)Cl]·2MeOH shows two bands at 1635 and 1630 cm^{-1}}. Again, as described for the copper(II)–uranyl(VI) complex there is a multiplicity of bands in the range 1595–1540 cm^{-1} due to v(C=O) (phenolate). A comparison between [CuLa(L$_A$)(NO$_3$)]·H$_2$O and [CuY(L$_A$)(NO$_3$)]·MeOH shows peaks due to bidentate nitrate groups at 1468 and 1265 cm^{-1} for the first complex, and at 1514 and 1302 cm^{-1} for the second. Both compounds show also a strong absorption respectively at 1385 and 1393 cm^{-1} attributable to ionic NO$_3$$^-$ groups; however, this may be due to exchange processes with KBr used in the pellet preparation, and the latter band disappears on using Nujol.

An X-ray structure of the [{CuYL$_A$(NO$_3$)(dmso)}$_2$]·2dmso complex shows the presence of bidentate nitrate groups only. The complex is a tetranuclear unit and its structure is reported in Fig. 3 together with the atom labelling for the asymmetric unit. The clathrate molecules are not depicted for clarity. The compound is neutral and forms a centrosymmetric dimeric complex in the crystal with the inversion centre located in the Y(1)–O(3)–Y(1^I)–O(3^I) core (symmetry operation I 1 − x, 2 − y, 1 − z). As shown in Fig. 3, the entire complex, apart from the nitrate and dmso groups co-ordinated to the yttrium atoms, is roughly planar, with maximum dihedral angles of about 24° between the two phenyl rings [C(1)–C(6) and C(11)–C(16)]. The co-ordination of the second metal introduces some differences in bond lengths, angles and spatial conformation in the organic moiety with respect to the mononuclear copper complex [Cu(H$_2$L$_A$)]. The copper ion has a quasi-square-planar configuration and is displaced by 0.04 Å from the co-ordination N$_2$O$_2$ plane. The ligand changes from a stepped to an 'umbrella' conformation[29] and the two halves are very similar to each other in bond lengths and angles but differ from those observed in the mononuclear complex. The angles (φ)[29] between the N$_2$O$_2$ co-ordination plane and the pentaatomic NCCCO chelating rings are 2.1 [for N(1),C(7),C(6),C(1),O(1)] and 17.3° [for N(2),C(10),C(11),C(16),O(2) mean plane]. The half step distances (σ)[29] from the copper ion to the above NCCCO planes are 0.00 and 0.35 Å respectively; the phenyl rings too are differently inclined with respect to the co-ordination plane forming dihedral angles of 3.1 [C(1)–C(6) ring] and 24.5° [C(11)–C(16)]. The atoms O(1) and O(2), now involved in a bridging co-ordination, change in contact distance from 2.63(1) Å, in the mononuclear, to 2.47(2) Å in the binuclear complex and, consequently, the angle O(1)–Cu–O(2) changes from 87.8 to 82.2(6)°.
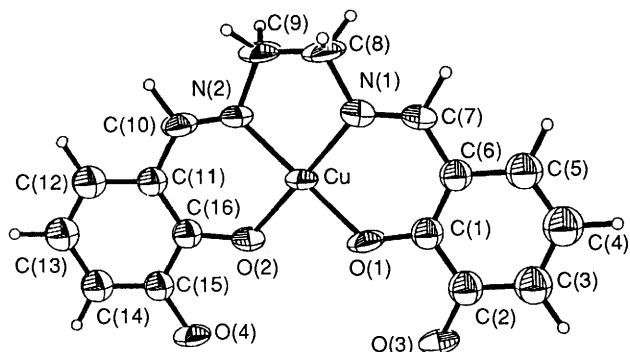
Fig. 1 An ORTEP view of [Cu(H₂L_A)]. The non-hydrogen atoms are represented by their 50% probability ellipsoids, hydrogen atoms by spheres of arbitrary size

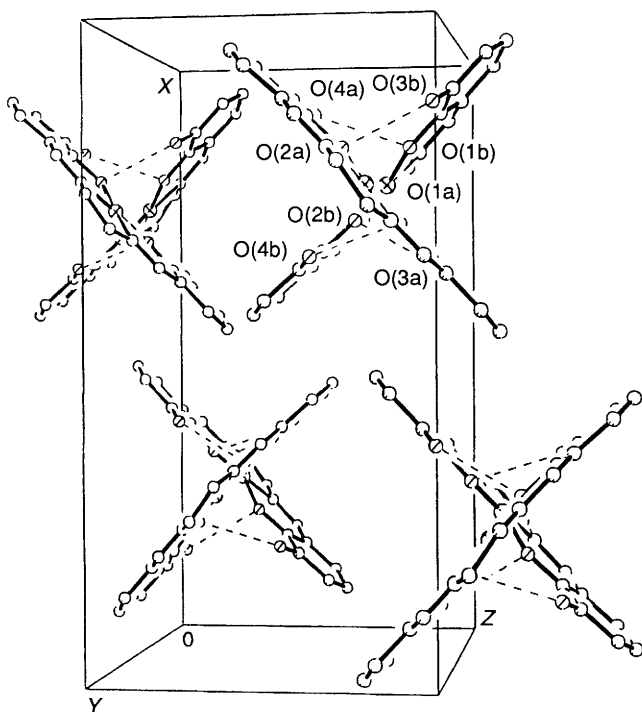**Fig. 2** The cell packing of [Cu(H₂L_A)] in the *b* projection; the labelling a and b indicates oxygen atoms of two different, hydrogen bonded molecules

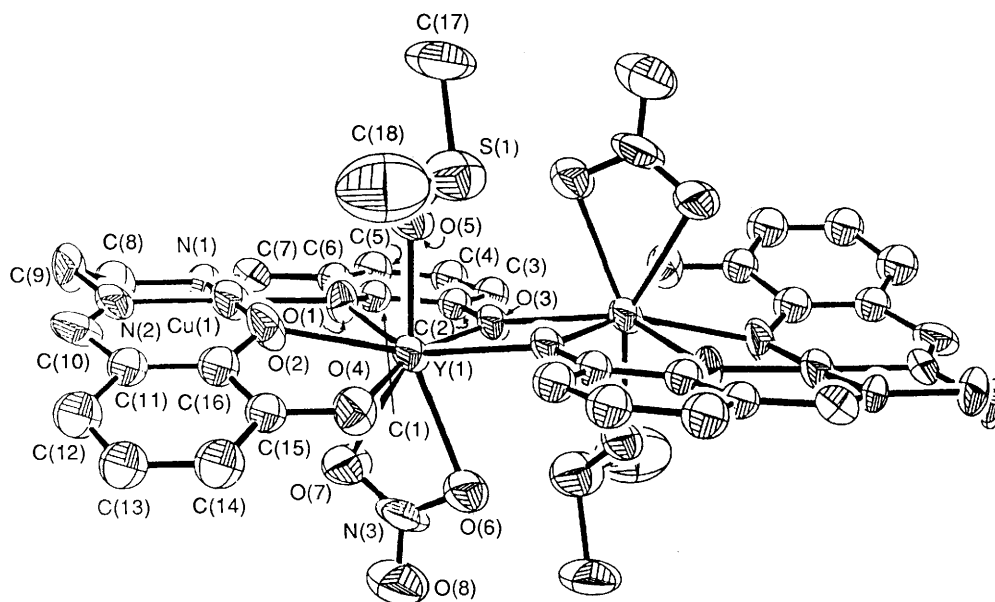The yttrium is eight-co-ordinated (Fig. 4) and, owing to the severe difference in the nature and charge between the donor oxygens, an approach to the description of the co-ordination polyhedron in a 'classical' way [31] is practically impossible. The geometry around the Y[III] can be well described as irregular pentagonal bipyramidal with atoms O(3),O(1),O(2),O(4),O(3¹) forming the equatorial plane; the two apical positions are occupied by O(5) of the co-ordinated dmso group on one side and by O(6) and O(7) of the bidentate nitrato group on the other side. This group, owing to its relatively short 'bite' [2.14(2) Å] of the two bonding oxygens, can be depicted as occupying a 'single' site of the polyhedron, similar and opposite to the dmso molecule. The lines O(5)(dmso)–Y(1) and M'(nitrate)–Y(1) [where M' is the middle point between O(6) and O(7)] are practically normal to the equatorial mean plane [O(3),O(1),O(2),O(4),O(3¹)], forming angles of 92.5 and 89.1° respectively.

The equatorial oxygens are bridging atoms apart from the terminal negatively charged O(4) which presents the shortest bond distance [2.29(1) Å] to the yttrium ion. The bonds Y–O(1) [2.32(1) Å] and Y–O(2) [2.36(1) Å] are comparable; Y–O(3) [2.40(1) Å] is very different from Y–O(3¹) [2.30(1) Å] showing that this oxygen is asymmetrically shared between the two yttrium atoms of the complex. The metal–metal separations are 3.397(3) Å for Cu···Y and 3.781(2) Å for Y···Y. The Y–O(ligand) bonds are in the range 2.29–2.40 Å, Y–O(dmso) is 2.31(1) Å and Y–O(nitrate) are 2.48 Å (mean).

The reaction of heterodinuclear complexation can be applied to other systems and by this procedure the heterodinuclear [CuBaL_A]·2H₂O complex has been prepared. Its infrared spectrum is quite similar to those of the other heterodinuclear complexes prepared: ν(C=N) lies at 1655 cm⁻¹ and the absorptions at 1589, 1564 and 1537 cm⁻¹ may be due to ν(C=O) (phenolate). These heterodinuclear complexes have been used as precursors in the synthesis, by thermal decomposition, of mixed oxides. Particular attention has been devoted to [CuY(L_A)(NO₃)]·MeOH and [CuLa(L_A)-(NO₃)]·H₂O.

Thermogravimetric measurements show that the [CuY(L_A)-(NO₃)]·MeOH complex loses the solvent molecule when the sample is under an air flux, and the nitrate group at 245 °C (weight loss 12.90, calc. 12.45%). At 290 and 325 °C the complex suffers an exothermic decomposition leading to a final compound which shows a stability range from 700 to 1100 °C (weight loss 62.70, calc. 62.30%) (Fig. 5) formulable, in
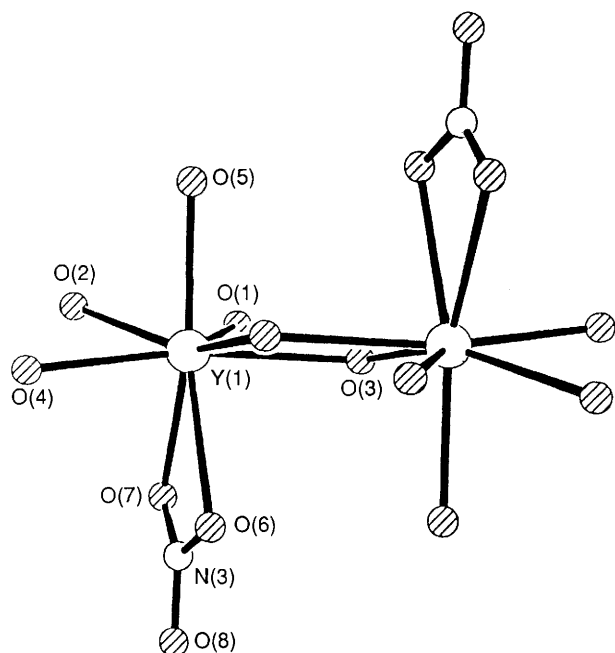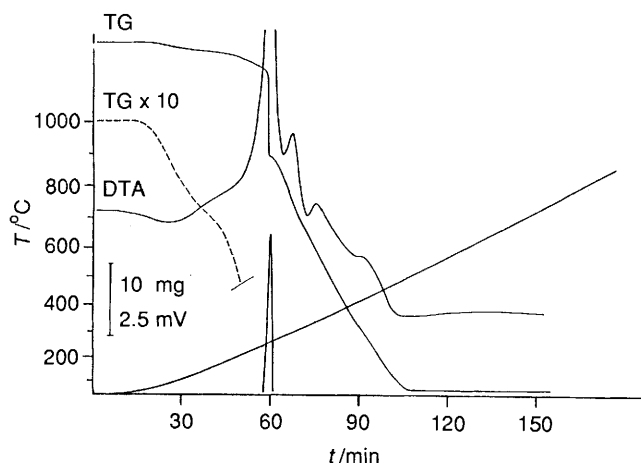

Fig. 3 An ORTEP diagram of [{CuYL_A(NO₃)(dmso)}₂]·2dmso with probability ellipsoids drawn at the 50% level. Lattice dmso and hydrogen atoms are not shown

Fig. 4 A view of the yttrium ion environment

Fig. 5 Thermal behaviour of [CuY(L$_A$)(NO$_3$)]·MeOH. The temperature variation T with time is estimated from the mV reading

Fig. 6 X-Ray fluorescence spectrum of [CuY(L$_A$)(NO$_3$)]·MeOH

Fig. 7 A SEM image (secondary electrons) of [CuY(L$_A$)(NO$_3$)]·MeOH marker 10μm)

Fig. 8 An SEM image (secondary electrons) of the compound formulable as CuY$_2$O$_4$ + CuO (marker 1 μm)

agreement with an electron microscopy investigation, as CuY$_2$O$_4$ + CuO (see below). The thermal behaviour of [CuLa(L$_A$)(NO$_3$)]·H$_2$O is comparable to that of [CuY(L$_A$)-(NO$_3$)]·MeOH, giving rise at 550 °C to a product formulable as CuLa$_2$O$_4$ + CuO stable up to about 700 °C as evidenced by the X-ray powder diffraction (XRD) analysis. The pattern for CuLa$_2$O$_4$ is completely in accord with an orthorhombic symmetry.

An investigation by scanning electron microscopy and X-ray fluorescence spot analyses was carried out on the starting complexes [CuY(L$_A$)(NO$_3$)]·MeOH, [CuLa(L$_A$)(NO$_3$)]·H$_2$O and the oxides obtained. By integration of back-scattered X-rays, metal ratios can be evaluated and the sample homogeneity checked. This technique gives multielement analyses on small volumes of the samples (about 1 μm^3 depending of the average atomic composition.[32,33] The complexes are homogeneous with a 1:1 metal ratio as shown in Fig. 6 for [CuY(L$_A$)(NO$_3$)]·MeOH. Fig. 7 shows the morphology of [CuY(L$_A$)(NO$_3$)]·MeOH; 1 μm microcrystals are clearly detectable, the sample being homogeneous. The copper–yttrium oxide is conveniently formulated as CuY$_2$O$_4$ + CuO as evidenced by the X-ray fluorescence spot analyses, carried out by using a windowless detector, on different particles of the sample (Figs. 8–10). The
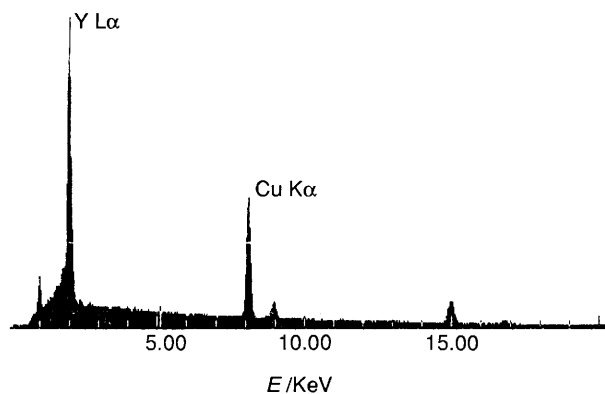
absence of carbon- and nitrogen-containing residues was also confirmed.

The thermal analysis of [CuBaL$_A$]·2H$_2$O shows that the compound loses solvent molecules under an air flux and suffers an immediate exothermic decomposition ending at 480 °C (weight loss 52.3, calc. 51.95%) leading to a final product formulable as CuBaO$_2$. Above 700 °C the compound suffers a further modification probably due to an oxygen deficiency. Further investigations are in progress with the aim of discovering new routes for the preparation of mixed oxides in the synthesis of ceramic superconductors.
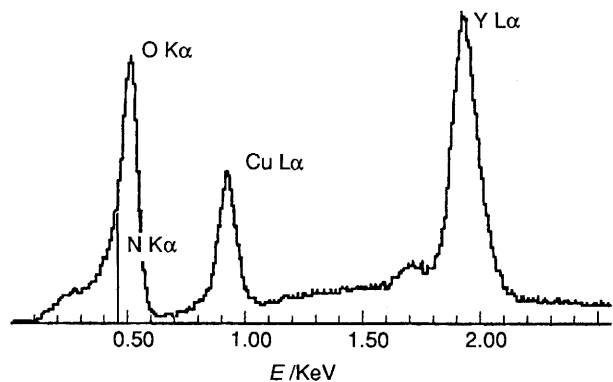
Fig. 9 X-Ray fluorescence spectrum of the CuY_2O_4 phase (a windowless detector was used in order to identify light elements)
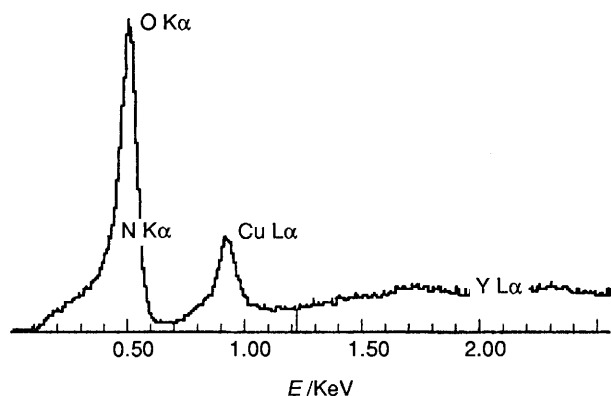

Fig. 10 X-Ray fluorescence spectrum of the CuO phase (details as in Fig. 9)

Acknowledgements

References

1 P. Guerriero, S. Sitran, P. A. Vigato, C. Marega, A. Marigo and R. Zannetti, *Inorg. Chim. Acta*, 1990, **171**, 103.
2 M. L. Steigerward and C. R. Sprinkle, *Organometallics*, 1988, **7**, 245.
3 J. G. Brennan, T. Siegrist, P. J. Carroll, S. M. Stuczynski, L. E. Brus and M. L. Steigerward, *J. Am. Chem. Soc.*, 1988, **110**, 4228.
4 M. L. Steigerward, *Chem. Mater.*, 1989, **1**, 52.
5 J. G. Brennan, T. Siegrist, S. M. Stuczynski, L. E. Brus and M. L. Steigerward, *J. Am. Chem. Soc.*, 1989, **111**, 9240.
6 D. R. Uhlmann, B. J. J. Zwlinski and G. E. Wnek, *Mater. Res. Soc. Symp. Proc.*, 1984, **32**, 59.
7 N. N. Sauer, E. Garcia, K. V. Salazar, R. R. Ryan and J. A. Martin, *J. Am. Chem. Soc.*, 1990, **112**, 1524.
8 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603.
9 K. D. Karlin, Q. Gan, A. Farooq, S. Lin and J. Zubieta, *Inorg. Chim. Acta*, 1989, **165**, 37.
10 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1985, 158.
11 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385.
12 D. E. Fenton, S. J. Kitchen, C. M. Spencer, S. Tamburini and P. A. Vigato, *J. Chem. Soc., Dalton Trans.*, 1988, 685.
13 A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392; O. Kahn, *Struct. Bonding (Berlin)*, 1987, **68**, 89.
14 P. Guerriero, P. A. Vigato, J.-C. G. Bünzli and E. Moret, *J. Chem. Soc., Dalton Trans.*, 1990, 647.
15 P. A. Vigato, S. Tambutini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25.
16 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1965, **24**, 351.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
18 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.
19 G. M. Sheldrick, SHELX, A System of Computer Programs for X-Ray Structure Determination, Göttingen, 1976.
20 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
21 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
22 H. st Rade, *J. Chem. Phys.*, 1973, **77**, 424.
23 Ch. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 208.
24 D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.*, 1977, 2101.
25 D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1982, **62**, 57.
26 D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1978, **27**, 9.
27 K. Ueno and A. E. Martell, *J. Chem. Phys.*, 1957, **61**, 257; J. P. Fackler, jun., *J. Am. Chem. Soc.*, 1962, **84**, 24; R. H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 5632.
28 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.
29 H. S. Maslen and T. N. Waters, *Coord. Chem. Rev.*, 1975, **17**, 137.
30 E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. A*, 1970, 406.
31 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.
32 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta*, 1986, **119**, 215.
33 P. Guerriero, P. A. Vigato and B. Burtet-Fabris, *Inorg. Chim. Acta*, 1989, **164**, 155.