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Mononuclear, homo- and heteropolynuclear complexes with acyclic compartmental Schiff bases

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Abstract

Acyclic compartmental Schiff bases (H_4L) have been synthesized by condensation of 2,3-dihydroxybenzaldehyde with the diamines NH_2–R–NH_2 (R = $-(CH_2)_2-$, H_4L_A; $-C(CH_3)_2-CH_2-$, H_4L_B; $-CH_2-C(CH_3)_2-CH_2-$, H_4L_C; $-C_6H_4-$, H_4L_D). Mononuclear complexes have been obtained by reaction of these hexadentate ligands with the appropriate metal(II) ions (copper(II), nickel(II), uranyl(VI) or lanthanium(III)) or by template procedure. The d metal ions coordinate into the inner N_2O_2 compartment, while uranyl(VI) or lanthanium(III) occupy the outer O_2O_2 site of the ligands. Crystals of Ni(H_2L_C), grown from a methanol/diethyl ether solution are triclinic, space group $P\bar{1}$ with $a=11.040(5)$, $b=13.645(5)$, $c=14.877(6)$ Å; $\alpha=71.93(4)$, $\beta=84.62(5)$, $\gamma=66.56(5)°$ for $Z=2$. The two chemically identical molecules of the nickel complex, present in the asymmetric portion of the cell, contain a methanol or a water molecule, respectively, linked by hydrogen bonds in the O_2O_2 outer site. The coordination around nickel ions, placed in the N_2O_2 sites, is not strictly planar, all atoms being tetrahedrally displaced from the mean coordination planes by about 0.047 and 0.093 Å (mean) for the two molecules A and B, respectively. The metal ion is displaced by 0.026 and 0.015 Å from the same planes. The average bond lengths for Ni–O and Ni–N are 1.84 Å. In the heteropolynuclear complexes $MLn(H_2L)(X)_3$, $[MLn(L)(NO_3)(S)]_2$ and $MUO_2(L)(S)$, ($M=Cu^{2+}$, Ni^{2+}; Ln = La, Gd; S = H_2O, MeOH, dmso), obtained by a step by step procedure, the smaller d ion always occupies the inner N_2O_2 chamber, while the larger f ion occupies the outer O_2O_2 chamber. The ligands and the complexes have been characterized by IR, ^1H and ^{13}C NMR, X-ray, mass spectrometric and magnetic susceptibility studies. The temperature dependence of the magnetic susceptibility of heterodinuclear and heterotetranuclear complexes containing copper(II) and gadolinium(III) ions, in the temperature range 4.2–300 K, shows a ferromagnetic interaction between the d and f metal ions ($J_{CuGd}=1.59(3)$ and $-3.76(4)$ cm^{-1} for $CuGd(H_2L_A)(NO_3)_3$ and $[CuGd(L_A)(NO_3)(H_2O)]_2$, respectively.

Introduction

Compartmental macrocyclic and macroacyclic ligands, containing two adjacent coordination chambers, and related homo- and heterodinuclear complexes have been widely studied and reviewed owing to their unusual structural features and their peculiar magnetic, optical or catalytic properties [1–9]. With suitable prescursors, the metal...metal distance can appropriately be fixed and hence the physicochemical properties of the complexes adequately tuned.

Recently homo- and heterodinuclear complexes containing lanthanide(III) ions have been prepared by using compartmental ligands of suitable dimensions. The increasing interest for a better knowledge of the properties of polynuclear complexes containing lanthanide ions is due to peculiar physicochemical properties of the various 4 f ions and to their use as essential components in the manufacture of new optical and magnetic materials.

In particular the macrocyclic H_2-**I**–H_2-**III** and the macroacyclic H_4-**IV** and H_4-**VIII** systems contain coordination chambers large enough to accommodate two equal or different coordination lanthanide ions [10–13].

In contrast macrocycles with a smaller cavity such as H_2-**IX** or H_2-**X** can accommodate only one lanthanide ion into the coordination cavity as confirmed also by X-ray structural determinations [14, 15]. In the complexes with H_2-**IX** a ring contraction of the free chamber, not involved in the coordination to the central metal ion, occurs with the formation of a five-membered imidazoline ring.

Analogously the acyclic ligands H_4-**XI** and H_4-**XII** coordinate d transition metal ions quite well into their

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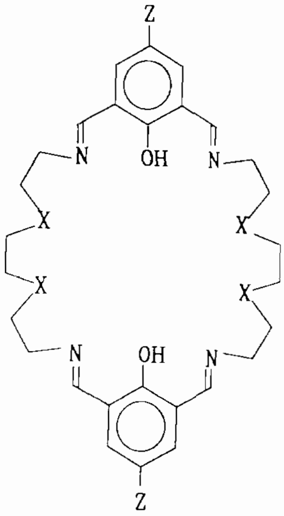
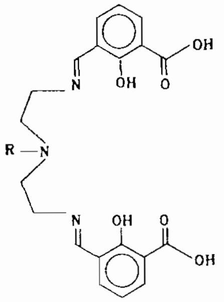
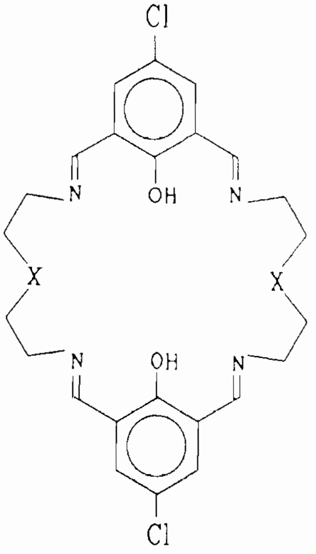


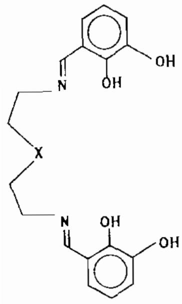
H$_2$-I (X=O, Z=CH$_3$)
H$_2$-II (X=O, Z=Cl)
H$_2$-III (X=NH, Z=CH$_3$)



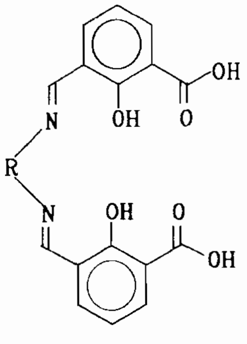
R= -(CH$_2$)$_{11}$-CH$_3$	H$_2$-IV
R= -H	H$_2$-V



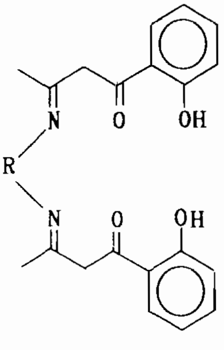
	X
H$_2$-IX	NH
H$_2$-X	S



X	
NH	H$_2$-VI
S	H$_2$-VII
N-(CH$_2$)$_{11}$-CH$_3$	H$_2$-VIII



H$_4$-XI



H$_4$-XII

(R = aliphatic or aromatic chain without donor atoms)

inner N_2O_2 coordination site but are unable to secure large f ions into this coordination moiety [16–23]. Thus on going from hepta- to hexa-acyclic ligands which differ from one another in denticity of the inner compartment, larger N_2XO_2 for the former and smaller N_2O_2 for the latter, while both ligands have the same O_2O_2 outer chamber (Fig. 1), it is possible to prepare f,f dinuclear complexes or d,f heterodinuclear complexes, respectively.

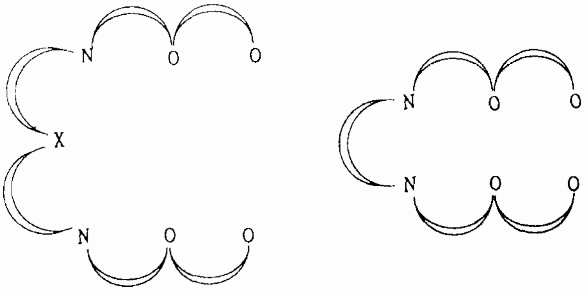
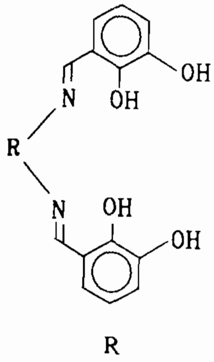


Fig. 1. Schematic representation of the two coordination chambers for hepta- (A) and hexa-acyclic ligands (B).

It has been verified that an antiferromagnetic interaction is operating in homodinuclear lanthanide(III) complexes. In particular for $Gd_2(VI)(NO_3)_2 \cdot 4H_2O$ the effective magnetic moment decreases with the lowering of the temperature, passing from 10.97 μ_B at room temperature to 7.96 μ_B at 4.2 K. For a *g* factor value of 1.975 an antiferromagnetic coupling constant $J = 0.211(4)$ cm^{-1} has been obtained and a super exchange mechanism through the oxygen bridges has been proposed [12].



$-(CH_2)_2-$	(H_4L_A)
$-C(CH_3)_2-CH_2-$	(H_4L_B)
$-CH_2-C(CH_3)_2-CH_2-$	(H_4L_C)
$-C_6H_4-$	(H_4L_D)

In order to estimate the interactions between d and f metal ions the potentially hexadentate Schiff bases, obtained by reaction of 2,3-dihydroxybenzaldehyde with the diamines NH_2-R-NH_2 ($R = -(CH_2)_2-$ (H_4L_A); $-C(CH_3)_2-CH_2-$ (H_4L_B); $-CH_2-C(CH_3)_2-CH_2-$ (H_4L_C); $-C_6H_4-$ (H_4L_D)) were prepared and their interactions with d and f metal ions studied.

Particular attention was devoted to the evaluation of the variation in NMR data (^1H and ^{13}C) on going from the free ligands to the heteropolynuclear complexes through the mononuclear analogues.

Finally the temperature dependence of the magnetic susceptibility for some of the prepared complexes, particularly those containing gadolinium(III) and copper(II) ions, has been investigated in the temperature range 4.2–300 K in order to ascertain the magnetic interaction that generates from the close proximity of paramagnetic d and f centres.

Experimental

Materials

1,2-Diaminoethane, 1,2-diamino-2-methylpropane, 1,3-diamino-2,2-dimethylpropane, 2,3-dihydroxybenzaldehyde, the solvents and the metal salts were commercial products, used without further purification, while 1,2-diaminobenzene was recrystallized from chloroform three times before use.

The elemental analyses of the ligands and related complexes are reported in Table 1.

Preparation of H_4L_A, H_4L_B, H_4L_C, H_4L_D

The ligands were prepared following the literature procedure [24, 25]. A typical experimental procedure is as follows. To a methanolic solution (50 ml) of 2,3-

TABLE 1. Elemental analysis of the prepared ligands and complexes

Compound	Calc. (%)			Found (%)		
	C	H	N	C	H	N
$H_4L_A\cdot 0.5MeOH$	62.65	5.74	8.86	62.98	5.75	9.08
$Ni(H_2L_A)$	53.83	3.95	7.84	54.45	4.32	7.49
$Cu(H_2L_A)$	52.51	4.06	7.19	53.01	3.09	7.70
$La(H_4L_A)(NO_3)_3(MeOH)$	31.07	3.06	10.65	30.74	3.19	10.64
$UO_2(H_2L_A)(MeOH)$	34.01	3.02	4.66	34.12	2.84	4.55
$Cu_2(LA)(MeOH)$	44.44	4.39	6.10	44.63	3.65	6.02
$[NiLa(H_2L_A)(NO_3)_3\cdot 2H_2O]$	26.77	2.52	9.75	26.58	2.61	9.43
$[NiGd(H_2L_A)(NO_3)_3\cdot 2H_2O]$	26.10	2.46	9.51	26.18	2.37	9.32
$[CuLa(H_2L_A)(NO_3)_3\cdot 2H_2O]$	26.59	2.51	9.69	26.45	2.48	9.53
$[CuGd(H_2L_A)(NO_3)_3\cdot 2H_2O]$	25.93	2.44	9.45	26.02	2.43	9.38
$[NiLa(H_2L_A)(Ac)_3\cdot 2H_2O]$	37.27	3.83	3.95	37.25	3.72	3.76
$[NiGd(H_2L_A)(Ac)_3\cdot 2H_2O]$	36.33	3.74	3.85	36.12	3.55	3.62
$[CuLa(H_2L_A)(Ac)_3\cdot 2H_2O]$	37.01	3.81	3.92	36.90	3.85	3.88
$[CuGd(H_2L_A)(Ac)_3\cdot 2H_2O]$	36.01	3.71	3.83	36.22	3.78	3.62
$[NiLa(H_2L_A)\cdot Cl_3\cdot 2H_2O]$	30.11	2.84	4.39	30.18	2.66	4.25
$[NiGd(H_2L_A)\cdot Cl_3\cdot 2H_2O]$	29.27	2.76	4.26	29.12	2.75	4.68
$[CuLa(H_2L_A)\cdot Cl_3\cdot 2H_2O]$	29.88	2.82	4.35	29.82	2.78	4.54
$[CuGd(H_2L_A)\cdot Cl_3\cdot 2H_2O]$	29.05	2.74	4.23	29.18	2.85	4.66
$[NiLa(H_2L_A)(ClO_4)_3\cdot 2H_2O]$	23.14	2.18	3.37	23.18	2.15	3.46
$[NiGd(H_2L_A)(ClO_4)_3\cdot 2H_2O]$	22.64	2.13	3.30	22.52	2.18	3.38
$[CuLa(H_2L_A)(ClO_4)_3\cdot 2H_2O]$	23.01	2.17	3.35	23.13	2.36	3.44
$[CuGd(H_2L_A)(ClO_4)_3\cdot 2H_2O]$	22.52	2.12	3.28	22.64	2.15	3.20
$[CuUO_2(L_A)(MeOH)]$	30.85	2.43	4.32	30.62	2.38	4.12
$[NiLa(L_A)(NO_3)(MeOH)]_2$	34.73	2.74	7.14	34.55	2.72	7.10
$[NiGd(L_A)(NO_3)(MeOH)]_2$	33.68	2.66	6.93	33.59	2.43	6.84
$[CuLa(L_A)(NO_3)(MeOH)]_2$	34.45	2.72	7.09	34.24	2.65	7.18
$[CuGd(L_A)(NO_3)(MeOH)]_2$	33.43	2.63	6.87	33.58	2.46	6.55
H_4L_B	65.84	6.14	8.53	65.29	6.31	8.44
$Cu(H_2L_B)\cdot 1.5H_2O$	51.86	5.08	6.72	51.76	4.80	6.86
$[CuLa(H_2L_B)(NO_3)_3\cdot 4H_2O]$	27.48	3.33	8.90	27.55	3.15	8.46
$[CuLa(L_B)(NO_3)\cdot H_2O]$	35.63	2.99	6.92	35.72	3.05	6.74
$[CuLa(H_2L_B)(Cl)_3\cdot 2H_2O]$	32.21	3.30	4.17	32.18	3.25	4.02
$[CuLa(H_2L_B)(Ac)_3\cdot 3H_2O]$	37.93	4.37	3.69	38.15	4.26	3.65
$[CuLa(H_2L_B)(ClO_4)_3\cdot 3H_2O]$	24.53	2.74	3.18	24.42	3.02	2.96
$[CuGd(H_2L_B)(Ac)_3\cdot 2H_2O]$	37.92	4.10	3.68	37.82	4.18	3.47
$[CuUO_2(L_B)(MeOH)]$	33.08	2.92	4.06	33.24	2.88	4.05
$Ni(H_2L_B)$	56.15	4.71	7.27	55.82	4.79	7.07
$[NiLa(H_2L_B)(NO_3)_3\cdot 4H_2O]$	27.65	3.35	8.95	27.55	3.12	8.72
$[NiLa(L_B)(NO_3)\cdot H_2O]$	35.92	3.01	6.98	35.88	3.22	7.15
$[NiLa(H_2L_B)(Cl)_3\cdot 2H_2O]$	32.45	3.32	4.20	32.79	3.15	4.60
$[NiLa(H_2L_B)(Ac)_3\cdot 3H_2O]$	38.17	4.40	3.71	38.22	4.55	3.68
$[NiLa(H_2L_B)(ClO_4)_3\cdot 4H_2O]$	24.17	2.93	3.13	24.45	2.88	3.24
$[NiGd(H_2L_B)(Ac)_3\cdot 1H_2O]$	39.09	3.96	3.80	39.27	3.76	3.65
$[NiUO_2(L_B)(MeOH)]$	33.31	2.94	4.09	33.24	2.75	4.43
H_4L_C	66.65	6.48	8.18	66.39	6.62	8.21
$Ni(H_2L_C)$	55.14	5.52	6.36	54.72	5.32	6.72
$Cu(H_2L_C)\cdot 1H_2O$	54.09	5.25	6.64	53.89	5.32	6.40
$[CuLa(L_C)(NO_3)\cdot 3H_2O]$	34.74	3.68	6.40	34.83	3.65	6.52
$[CuLa(H_2L_C)(NO_3)_3\cdot 3H_2O]$	29.15	3.34	8.94	29.32	3.30	8.68
$[NiLa(H_2L_C)(NO_3)\cdot 2H_2O]$	30.03	3.18	9.21	29.91	3.12	9.15
H_4L_D	68.69	4.62	8.04	68.90	4.89	8.05
$[Ni(H_2L_D)\cdot 0.5H_2O]$	58.44	3.59	6.81	58.47	3.61	6.78
$[NiLa(H_2L_D)(NO_3)_3\cdot H_2O]$	32.20	1.89	9.39	32.36	2.05	9.02
$[NiLa(H_2L_D)(Ac)_3\cdot 2H_2O]$	41.36	3.34	3.71	41.22	3.26	3.69
$[NiLa(H_2L_D)(Cl)_3\cdot H_2O]$	32.44	2.77	3.60	32.48	2.81	3.64

(*continued*)

TABLE 1. (*continued*)

Compound	Calc. (%)			Found (%)		
	C	H	N	C	H	N
$[NiUO_2(L_D) \cdot H_2O]$	34.76	2.04	4.05	34.52	2.32	4.18
$[NiGd(H_2L_D)(NO_3)_3 \cdot H_2O]$	31.35	2.10	9.14	31.22	2.36	9.42
$[NiLa(L_D)(Ac) \cdot H_2O]$	41.14	2.66	4.36	41.28	2.65	4.32
$[NiLa(H_2L_D)(Ac)_3 \cdot 2H_2O]$	42.07	2.85	3.77	42.03	2.72	3.68
$[NiGd(H_2L_D)(Ac)_3 \cdot 2H_2O]$	40.03	3.48	3.59	39.88	3.32	3.61
$[Cu(H_2L_D) \cdot 0.5H_2O]$	57.35	3.60	6.68	57.17	3.53	6.65
$[CuLa(H_2L_D)(NO_3)_3]$	30.53	2.30	8.90	30.98	2.32	9.00
$[CuLa(H_2L_D)(Ac)_3 \cdot 2H_2O]$	41.09	3.31	3.68	41.12	3.18	3.55
$[CuLa(H_2L_D)(Cl)_3 \cdot 4H_2O]$	33.03	3.04	3.85	33.13	3.22	3.77
$[CuUO_2(L_D) \cdot H_2O]$	34.52	2.02	4.02	34.48	2.12	4.16

dihydroxybenzaldehyde (2 mmol), the appropriate diamine (1 mmol) in methanol (30 ml) was added. The solution was refluxed for 2 h. The solvent was partially evaporated under reduced pressure and the yellow (H_4L_A–H_4L_C) or red (H_4L_D) precipitate filtered off, washed with methanol and dried *in vacuo*. The crude product can be recrystallized from methanol or chloroform.

Preparation of $M(H_2L) \cdot nS$ $(M=Cu^{2+}, Ni^{2+}; S=H_2O; n=0\text{–}1.5)$

To a methanolic solution (50 ml) of 2,3-dihydroxybenzaldehyde (2 mmol), the appropriate diamine (1 mmol) in methanol (30 ml) was added. To the resulting solution the desired metal(II) acetate (1 mmol) and LiOH (2 mmol) in methanol (50 ml) were added. The resulting solution (or suspension) was refluxed for 1 h and reduced in volume. The precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

The same mononuclear complexes can be prepared when the preformed ligands (H_4L_A–H_4L_D) are used instead of the related precursors.

The complexes can be recrystallized from a methanol/diethyl ether solution.

Preparation of $UO_2(H_2L_A)(CH_3OH)$

To a warm solution (50 ml) of 2,3-dihydroxybenzaldehyde (2 mmol) ethylenediamine (1 mmol) in methanol (50 ml) was added dropwise. After the addition of uranyl(VI) acetate in methanol, the resulting suspension was refluxed for 1 h. The orange–brown precipitate was filtered off, washed with methanol and dried *in vacuo*.

The same complex has been prepared from the preformed ligand H_2L_A and uranyl(VI) diacetate in refluxing methanol.

Preparation of $La(H_4L_A)(NO_3)_3 \cdot CH_3OH$

The same procedure used to obtain the mononuclear uranyl(VI) complex was employed to obtain $La(H_4L_A)(NO_3)_3$. The yellow solid, formed by template procedure or by addition of lanthanum(III) nitrate to the preformed ligand, was filtered off, washed with methanol and dried *in vacuo*.

Preparation of $Cu_2(L_A)(CH_3OH)$

To 1,2-diaminoethane (1 mmol) in methanol (50 ml) 2,3-dihydroxybenzaldehyde (2 mmol) in methanol (50 ml) was added. To the resulting yellow solution, after a reflux of 15 min, copper(II) acetate tetrahydrate (2 mmol) and LiOH (4 mmol) were added. The solution turned to brown and separated a brown precipitate. The suspension was refluxed for 2 h; then the brown precipitate was filtered off, washed with methanol and dried *in vacuo*.

Preparation of heterodinuclear complexes $MLn(H_2L)(X)_3 \cdot nH_2O$ $(M=Cu^{2+}, Ni^{2+}; Ln=La^{3+}, Gd^{3+}; X=NO_3^-, Cl^-, CH_3COO^-, ClO_4^-; n=1\text{–}4)$

To a methanolic suspension of the appropriate mononuclear complex $M(H_2L)$ (1 mmol), a methanolic solution (100 ml) of the appropriate lanthanide(III) salt (1 mmol) was added. The suspension was refluxed for 2 h. The resulting red solution was evaporated to dryness and the residue was treated with methanol, filtered off, washed with methanol and dried *in vacuo*.

$CuLa(H_2L_A)(NO_3)_3$ and $CuLa(H_2L_D)(NO_3)_3$ were also obtained by addition of copper(II) acetate (1 mmol) and lanthanum(III) nitrate (1 mmol), in that order, to the appropriate preformed ligand (1 mmol). The resulting solution was refluxed for 2 h, then evaporated to dryness. The residue was treated with methanol, filtered off, washed with methanol and dried *in vacuo*.

N.B. Experimental procedures where the order of the reactants was not followed, produced the same complexes.

Preparation of $CuUO_2(L_A)(CH_3OH)$, $CuUO_2(L_B)(CH_3OH)$ *and* $CuUO_2(L_D)(CH_3OH)$

(a) To a methanolic solution (50 ml) of the appropriate mononuclear copper(II) complex (1 mmol), uranyl(VI) acetate (1 mmol) in methanol (50 ml) was added. The solution was refluxed for 2 h, and the orange–brown precipitate obtained was collected by filtration, washed with methanol and dried *in vacuo*.

(b) To a methanolic solution (50 ml) of the appropriate ligand (1 mmol) or of the formyl (2 mmol) and amine (1 mmol) precursors, copper(II) acetate (1 mmol) and uranyl(VI) acetate (1 mmol) were added in order. The resulting solution, refluxed for 2 h, separated an orange–brown precipitate which was filtered off, washed with methanol and dried *in vacuo*.

Preparation of [$MLn(L_A)(NO_3)(S)]_2$ ($M = Cu^{2+}$, Ni^{2+}; $Ln = La^{3+}$, Gd^{3+}; $S = H_2O$, dmso, CH_3OH)

To a methanolic solution (100 ml) of the appropriate mononuclear complex (1 mmol), LiOH (2 mmol) was added. The suspension obtained was refluxed for 2 h. To the solution obtained the appropriate lanthanide(III) nitrate (1 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 and dried *in vacuo*.

X-ray crystallography

A crystal of dimensions 0.10×0.12×0.08 mm was used for X-ray measurements. Data collection was performed on a Philips PW1100 automatic diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å). Cell dimensions were determined by a least-square refinement of 25 medium-angle settings.

Crystal data for $C_{37}H_{42}N_4O_{10}Ni_2$: $MW = 820.1$, triclinic, space group $P\bar{1}$, $a = 11.040(5)$, $b = 13.645(5)$, $c = 14.877(6)$ Å; $\alpha = 71.93(4)$, $\beta = 84.62(5)$, $\gamma = 66.56(5)$°; $V = 1953.6(9)$ Å^3, $D_c = 1.41$ g cm^{-3}, for $Z = 2$, μ(Mo Kα) = 9.8 cm^{-1}, $F(000) = 840$. The crystal was stable under irradiation, but of a total of 5696 reflections read, only 2570 with $I > 3\sigma(I)$ could be considered as observed, indicating a relatively low degree of crystallinity of the compound.

Resolution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. Phenyl groups were refined as rigid bodies; hydrogen atoms were introduced in calculated positions with fixed thermal parameter ($U_{iso} = 0.08$ Å^2).

At convergence, the residual conventional R factor was 0.066 based on observed reflections. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. The SHELX program package [26] and its scattering factors were used in the calculations but scattering factors for Ni were those of ref. 27. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2; selected bond lengths, angles and possible contacts are reported in Table 3.

Physicochemical measurements

IR spectra were recorded as KBr pellets on a Philips PU 9624 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM200 spectrometer equipped with an Aspect 3000 computer. 2D Nuclear Overhauser effect experiments were made on degassed samples in $CDCl_3$ or acetone-d_6 and were carried out using a standard Bruker microprogram with a mixing time of 800 ms. All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG analytical Ltd) operating in electron impact (EI) (70 eV, 200 mA, ion source temperature 200 °C) and fast atom bombardment (FAB) (8 KeV Xe atom bombarding a thioglicerol/acetic solution of the sample) conditions [28, 29].

The homogeneity of the heteropolynuclear samples was checked with a Philips SEM XL40 model scanning electron microscope equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal ratios were determined by the integral counting of back scattered X-ray fluorescence radiation [30].

X-ray diffraction patterns were recorded by 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 Kα_1 radiation was employed. The step-scanning recording was performed in the 5–60° (2θ) range at 0.02° steps and with a counting time of 15 s per step.

Magnetic susceptibilities were measured using a Metronique Ingegnerie SQUID magnetometer operating at 1.0 T. The apparatus was calibrated using $Gd_2(SO_4)_3$ (Aldrich, Gold Label) [31]. Diamagnetic corrections were made by using Pascal's constants [32].

Results and discussion

Mononuclear complexes

The condensation reaction, in alcoholic solution, of the formyl precursor 2,3-dihydroxybenzaldehyde with the appropriate diamine forms the Schiff bases H_4L_A–H_4L_D of Scheme 1. These compounds are yellow (H_4L_A–H_4L_C) or red (H_4L_D) solids stable in air and soluble in the most common organic solvents. Their electron impact mass spectra show the peaks of both molecular and fragmentation products related to the structure proposed in Scheme 1 and confirmed for H_4L_C by an X-ray diffractometric investigation [25].

These hexadentate compartmental Schiff bases react with d or f metal ions to give complexes which clearly show coordination selectivity towards the different metal ions. The tetradentate nature of the inner chamber favours the coordination of transition metal ions, as copper(II) or nickel(II), in this N_2O_2 compartment, while the external O_2O_2 chamber remains particularly designed for f metal ions and favours the coordination of lanthanide(III) or uranyl(VI) ions in this site.

The mononuclear complexes can be obtained by reaction of the preformed ligands or of the formyl and amine precursors in the presence of the appropriate metal acetate. In these complexes copper(II) and nickel(II) are square planar, as confirmed by the X-ray structure of the copper(II) complex with the ligand H_4L_A [24] and by magnetic data on nickel(II) complexes, which are diamagnetic.

TABLE 2. Fractional coordinates with isotropic (denoted by*) or equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	$U_{iso/eq}$^{a}
Ni(1)	0.6396(1)	1.0116(1)	0.5320(1)	0.0480(7)
O(1)	0.7037(7)	0.9060(6)	0.4660(5)	0.050(1)
O(2)	0.8009(8)	0.7838(7)	0.3453(6)	0.070(1)
C(3)*	0.8416(5)	0.6179(5)	0.4708(4)	0.057(1)
C(4)*	0.8377(5)	0.5635(5)	0.5667(4)	0.065(2)
C(5)*	0.7878(5)	0.6257(5)	0.6303(4)	0.065(2)
C(6)*	0.7418(5)	0.7422(5)	0.5980(4)	0.048(1)
C(1)*	0.7457(5)	0.7966(5)	0.5021(4)	0.043(1)
C(2)*	0.7956(5)	0.7344(5)	0.4385(4)	0.053(1)
C(7)	0.6849(9)	0.8013(9)	0.6675(8)	0.052(1)
N(1)	0.6391(8)	0.9104(7)	0.6438(6)	0.043(1)
C(8)	0.5723(10)	0.9597(8)	0.7207(8)	0.053(1)
C(9)	0.6087(9)	1.0600(9)	0.7048(8)	0.054(1)
C(10)	0.7502(9)	1.0250(9)	0.7318(9)	0.066(1)
C(11)	0.5168(11)	1.1369(9)	0.7615(9)	0.083(1)
N(2)	0.5887(8)	1.1157(7)	0.6004(7)	0.046(1)
C(12)*	0.5494(9)	1.2235(8)	0.5605(8)	0.048(1)
C(14)*	0.4873(5)	1.3978(5)	0.4392(4)	0.068(2)
C(15)*	0.4779(5)	1.4591(5)	0.3438(4)	0.073(2)
C(16)*	0.5227(5)	1.4036(5)	0.2752(4)	0.066(2)
C(17)*	0.5768(5)	1.2869(5)	0.3020(4)	0.058(1)
C(18)*	0.5861(5)	1.2256(5)	0.3974(4)	0.056(1)
C(13)*	0.5414(5)	1.2811(5)	0.4660(4)	0.048(1)
O(3)	0.6364(7)	1.1133(6)	0.4184(5)	0.047(1)
O(4)	0.6172(8)	1.2360(7)	0.2328(7)	0.080(1)
Ni(2)	0.0784(1)	0.4252(1)	0.1129(1)	0.0421(6)
O(5)	0.2024(6)	0.3174(6)	0.0645(6)	0.055(1)
O(6)	0.4164(7)	0.1687(6)	0.0098(6)	0.068(1)
O(7)	0.2097(6)	0.4782(6)	0.1064(5)	0.046(1)
O(8)	0.3931(7)	0.5612(6)	0.0397(6)	0.057(1)
N(3)	−0.0526(8)	0.3787(7)	0.1078(7)	0.051(1)
N(4)	−0.0392(7)	0.5225(7)	0.1756(6)	0.043(1)
C(21)*	0.2904(5)	0.0693(4)	−0.0072(4)	0.054(1)
C(22)*	0.1714(5)	0.0546(4)	0.0008(4)	0.062(2)
C(23)*	0.0597(5)	0.1295(4)	0.0310(4)	0.059(2)
C(24)*	0.0670(5)	0.2192(4)	0.0532(4)	0.046(1)
C(19)*	0.1860(5)	0.2339(4)	0.0452(4)	0.046(1)
C(20)*	0.2977(5)	0.1589(4)	0.0150(4)	0.050(1)
C(25)	−0.0476(10)	0.2920(9)	0.0859(8)	0.057(1)
C(26)	−0.1867(9)	0.4570(9)	0.1295(8)	0.059(1)
C(27)	−0.1578(9)	0.4965(8)	0.2082(8)	0.048(1)
C(28)	−0.2822(9)	0.6025(9)	0.2121(9)	0.068(1)
C(29)	−0.1237(10)	0.4056(9)	0.3030(8)	0.060(1)
C(30)	−0.0184(9)	0.6017(8)	0.1944(8)	0.047(1)
C(32)*	0.0864(5)	0.7256(5)	0.1907(4)	0.051(1)
C(33)*	0.1866(5)	0.7651(5)	0.1608(4)	0.056(1)
C(34)*	0.2911(5)	0.7101(5)	0.1108(4)	0.051(1)
C(35)*	0.2954(5)	0.6155(5)	0.0907(4)	0.043(1)
C(36)*	0.1952(5)	0.5760(5)	0.1205(4)	0.039(1)
C(31)*	0.0907(5)	0.6311(5)	0.1706(4)	0.044(1)
O(10)*	0.4632(7)	0.3245(6)	0.0642(6)	0.054(1)
O(9)*	0.7741(8)	1.0085(7)	0.2829(6)	0.075(1)
C(37)*	0.8937(11)	1.0129(10)	0.2439(10)	0.095(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond distances (Å), angles (°) and contacts (Å) for $Ni(H_2L_C)$

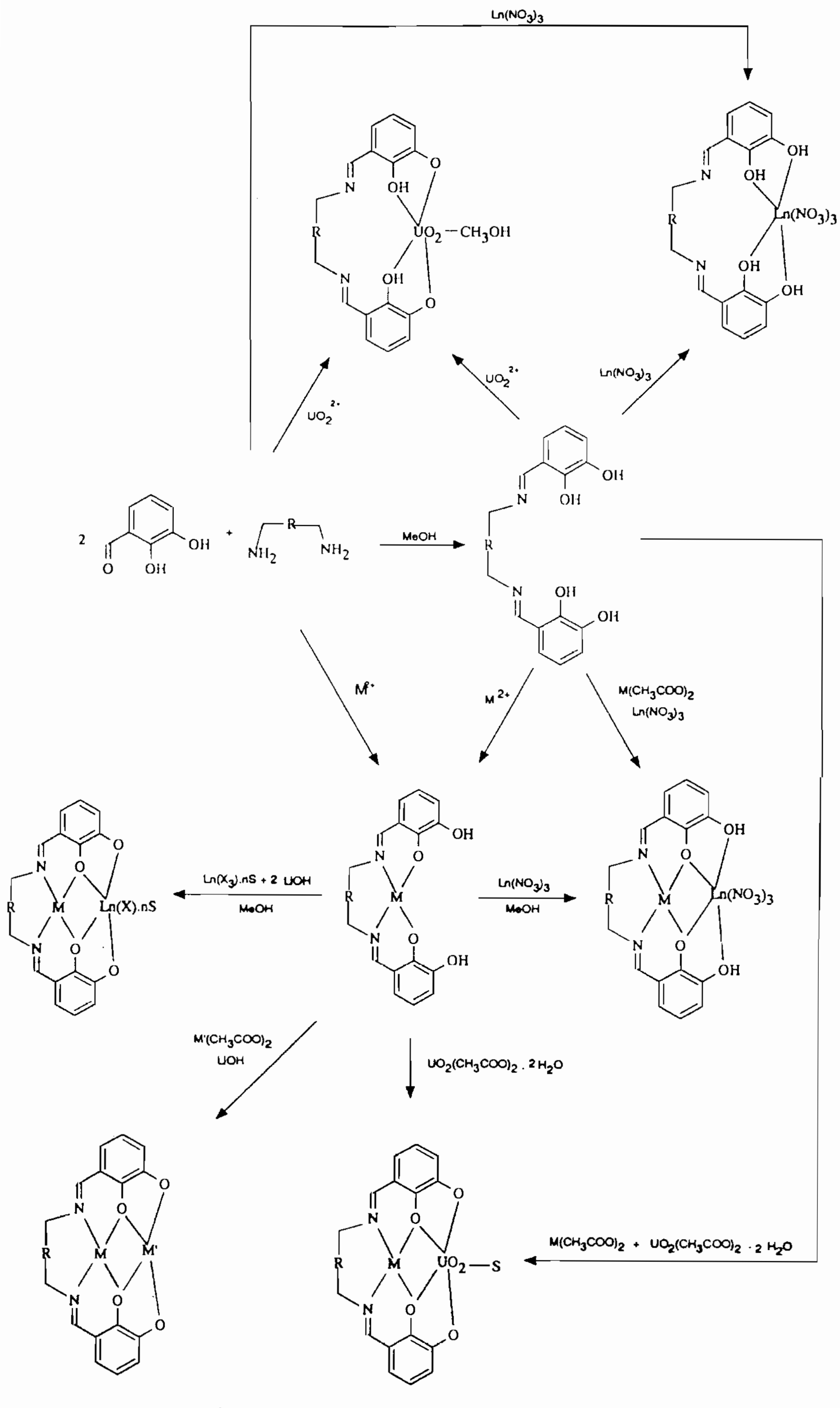
Bond distances (Å)			
Ni(1)–O(1)	1.865(7)	Ni(2)–O(5)	1.851(6)
Ni(1)–N(1)	1.804(9)	Ni(2)–N(3)	1.810(8)
Ni(1)–N(2)	1.877(8)	Ni(2)–N(4)	1.868(7)
Ni(1)–O(3)	1.817(8)	Ni(2)–O(7)	1.844(7)
O(1)–C(1)	1.316(9)	O(5)–C(19)	1.338(8)
O(2)–C(2)	1.35(1)	O(6)–C(20)	1.362(9)
C(6)–C(7)	1.45(1)	C(24)–C(25)	1.42(1)
C(7)–N(1)	1.30(1)	N(3)–C(25)	1.30(1)
N(1)–C(8)	1.49(1)	N(3)–C(26)	1.52(1)
C(9)–N(2)	1.50(1)	N(4)–C(27)	1.49(1)
N(2)–C(12)	1.30(1)	N(4)–C(30)	1.30(1)
C(12)–C(13)	1.37(1)	C(30)–C(31)	1.40(1)
C(18)–O(3)	1.346(9)	O(7)–C(36)	1.360(8)
C(17)–O(4)	1.361(9)	O(8)–C(35)	1.358(8)
O(9)–C(37)	1.41(1)		
Bond angles (°)			
O(1)–Ni(1)–O(3)	85.4(3)	O(5)–Ni(2)–O(7)	84.8(3)
N(1)–Ni(1)–N(2)	85.8(4)	N(3)–Ni(2)–N(4)	86.7(3)
O(1)–Ni(1)–N(1)	94.2(3)	O(5)–Ni(2)–N(3)	93.9(3)
N(2)–Ni(1)–O(3)	94.7(4)	O(7)–Ni(2)–N(4)	95.2(3)
C(6)–C(7)–N(1)	121(1)	N(3)–C(25)–C(24)	124(1)
C(7)–N(1)–C(8)	115.0(9)	C(25)–N(3)–C(26)	117(1)
C(9)–N(2)–C(12)	124(1)	C(27)–N(4)–C(30)	122(1)
Ni(1)–N(1)–C(7)	130.4(8)	Ni(2)–N(3)–C(25)	129.4(9)
Ni(1)–N(1)–C(8)	114.6(7)	Ni(2)–N(3)–C(26)	113.1(8)
Ni(1)–N(2)–C(9)	112.1(7)	Ni(2)–N(4)–C(27)	113.2(7)
Ni(1)–N(2)–C(12)	123.4(8)	Ni(2)–N(4)–C(30)	124.4(8)
N(2)–C(12)–C(13)	129(1)	N(4)–C(30)–C(31)	127(1)
Possible contacts and hydrogen bonds (Å)			
Ni(1)...Ni(1^a)	3.467(3)	Ni(2)...Ni(2^b)	3.532(3)
Ni(1)...O(1^a)	3.50(1)	Ni(2)...N(3^b)	3.485(9)
O(1)...O(9)	2.84(1)	O(5)...O(10)	2.92(1)
O(2)...O(9)	2.81(1)	O(6)...O(10)	2.73(1)
O(3)...O(9)	2.81(1)	O(7)...O(10)	2.905(9)
O(4)...O(9)	2.78(1)	O(8)...O(10)	2.91(1)
O(4)...O(10^d)	2.81(1)	O(8)...O(8^c)	2.71(1)

$^a = 1-x,\ 2-y,\ 1-z.$ $^b = -x,\ 1-y,\ -z.$ $^c = 1-x,\ 1-y,\ -z.$ $^d = x,\ 1+y,\ z.$

The different solvation or the elongation of the aliphatic chain do not influence the coordination about the central metal ion in the mononuclear nickel complexes.

Two mononuclear nickel(II) complexes, one green and the other red, with the ligand H_4L_B have been obtained: they differ in the presence of a CH_3COOH molecule in the red complex. This molecule, as ascertained by ^1H NMR, elemental analysis and thermal analysis, is easily lost on grinding or on washing the crude powder with diethyl ether. For this reason the IR spectra of the two complexes, as KBr pellets, are identical.

The condensation reaction of 2,3-dihydroxybenzaldehyde and ethylenediamine, using uranyl(VI) or lanthanide(III) ions as templating agents, leads to the



X = NO_3^-, CH_3COO^-, Cl^-, ClO_4^-
S = H_2O, MeOH, dmso
M^{2+} = Cu^{2+}, Ni^{2+}

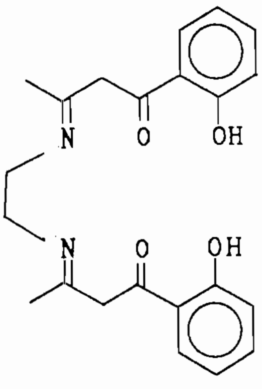
R	
$-(CH_2)_2-$	**(H_4L_A)**
$-C(CH_3)_2-CH_2-$	**(H_4L_B)**
$-CH_2-(CH_3)_2-CH_2-$	**(H_4L_C)**
$-C_6H_4-$	**(H_4L_D)**

Scheme 1. Reaction pathway for the formation of the Schiff base ligands H_4L_A–H_4L_D and related complexes.

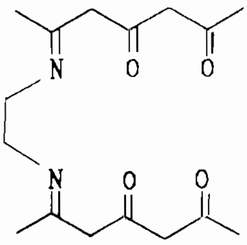
formation of $UO_2(H_2L_A)(MeOH)$ and $Ln(H_4L_A)(NO_3)_3$; as already observed [9], under similar experimental conditions, the Schiff base coordinates as neutral in the lanthanide(III) complex and as dinegative in the uranyl(VI) one.

In these complexes the metal ion is suggested to be in the outer O_2O_2 compartment with a solvent molecule occupying the fifth equatorial site of a pentagonal bipyramid for the uranyl(VI) compounds and with nitrate anions filling the coordination sphere for the lanthanide(III) ones.

The outer O_2O_2 preference for the uranyl(VI) ion in complexes with the potentially hexadentate side-off Schiff bases H_4L_E and H_4L_F has been already ascertained by X-ray structural analyses [33, 34].



H_4L_F



H_4L_E

Structure of Ni(H₂L_C)

Crystals of $Ni(H_2L_C)$, suitable for an X-ray investigation, were grown from a methanol/diethyl ether solution. Two chemically identical molecules of the nickel complex are present in the asymmetric portion of the cell and are reported as A and B in Fig. 2, together with the atomic numbering scheme. Apart from some insignificant details, the main difference between A and B consists of the presence of a methanol molecule linked by hydrogen bonds in the O_2O_2 site of molecule A, and a water molecule in the same site of molecule B.

The coordination around nickel ions, placed in the N_2O_2 sites, is not strictly planar, all atoms being tetrahedrally displaced from the mean coordination planes by about 0.047 and 0.093 Å (mean) for A and B, respectively. The metal ion is displaced by 0.026 and 0.015 Å from the same planes.

The configuration of the molecules is 'stepped'; the dihedral angle between the planes defined by the two hydroxysalycilideneimine residues is 4.4° in A and 13.9° in B and the angles that these planes form with the corresponding coordination planes are 6.6 and 10° for A and 6.6 and 16.6° for B. The torsion angle around the C(8)–C(9) and C(26)–C(27) isobutyl bridges is 45(1) and 44(1)°, respectively.

The average values of the distances Ni–O (1.84 Å) and Ni–N (1.84 Å) are not significantly different from the values already found in similar complexes [36]. A brief remark has to be made about coordinated nitrogen atoms that present a different environment; N(2) and N(4) are in fact bonded to a tertiary carbon atom. The C(9)–N(2)–C(12) and C(27)–N(4)–C(30) bond angles (123° mean) are larger than the corresponding angles (116° mean) subtended by N(1) and N(3) that are bonded to a primary carbon atom. This different type of steric hindrance leads to the lengthening of the coordination bond to the central metal ion: 1.877(8) and 1.868(7) Å for N(2) and N(4), respectively, while the corresponding values are 1.804(9) and 1.810 Å for N(1) and N(3), respectively.

Linking of adjacent molecules through hydrogen bonds and contacts produces a complicated network of interactions which provides considerable compactness to the crystal (Fig. 3).

Dinuclear and tetranuclear complexes

By reaction of $M(H_2L_A)$ with $Ln(NO_3)\cdot 6H_2O$, the dinuclear $MLn(H_2L_A)(NO_3)_3$ complexes are obtained, while the same reaction in the presence of two equivalent of LiOH produces the tetranuclear complexes $[MLn(L_A)(NO_3)(S)]_2$ ($S = MeOH$, H_2O, dmso). The same results are obtained with the ligands H_4L_B, H_4L_C and H_4L_D. The X-ray structure of $[CuY(L_A)(NO_3)(dmso)]_2$ confirms the tetranuclear nature of the compounds, where two binuclear units are held together by phenolate oxygen bridges [24]. The copper ion remains square planar, while yttrium(III) is eight-coordinate, being bonded to the O_2O_2 donor atoms of the outer compartment, to two bridging oxygens, to one bidentate nitrate group and one oxygen of a dimethyl sulfoxide molecule [24].

Heterodinuclear complexes, containing uranyl(VI) ion, have been obtained by reaction of the appropriate mononuclear d complex with uranyl(VI) salts. In these complexes the O–U–O group reaches its pentacoordination through the coordination of the outer O_2O_2 donor set of the Schiff base and of a solvent molecule as in the mononuclear $UO_2(H_2L_A)(CH_3OH)$.

The enhanced selectivity of the two chambers of these ligands towards the different metal ions is evidenced by their capability to form pure heterodinuclear complexes also when a transition metal ion (i.e. copper(II) or nickel(II)) and an f metal ion (i.e. lanthanum(III) or uranyl(VI)) are added in sequence to the ligands without previous separation and purification of the mononuclear species. The transition metal ion always occupies the inner and the f ion the outer chamber.

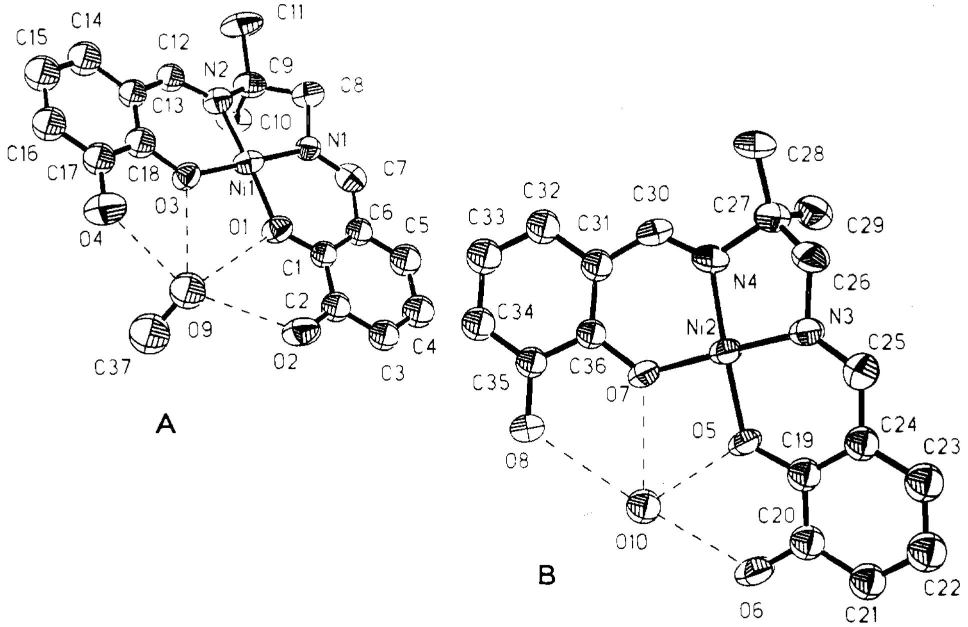


Fig. 2. ORTEP [35] representation of the two independent molecules of the nickel complex Ni(H_2L_C). The thermal ellipsoids are at the 50% probability level.

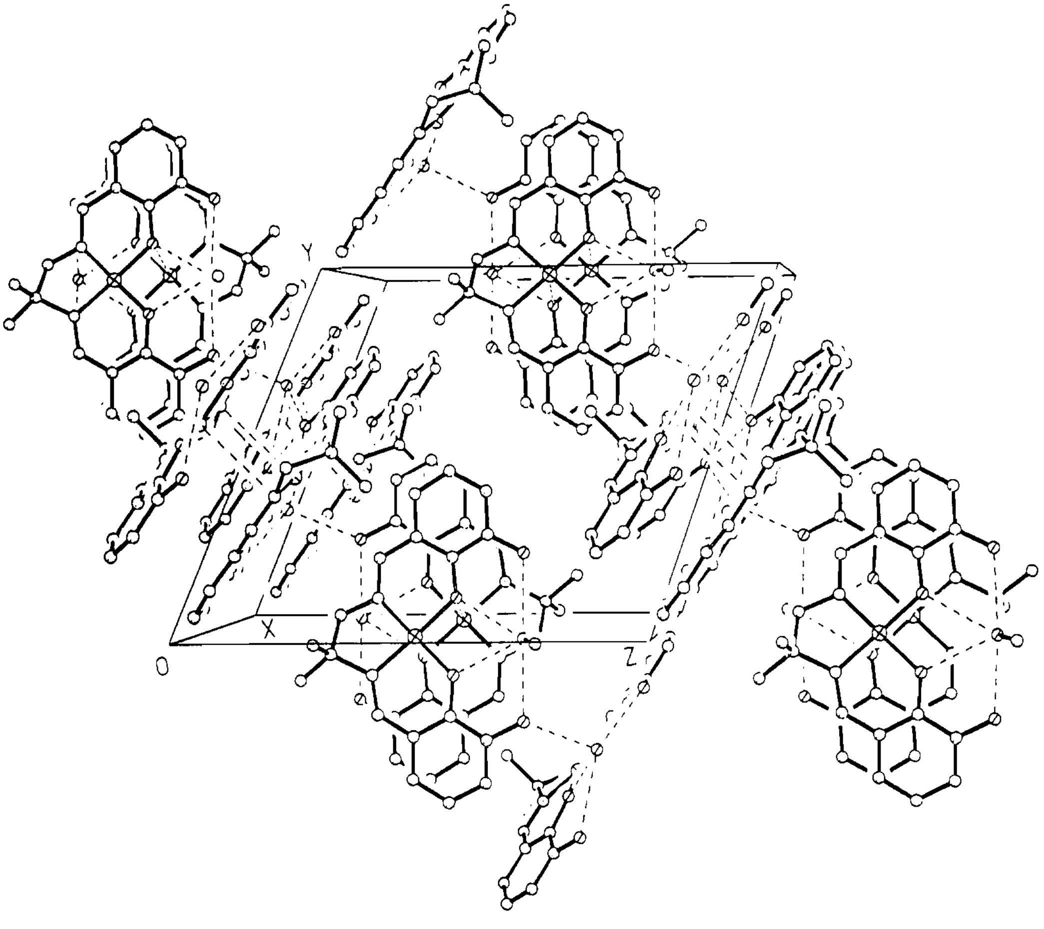


Fig. 3. Packing of the Ni(H_2L_C) molecules within the unit cell.

The similar heterodinuclear complexes $MLa(L_A)(X)_3$ or $MLa(L_D)(X)_3$, ($X=Cl^-$, CH_3COO^-) have been prepared using lanthanum(III) acetate or chloride instead of the nitrate and $M(H_2L_A)$ or $M(H_2L_D)$ as mononuclear precursors. These complexes are also stable in air and do not hydrolyze in solution as shown by the correct metal ratio estimated by X-ray microprobe analyses. The substitution of the nitrate anions with acetates or chlorides increases the solubility of these complexes in alcoholic solutions.

On using lanthanum(III) perchlorate and $Ni(H_2L_A)$ an oil was obtained; repeated attempts to obtain solid products, by treating the oil with different solvents (e.g. chloroform) lead to the formation of an orange solid formulable as $NiLa(L_A)(ClO_4)_3\cdot 4H_2O$. Again the X-ray microprobe analysis shows the compound is homogeneous with a Ni:La:Cl ratio 1:1:3, in agreement with the formulation proposed.

Under particular experimental conditions (presence of LiOH and prolonged reflux of the solution) the homodinuclear copper(II) complex $Cu_2(L_A)(MeOH)$, but not the analogous nickel(II) complex, was obtained. Using nickel(II) acetate the mononuclear $Ni(H_2L_A)$ complex was always recovered.

H_4L_D does not form homodinuclear copper(II) or nickel(II) complexes. All attempts resulted in the recovery of the mononuclear complexes only.

These reactions can be explained by the different chemical behaviour of copper(II) and nickel(II) towards ligands containing N_2O_2 and O_2O_2 sites. Copper(II) can coordinate also in the outer O_2O_2 site, but only with H_2L_A which show enough flexibility to modify such a site to make it suitable for coordination of copper(II). It must be noted that, with similar potentially hexadentate compartmental Schiff bases, copper(II) was found to form mononuclear positional isomers depending on the solvent used [2]; nickel(II), on the contrary, strongly prefers the inner N_2O_2 site [2].

The reduced flexibility of H_4L_D in comparison with H_4L_A might explain the different chemical behaviour of the two ligands towards the formation of homodinuclear copper(II) complexes. This is not a general trend: both ligands easily form homodinuclear iron(III) complexes when reacted in air with iron(II) acetate and LiOH in a 1:2:4 molar ratio. The presence of iron(III) was ascertained by Mössbauer spectroscopy. Analogously heterodinuclear copper(II)–iron(III) or copper(II)–manganese(III) complexes were easily obtained when the mononuclear copper complex was reacted with the appropriate metal acetate [37].

IR and NMR data

The strong νC=N absorptions, present at 1640 cm^{-1} for H_4L_A, at 1655 and 1634 cm^{-1} for H_4L_B, at 1651 cm^{-1} for H_4L_C and at 1616 cm^{-1} for H_4L_D, are lowered in the mononuclear copper(II) or nickel(II) complexes while the introduction of the lanthanide(III) ion and different anions in the outer O_2O_2 chamber does not cause further significant shift. For instance in $NiLa(L_B)(X)_3$, νC=N lies at 1622 ($X=NO_3^-$), 1619 ($X=CH_3COO^-$) and 1621 ($X=ClO_4^-$) cm^{-1}; analogously for $NiLa(L_D)(X)_3$ νC=N is at 1612 ($X=NO_3^-$) and 1609 ($X=Cl^-$) cm^{-1}.

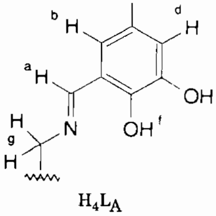
For the mononuclear O_2O_2 complexes $La(H_4L_A)(NO_3)_3$ and $UO_2(H_2L_A)(CH_3OH)$ the νC=N lies at 1639 and at 1647 and 1627 cm^{-1}, respectively.

IR and Raman investigations rule out the presence of ionic nitrate groups and show they coordinate as bidentate to the lanthanide(III) ion: absorption peaks at 1488–1468 (ν_1) and 1320–1304 (ν_4) cm^{-1} of comparable intensity are present in the IR and Raman spectra.

An analogous behaviour can be proposed for the CH_3COO^- groups; again absorption peaks at 1464 and 1278 cm^{-1} due to antisymmetric and symmetric stretchings of the COO^- groups, of comparable intensity, justify a bidentate coordination of these groups to the lanthanum(III) metal ion.

TABLE 4. ^1H and ^{13}C NMR data of H_4L_A, $Ni(H_2L_A)$ and $NiLa(H_2L_A)(NO_3)_3$ in dmso-d_6

	H_4L_A			$Ni(H_2L_A)$			$NiLa(H_2L_A)(NO_3)_3$		
^1H	ppm	int.	mult	ppm	int.	mult	ppm	int.	mult
a	8.53	2	s	7.87	2	s	8.11	2	s
b	6.83	2	q	6.73	2	q	7.01	2	q
c	6.63	2	t	6.36	2	t	6.61	2	t
d	6.81	2	q	6.65	2	q	6.91	2	q
g	3.91	4	s	3.42	4	s	3.66	4	s
e	8.9	2	s(br)	8.12	2	br	8.36	2	br
f	13.3	2	s(br)						
^{13}C	ppm	mult		ppm	mult		ppm	mult	
a	167.1	d		162.75	d		170.27	d	
b	117.6	d		114.3	d		114.35	d	
c	121.8	d		121.94	d		121.9	d	
d	117.6	d		114.4	d		114.4	d	
e	151.5	s		152.79	s		158.4	s	
f	145.8	s		147.67	s		147.6	s	
g	118.05	s		119.32	s		119.13	s	
h	57.96	s		58.3	s		57.98	s	



H_4L_A

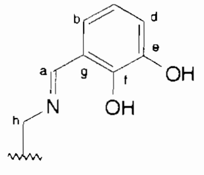
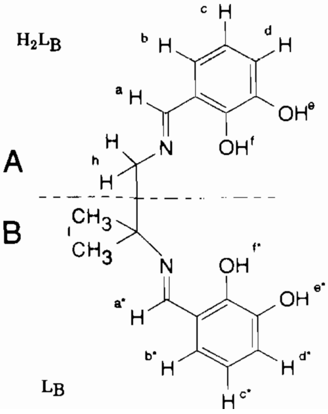


TABLE 5. ^1H and ^{13}C NMR data of H_4L_B, $Ni(H_2L_B)$ and $NiLa(H_2L_B)(NO_3)_3$

	H_4L_B (acetone-d_6)				$Ni(H_2L_B)$ (acetone-d_6)				$NiLa(H_2L_B)(NO_3)_3$ (acetone-d_6)			
^1H	ppm	int.	mult	J (Hz)	ppm	int.	mult	J (Hz)	ppm	int.	mult	J (Hz)
a	8.51	1	t	0.88 H^a-H^h	7.74	1	t	1.5	7.98	1	t	1.4
a*	8.57	1	s		7.76	1	s		7.98	1	s	
b	6.87	1	q	1.3 H^b-H^d	6.71	1	q	1.7	7.17	1	m	
b*	6.88	1	q	1.3 H^{b*}-H^{d*}	6.79	1	q	1.7	7.17	1	m	
c	6.69	1	t	7.9 H^c-H^d	6.39	1	t	7.91	6.76	1	t	7.91
c*	6.64	1	t	7.3 H^{c*}-H^{d*}	6.4	1	t	7.9	6.76	1	t	7.9
d	6.85	1	q	1.3 H^b-H^d	6.68	1	q	1.7	7.13	1	q	
d*	6.86	1	q	1.3 H^{b*}-H^{d*}	6.68	1	q	1.7	7.13	1	q	
e	–				7.61	1	br		–			
e*	–				7.61	1	br		–			
f	–				–				–			
f*	–				–				–			
h	3.88	2	d	0.88 H^a-H^h	3.44	2	d	1.5	3.63	2	d	1.4
l	1.48	6	s		1.56	6	s		1.96	6	s	

	H_4L_B ($CDCl_3$)		$Ni(H_2L_B)$ (methanol-d_4)		$NiLa(H_2L_B)(NO_3)_3$ (methanol-d_4)	
^{13}C	ppm	mult	ppm	mult	ppm	mult
a	166.78	d	164.2	d	165.7	d
a*	161.47	d	160.9	d	162.7	d
b	122.24	d	124.7	d	127.0	d
b*	122.24	d	124.1	d	126.5	d
c	118.18	d	117.4	d	119.4	d
c*	117.1	d	116.4	d	119.4	d
d	117.1	d	117.3	d	119.4	d
d*	116.2	d	116.3	d	119.4	d
e	149.3	s	148	s	147.3	s
e*	147.1	s	148	s	147.3	s
f	157.8	s	153.3	s	149.2	s
f*	155.0	s	153.3	s	148.6	s
g	118.2	s	121.7	s	121.7	s
g*	118.2	s	121.5	s	121.7	s
h	68.8	t	71.8	t	71.7	t
i	68.4	s	67.1	s	68.6	s
l	25.2	q	25.7	q	25.6	q



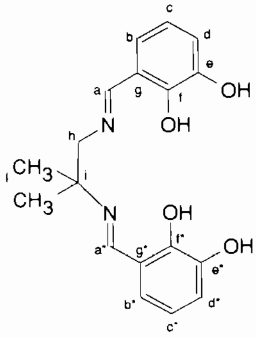
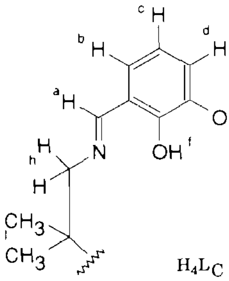
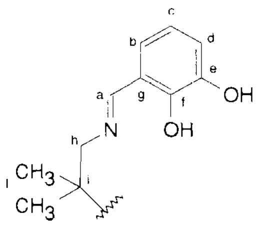


TABLE 6. ^1H and ^{13}C NMR data of H_4L_C and $Ni(H_2L_C)$ in acetone-d_6

	H_4L_C			$Ni(H_2L_C)$			
^1H	ppm	int.	mult	ppm	int.	mult	J (Hz)
a	8.51	2	s	7.74	2	s	1.5 H^a-H^h
b	6.92	2	q	6.88	2	q	1.7 H^b-H^d
c	6.7	2	t	6.3	2	t	7.91 H^c-$H^{d,b}$
d	6.88	2	q	6.76	2	q	1.7 H^b-H^d
e	14.2	2	br	10.5	2	br	
f	7.8	2	br				
h	3.6	4	s	4.6	4	s	1.5 H^a-H^h
l	1.1	6	s	1.01	6	s	
^{13}C	ppm		mult	ppm		mult	
a	167.59		d	168.17		d	
b	118.48		d	116.3		d	
c	122.92		d	122.64		d	
d	117.8		d	116.3		d	
e	147.8		s	143.14		s	
f	150.5		s	154.56		s	
g	123.19		s	123.19		s	
h	67.13		d	71.13		d	
i	37.2		s	35.58		s	
l	24.11		q	25.25		q	



H_4L_C



The IR spectra of $NiLn(L_A)(ClO_4)_3$ show three very strong absorption peaks in the range 1150–1050 cm^{-1} due to ν_3 of the perchlorate groups. These peaks indicate an interaction of the perchlorates with the central metal ion which causes a reduction of symmetry from T_d to C_{2v} or even lower than C_{2v}. Additional absorption peaks at 628 cm^{-1} due to ν_4 support the interaction proposed.

In $UO_2(H_2L_A)(CH_3OH)$ and $CuUO_2(L_A)(CH_3OH)$ a very strong IR band at 900 and 914, 904 cm^{-1}, respectively, due to the ν_3 O–U–O is detectable.

The ^1H and ^{13}C NMR spectra were recorded in different solvents for the ligands H_4L_A–H_4L_D and related mononuclear nickel(II) and heterodinuclear nickel(II)-lanthanum(III) complexes (Tables 4–7). Particular attention was devoted to H_4L_B and related complexes owing to their non-symmetry, named A and B in Table 5, of the aliphatic chain of the ligand.

Using acetone-d_6 as solvent the presence of the $(CH_3)_2$–C group in side B makes more basic the vicinal ketoiminic nitrogen in comparison with the analogous nitrogen in side A. This causes a deshielding of H^{a*} with respect to H^a and makes the hydrogen bond O--H--N of the free ligand stronger than that in side A, with the resulting effect to deshield the proton H^{c*} with respect to H^c.

The complexation of nickel(II) into the inner N_2O_2 chamber considerably reduces the difference between A and B sides, and the chemical shifts of the similar protons for sides A and B are almost identical. An upfield shift is observed for all the proton (and for some carbons) signals of $Ni(H_2L_B)$ with respect to H_4L_B.

The subsequent introduction of $La(NO_3)_3$ into the outer O_2O_2 chamber, with the consequent formation of the heterodinuclear complex $NiLa(H_2L_B)(NO_3)_3$, causes a significant electron withdrawing towards the lanthanide(III) ion with a downfield shift of all the proton and carbon signals. The introduction of the second metal ion makes sides A and B of the organic moiety identical to each other (at least in acetone solution). A bidimensional XHCORR experiment, carried out in methanol-d_4, was performed in order to assign correctly the carbon signals for the complex $NiLa(H_2L_B)(NO_3)_3$.

The OH protons are not detectable in the free and in the dinuclear species while a broad peak at 7.61 ppm can be seen in the spectrum of $Ni(H_2L_B)$.

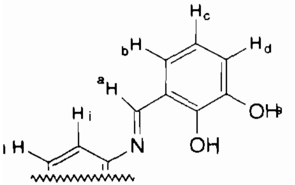
Downfield shifts for the carbon atoms C^b, C^{b*}, C^c, C^{c*}, C^d, C^{d*}, C^g and C^{g*} (2–6 ppm) are observed on going from H_4L_B and mono- to heterodinuclear species while C^f and C^{f*} behave in the opposite way. C^e and C^{e*} lie at the same values for the three compounds.

COSY experiments were carried out for the ligand H_4L_B and the complexes $Ni(H_2L_B)$ and $NiLa(H_2L_B)(NO_3)_3$ while NOESY experiments were made only for H_4L_B and $Ni(H_2L_B)$ in order to assign correctly the chemical shifts and the coupling among protons and recover some useful information about the structure and conformation in solution of the species under investigation. These bidimensional contour plots evidence a long range coupling between the methylic and the methylenic groups, not observed in the monodimensional spectra, and, for the NOESY of the free ligand and of the mononuclear complex, between the methylenic and the iminic protons (line a of Figs. 4 and 5), and between the methylic and iminic ones (line b of Figs. 4 and 5) showing that the free ligand has the same conformation as the almost planar mononuclear one.

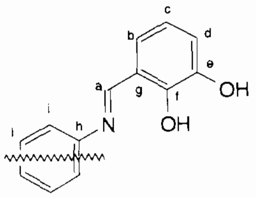
TABLE 7. ^1H and ^{13}C NMR data of H_4L_D, $Ni(H_2L_D)$ and $NiLa(H_2L_D)(NO_3)_3$

	H_4L_D (methanol-d_4)				$Ni(H_2L_D)$ (methanol-d_4)				$NiLa(H_2L_D)(NO_3)_3$ (methanol-d_4)			
^1H	ppm	int.	mult	J (Hz)	ppm	int.	mult	J (Hz)	ppm	int.	mult	J (Hz)
a	8.79	2	s		8.84	2	s			2	s	
b	7	2	q	1.73 H^b-H^d	7.1	2	q	1.6	7.28	2	q	1.7
c	6.79	2	t	7.67 H^c-$H^{d,b}$	6.59	2	t	7.8	6.83	2	t	7.6
d	6.92	2	q	1.72 H^b-H^d	6.86	2	q	1.6	7.28	2	q	1.7
i	7.39	2	m	0.01 H^i-H^l	7.36	2	q	132.3	7.55	2	q	106
l	7.39	2	m	0.01 H^i-H^l	8.02	2	q		8.07	2	q	
e	–	2	s		–				–			
f	–	2	s		–				–			

	H_4L_D (acetone-d_6)		$Ni(H_2L_D)$ (dmso-d_6)		$NiLa(H_2L_D)(NO_3)_3$ (dmso-d_6)	
^{13}C	ppm	mult	ppm	mult	ppm	mult
a	165.8	d	156.6	d	179	d
b	119.7	d	116.1	d	120.5	d
c	120.83	d	115.5	d	119	d
d	119.4	d	116.1	d	119.9	d
i	128.7	d	127.7	d	130.9	d
l	124.2	d	123.6	d	127	d
e	146.6	s	147.8	s	150.4	s
f	143.2	s	141.96	s	140.1	s
g	119.9	s	119.33	s	123.64	s
h	150.6	s	154.3	s	159.8	s



H_4L_D



A coupling H^aH^b and $H^{a*}H^{b*}$ can be detected only in COSY and NOESY of the mononuclear complex (line c of Fig. 5) and in NOESY of the free ligand, when performed in $CHCl_3$ (line c of Fig. 4). This last information together with the correlations recovered from the contour plot of a XHCORR experiment in $CHCl_3$ (Fig. 6), allow the peaks of the ^{13}C spectrum of the free ligand to be correctly assigned. In particular it can be seen that C^b and C^{b*} are downfield by about 4 ppm with respect to the C^c, C^{c*}, C^d and C^{d*} signals (line a of Fig. 6). This behaviour is opposite to the proton one where the H^d and H^{d*} signals are downfield with respect to the other aromatic signals.

Again, in the COSY experiments, a long range J^4 coupling between the methyl and the iminic protons is detectable for H_4L_B and $Ni(H_2L_B)$ but not for $NiLa(H_2L_B)(NO_3)_3$, this being attributed to a more pronounced deshielding (1.96 ppm for the NiLa complex versus 1.48 for the free ligand and 1.50 for the mononuclear complexes) of the CH_3^- groups in the binuclear complex.

Finally a ^5J coupling between methylenic and H^b is observed in COSY experiments of $Ni(H_2L_B)$.

A similar behaviour was also observed for the other ligands H_4L_A, H_4L_C and H_4L_D and related mononuclear nickel(II) and heterodinuclear nickel(II)–lanthanum-

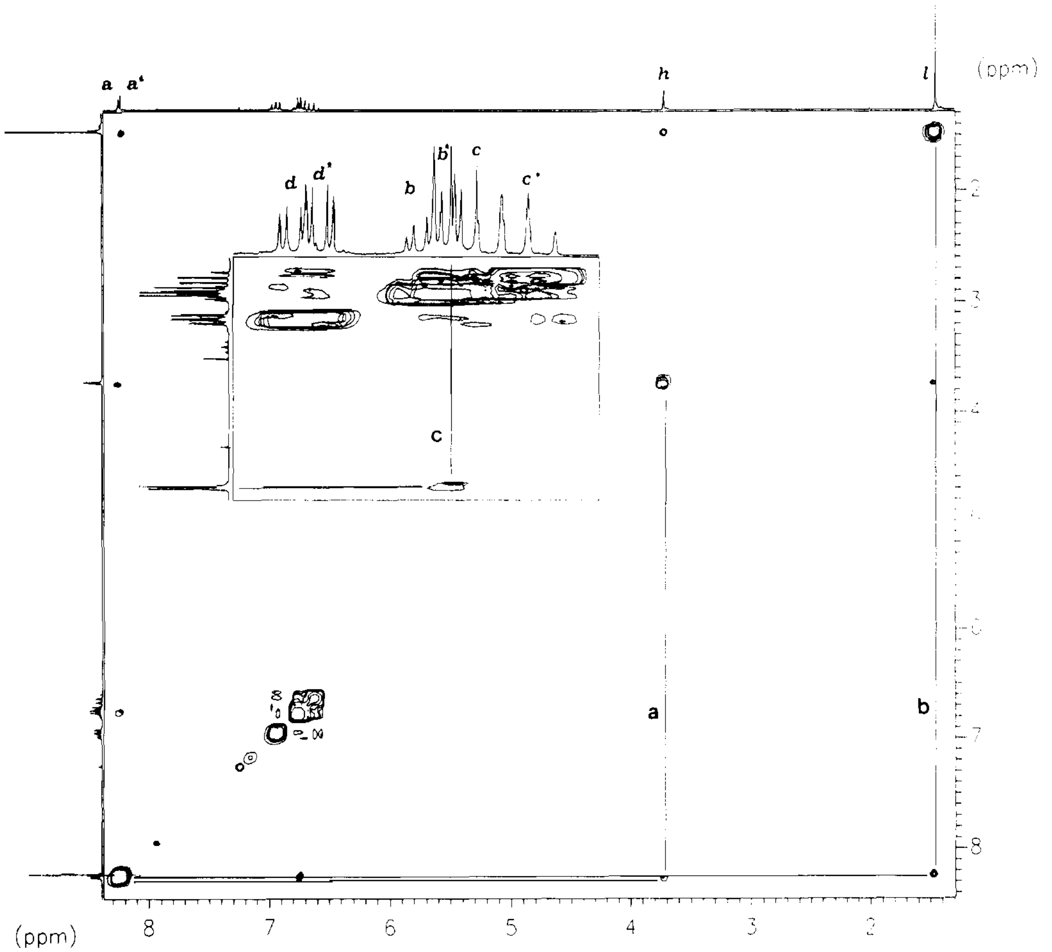


Fig. 4. 2D NMR NOESY contour plot of H_4L_B in $CDCl_3$.

(III) complexes. A noticeable chemical shift variation for H^i and H^l was observed upon complexation for H_4L_D. The signals, superimposable in the free ligand, are separated from each other by about 0.5 ppm in the complexes.

A remarkable behaviour was observed for the HC=N group. In $Ni(H_2L_D)$ the proton signal is moderately downfield with respect to H_4L_D and completely disappears in $NiLa(H_2L_D)(NO_3)_3$. The extended mesomeric system may favour an acidity increase of this proton with a possible exchange with alcoholic deuterium of the solvent. Reaction at –C=N, already observed in similar systems [25, 38, 39], must be ruled out, owing to the presence in the ^{13}C spectrum of the binuclear species of a signal at 23 ppm downfield with respect to the free ligand due to the –C=N group. Moreover no signals due to reduction or addition to C=N are detectable in the ^1H or ^{13}C spectra of $NiLa(H_2L_D)(NO_3)_3$. NMR data evidence also that in coordinating solvents (S = dmso or dmf) a demetallation reaction of the type

$$NiLa(H_2L_D)(NO_3)_3 \xrightarrow{S} Ni(H_2L_D) + La(NO_3)_3 \cdot nS$$

takes place. The other heterodinuclear complexes do not suffer this reaction, possibly owing to the higher flexibility of H_4L_A–H_4L_C in comparison with H_4L_D. This flexibility can better accommodate the outer O_2O_2 coordination site for a stronger coordination of $La(NO_3)_3$.

Magnetic properties

X-ray powder diffraction studies on copper(II)–yttrium(III) and copper(II)–gadolinium(III) complexes $[CuLn(L_A)(NO_3)(H_2O_2)]_2$ show that they are isostructural, hence both can be assumed to be tetranuclear, with a structure similar to that of $[CuY(L_A)(NO_3)(dmso)]_2$. Preliminary X-ray structural data confirm the complexes $CuLn(H_2L_A)(NO_3)_3$ and $CuLn(H_2L_D)(NO_3)_3$ are dinuclear: the copper(II)...lanthanide(III) distance is comparable in both tetranuclear and dinuclear structures. The nitrate groups completely fill the coordination sphere about the lanthanide(III) ion, this

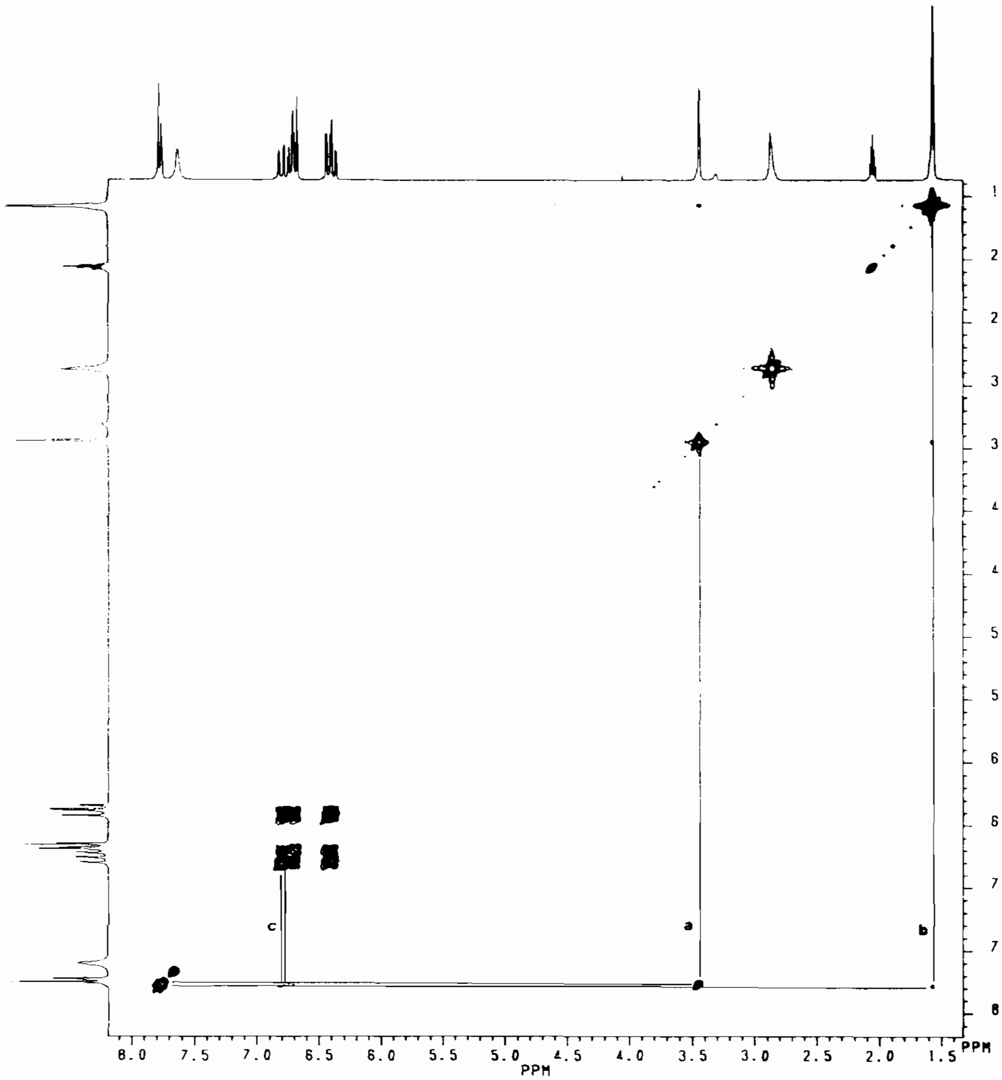


Fig. 5. 2D NMR NOESY contour plot of Ni(H_2L_B) in methanol-d_4.

precluding any oligomerization. However paucity of data and partial decomposition of the crystals, during data collection, prevent a satisfactory refinement of the structure.

The temperature dependence of the magnetic susceptibility of NiGd(H_2L_A)(NO_3)$_3$ and CuGd(H_2L_A)(NO_3)$_3$ complexes was measured in the 2.5–200 and 2.65–100 K ranges, respectively. The former derivative follows a Curie behaviour down to 15 K; below this temperature saturation effect might be at the origin of a slight deviation. The observed magnetic moment (7.55 μ_B) is slightly lower than expected for isolated Gd(III) ions (7.80 μ_B), but in any case is indicative that the Ni(II) ion is in a square planar environment and, therefore, in a low spin configuration. The lower value of the effective magnetic moment is probably due to the presence of some unreacted Ni(II) monomer (the monomeric impurity is around 10%), in analogy with that observed for the Cu(II) analogue described below.

The effective magnetic moment of CuGd(H_2L_A)(NO_3)$_3$ at various temperatures is shown in Fig. 7 in the χT versus T fashion. The χT values for the dimer increase on lowering the temperature, pass through a maximum at about 4.7 K and then decrease. Either scanning electron microprobe analyses and EPR spectroscopy revealed the presence in all the examined samples of the starting Cu(II) mononuclear complex. The polycrystalline powder EPR spectra showed, at 4.2 K and at room temperature, an unresolved feature, attributable to the ground state of the dimer with a high spin multiplicity. In addition a signal centered at a g value of about 2.1 was observed and we attribute this signal to isolated Cu(II) ions. The sample used for the analysis of the magnetic behaviour was chosen on the basis of the lowest level of monomeric impurity,

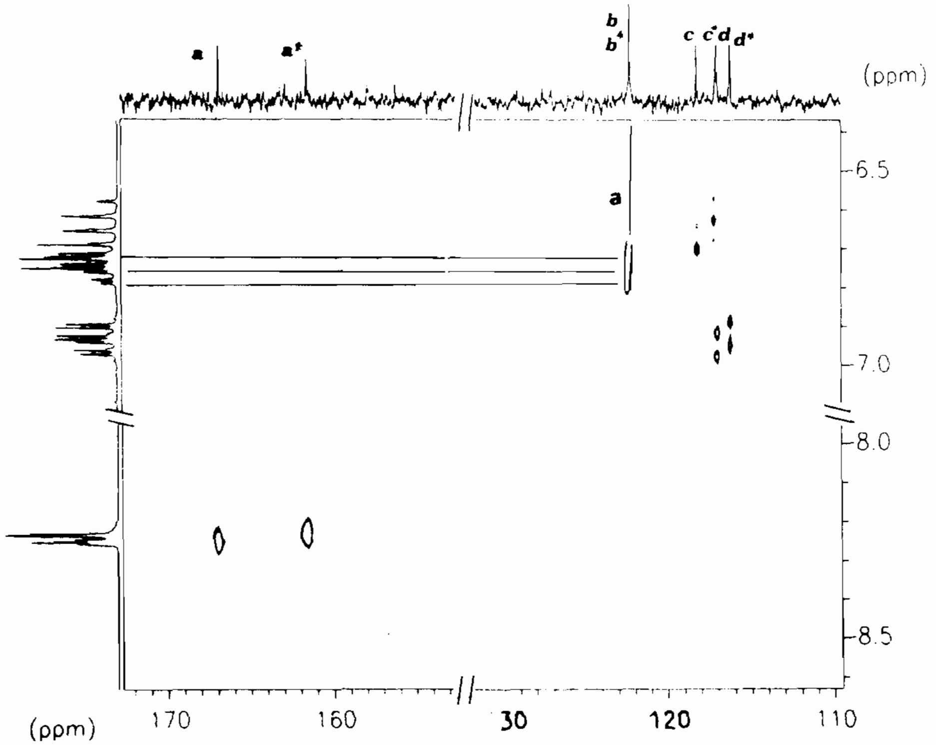


Fig. 6. 2D NMR XHCORR contour plot of H_4L_B in $CDCl_3$. The ^{13}C projection shows only CH, CH_2 and CH_3 signals obtained with a standard DEPT45 experiment.

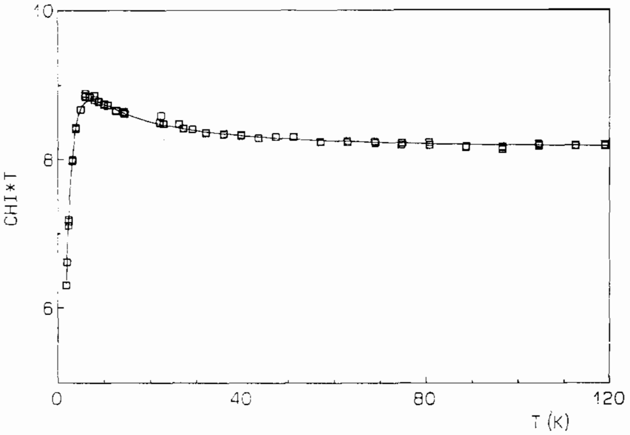


Fig. 7. χT vs. T for the dinuclear $CuGd(H_2L_A)(NO_3)_3$ complex.

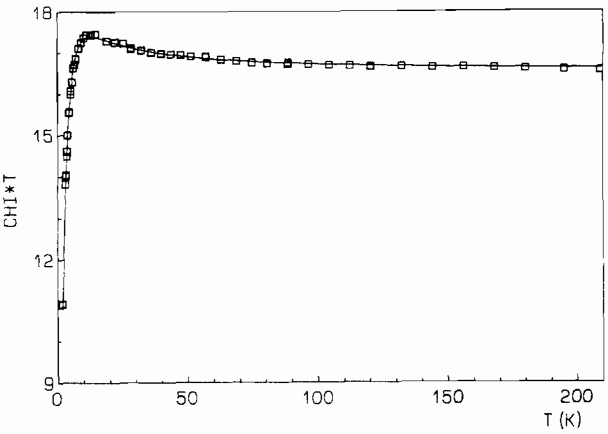


Fig. 8. χT vs. T for the dinuclear $[CuGd(L_A)(NO_3)(H_2O)]_2$ complex.

which was determined by electron microprobe analyses. The expression for calculating the magnetic susceptibility was derived by using an isotropic spin Hamiltonian ($H = J_{CuGd}S_1S_2$) corrected to account for the amount of monomeric species. The best fit parameters were $J_{CuGd} = -1.59(3)$ cm^{-1} and an amount of Cu(II) monomer of 6.9(2)% with fixed $g = 2.05$ and $g = 1.98$ values for Cu(II) and Gd(III) ions, respectively.

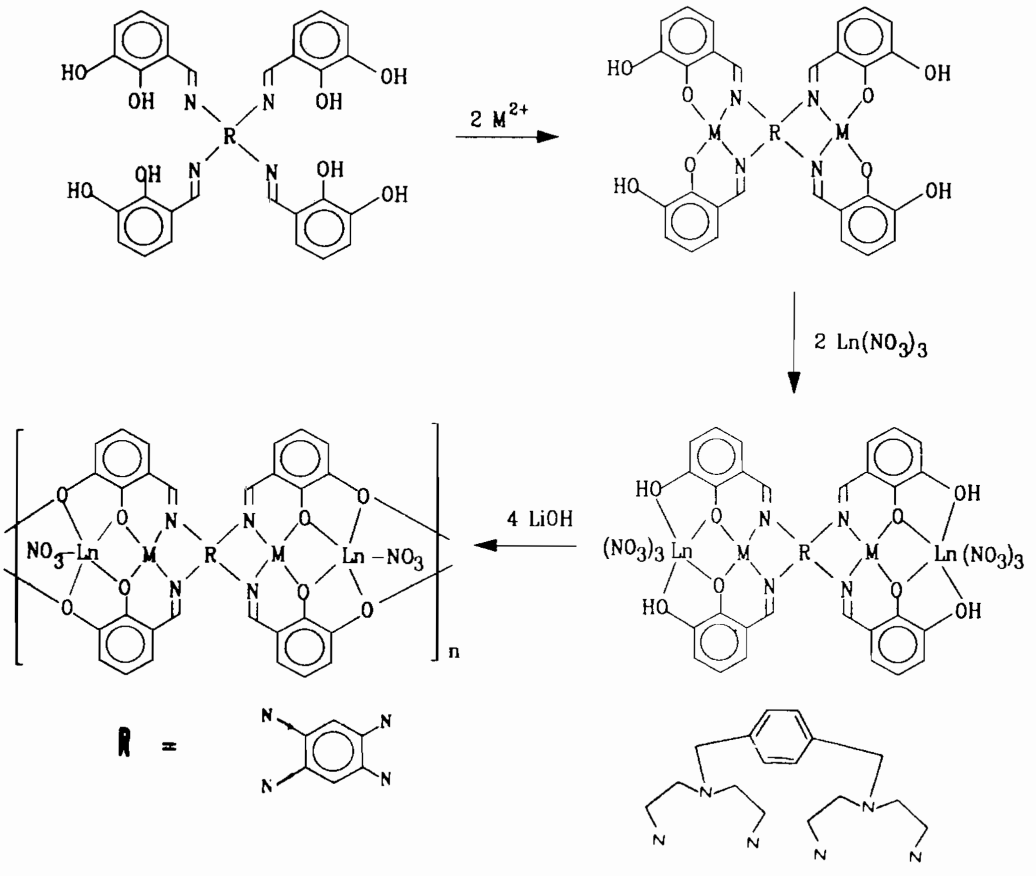
The magnetic behaviour of the tetranuclear $[CuGd(L_A)(NO_3)(H_2O)]_2$ (Fig. 8) is similar to that of the dimeric system. Again on lowering the temperature an increase of the χT values is observed with a maximum around 14.5 K: the decrease below this temperature is more dramatic than in the previous case. Assuming that the molecular structure of the compound is similar to that of the yttrium analogue, the magnetic behaviour can be interpreted as due to the magnetic coupling in a tetrameric linear unit where one Gd–Gd and two equivalent Gd–Cu interactions are operative. By using the appropriate spin Hamiltonian ($H = J_{CuGd}(S_1S_2 + S_3S_4) + J_{CuGd}S_2S_3$) and including a term to account for the presence of the external magnetic field, it is possible to fit the experimental data through a least-squares procedure. The best fit parameters are: $J_{CuGd} = -3.76(4)$ cm^{-1}, $J_{GdGd} = 0.16(5)$ cm^{-1} with the previously reported *g* values for the two ions.

All these calculated coupling constants are in agreement with previous findings; a ferromagnetic interaction is, even in this system, operative within the Gd(III)–Cu(II) pairs with a mechanism which does not depend on the geometry and nature of the bridging atoms. This result seems to confirm the presence of the proposed spin polarization mechanism in 3d–4f pairs [40–42]. The observed antiferromagnetic Gd(III)–Gd(III) coupling is weak but in any case the observed coupling constant is indicative that some exchange mechanism is operative together with the pure dipolar one.

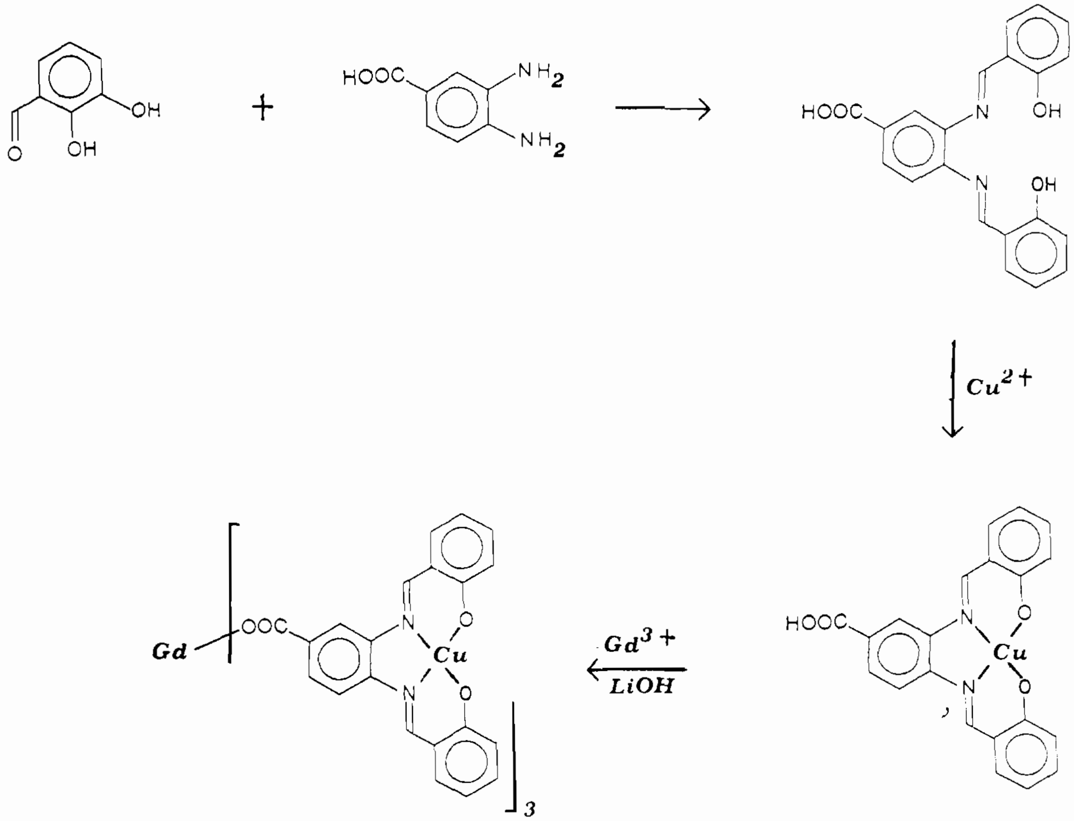
In conclusion it was verified that it is easy to prepare from suitable, potentially hexadentate, compartmental Schiff bases, with a inner N_2O_2 and an outer O_2O_2 compartment, heterodinuclear complexes containing d and f ions. The d ion, copper(II) or nickel(II) always occupies the N_2O_2 site in a square planar coordination and these mononuclear complexes can be used as ligands for the further coordination of an f ion, (uranyl(VI) or lanthanide(III)), in the outer O_2O_2 site.

Heteropolynuclear complexes

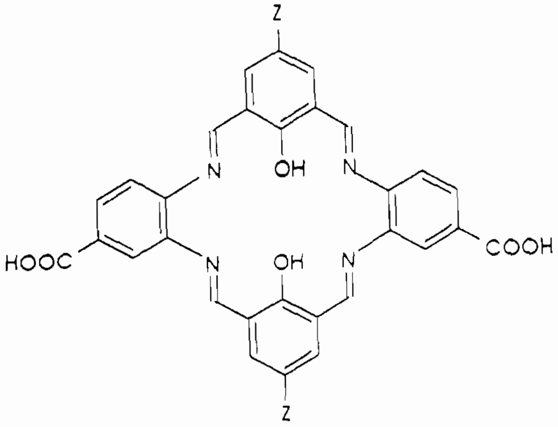
In the heterodinuclear complexes containing lanthanide(III) ions, the anions complete the coordination sphere about the central f ion. When these anions are partially removed by addition of a base (i.e. LiOH) oligomerization occurs, with the formation of tetranuclear species. Recently it was verified that the 'tripodal' heptadentate amine phenol ligand tris(((2-hydroxybenzyl)amino)ethyl) amine forms with gadolinium(III) nitrate in the presence of base a homodinuclear eight-coordinate complex where the two gadolinium atoms are bridged by phenolate oxygen atoms, one from each heptadentate ligand [43]. This seems to be a route for the synthesis of heteropolynuclear complexes, with predetermined properties, and preliminary synthetic data show that, it is possible to obtain polynuclear complexes by reaction of appropriate polyamines and formyl precursors in the presence of the desired metal ions and bases (Scheme 2).



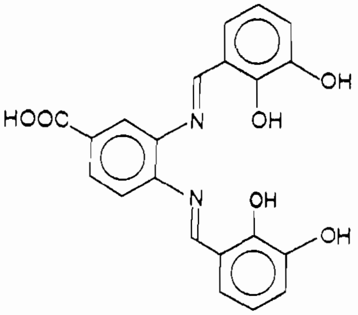
Scheme 2. Reaction pathway for the formation of heteropolynuclear complexes.



Scheme 3. Reaction pathway for the formation of $Gd[Cu_3(L_G)]_3 \cdot 6H_2O$.



H_2L_H



H_5L_I

Another route for obtaining polynuclear species is to use macrocyclic or macroacyclic ligands containing additional coordinating groups at the periphery of the coordination moiety. For example the tetranuclear complex $Gd[Cu_3(L_E)]_3 \cdot 6H_2O$ has been prepared according to Scheme 3.

X-ray microprobe analysis shows $Gd[Cu_3(L_G)]_3 \cdot 6H_2O$ is homogeneous with a Cu:Gd ratio 3:1 in agreement with the formulation proposed and well detectable peaks at the appropriate *m/z* value in the FAB mass spectra of H_3L_G and $Cu(HL_G)$ confirms the compounds proposed in Scheme 3.

The IR spectra of the free ligand H_5L_G and the mononuclear $Cu(HL_G)$ show $\nu C{=}O$ of the carboxylic group at 1688 and 1703 cm^{-1}, respectively. The subsequent coordination of gadolinium(III) ion to the carboxylic group to form $Gd[Cu_3(L_G)]_3 \cdot 6H_2O$ makes the two C–O bonds equivalent and this causes a shift of the ν antisymmetric and symmetric COO stretchings at 1611 and 1372 cm^{-1}. The $\nu C{=}N$, at 1616 cm^{-1} in the free ligand, suffer a small shift to 1611 cm^{-1} in both complexes.

The distance between the copper(II) and gadolinium(III) ions is too long to give rise to a significant spin coupling.

Analogously heteropolynuclear complexes have been obtained with the polyfunctional macrocyclic or macroacyclic ligands H_2L_H and H_5L_I or the reduced analogues.

Both ligands show strong peaks in the range 1630–1615 cm^{-1} due to $\nu C{=}N$ and a strong peak at 1700–1680 cm^{-1} due to $\nu C{=}O$ of the carboxylic group.

The macrocyclic nature of H_2L_H was confirmed by mass spectrometry. Its FAB mass spectrum, recorded using nitrobenzylalcohol as matrix, is characterized by the presence of abundant protonated molecular ion, $[M+H]^+$, at m/z 561 (100%). The MIKE spectrum of $[M+H]^+$ species shows the primary losses of H_2O, CO, CO_2 and the formation of $[M/2]^{\cdot+}$ ionic species.

The FAB mass spectrum of H_5L_I, recorded using nitrobenzylalcohol (NBA) as matrix, shows the presence of the following ionic species: $[M+H]^+$ at m/z 393 (100%), $M^{\cdot+}$ at m/z 392 (83%), $[M-H]^+$ at m/z 391 (72%) and $[M+H-C_7H_4O_2]^+$ at m/z 271 (65%). The MIKE spectrum of $[M+H]^+$ shows the primary losses of H_2O, CO, CO_2 and $C_7H_6O_2$.

H_5L_I easy coordinates copper(II) into the inner N_2O_2 chamber, the FAB mass spectrum of the resulting mononuclear compound $Cu(H_3L_I)$, recorded using NBA as matrix, shows the presence of the following ionic species: $M^{\cdot+}$ at m/z 453 (24%), $[M-CO]^{\cdot+}$ at m/z 425 (20%), $[M-CO_2]^{\cdot+}$ at m/z 409 (20%) and $[M+H-Cu]^+$ at m/z 391 (100%). The MIKE spectrum of $[M]^{\cdot+}$ ions shows the primary losses of H_2O, CO, CO_2 and $C_7H_5NO_2Cu$.

$Cu(H_3L_I)$ is the starting ligand for obtaining pure polynuclear complexes; their full characterization is currently under investigation.

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