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Mono-, homo- and hetero-dinuclear lanthanide(III) complexes with new acyclic compartmental Schiff bases

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Abstract

A series of homo-dinuclear lanthanide(III) complexes of the type: $Ln_2(L_A)(X)_2 \cdot n(H_2O)$ and $Ln_2(L_B)(X)_2 \cdot n(H_2O)$ (H_4L_A and H_4L_B are the Schiff bases obtained by condensation of 3-formylsalicylic acid and 4-*N*-dodecyldiethylenetriamine or 1,5-diamino-3-azapentane, respectively; $X = NO_3^-$, Cl^-; $n = 3$–8;) has been prepared and characterized. The synthesis of mono- and hetero-dinuclear complexes failed. On the contrary, mono-, homo- and hetero-dinuclear lanthanide(III) complexes, $Ln(H_4L_C)(NO_3)_3 \cdot nS$, $Ln(H_4L_D)(NO_3)_3 \cdot nS$ or $La(H_4L_E)(NO_3)_3 \cdot 4H_2O$, $Ln_2(L_C)(NO_3)_2 \cdot nS$, $Ln_2(L_D)(NO_3)_2 \cdot nS$ or $La_2(L_E)(NO_3)_2 \cdot 4H_2O$, $Ln^1\text{-}Ln^2(L_C)(NO_3)_2 \cdot nS$ or $Ln^1\text{-}Ln^2(L_D)(NO_3)_2 \cdot nS$ ($n = 1$–3; $S = H_2O$, CH_3OH), respectively, have been prepared by using the ligands H_4L_C, H_4L_D and H_4L_E, which are the Schiff bases derived by condensation of 2,3-dihydroxybenzaldehyde with 1,5-diamino-3-azapentane, 1,5-diamino-3-thiapentane or 4-*N*-dodecyldiethylenetriamine, respectively. The metal/metal ratio and the homogeneity of the hetero-dinuclear complexes have been evaluated also by electron microscopy together with X-ray fluorescence microprobe. The physicochemical properties of the prepared complexes have been compared with those of similar macrocyclic complexes. The magnetic behaviour of the complex $Gd_2(L_A)(NO_3)_2 \cdot 4H_2O$ has revealed a decrease in the effective magnetic moment from 10.97 μ_B at room temperature to 7.96 μ_B at 4.2 K, and an antiferromagnetic coupling constant $J = 0.211(4)$ cm^{-1}. A superexchange mechanism through the bridging atoms has been proposed.

Introduction

The possibility to prepare homo- and hetero-dinuclear complexes, containing lanthanide ions, has been recently established, by the use of the macrocyclic or macroacyclic compartmental ligands H_4-**I** $\cdots H_2$-**V** [1–8].

With the acyclic ligands H_4-**I** [1, 2] and H_4-**II** [3, 4], only hetero-dinuclear d–f complexes have been prepared. In particular for the complexes $[MLn(\mathbf{II}) \cdot X \cdot nH_2O]$ ($M = Cu^{2+}$, Ni^{2+}, $X = NO_3^-$, OH^-) the magnetic and optical properties have been tested and it was found that the transition metal(II) ion occupies the internal N_2O_2 chamber while the lanthanide(III) ion occupies the outer O_2O_2 coordination site. The presence of any magnetic interactions between the two metal ions was ruled out on the basis of the observed room temperature magnetic moments which were found very close to the values expected for two uncorrelated spins. Further these magnetic moments did not vary on decreasing the temperature in the 77–300 K range. As the exchange interactions, if present, are expected to be rather weak [9], magnetic measurements at temperatures lower than the liquid nitrogen limit, are required to ascertain if the reported assumptions are correct or not.

With the macrocyclic ligands H_2-**III** $\cdots H_2$-**V** [5–8] homo- and hetero-dinuclear lanthanide complexes have been prepared and their magnetic and optical properties studied. In particular the possible structure and the interaction between the metal ions for the complexes $Ln_2(\mathbf{IV})(NO_3)_4 \cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, Dy; $n = 1$, 2) and $Ln^1_x\text{–}Ln2_{(2-x)}(\mathbf{IV})(NO_3)_4 \cdot nH_2O$ ($Ln^1\text{–}Ln^2$ = La–Sm, La–Gd, La–Dy, La–Eu, Dy–Gd, Dy–Eu, Gd–Eu, Gd–Tb, Eu–Tb, La–Tb; $n = 1$, 2), have been inferred from spectroscopic, mass spectrometry and magnetic data together with scanning electron microprobe analyses [7].

Spectroscopic investigations on the heterodinuclear complex $[Tb\text{–}Eu(\mathbf{IV})(NO_3)_4] \cdot nH_2O$ have quantified the ligand → Ln(III) and Tb(III) to Eu(III) energy

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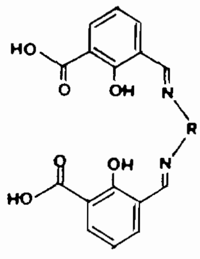
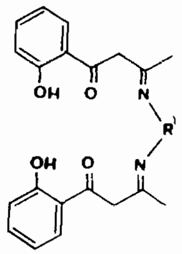
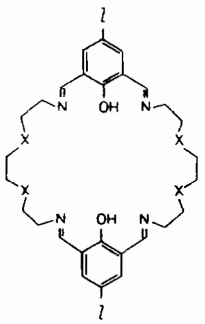


H_4-I



H_4-II



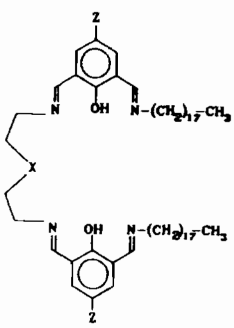
H_2-III (X=O, Z=CH_3)
H_2-IV (X=O, Z=Cl)
H_2-V (X=NH, Z=CH_3)

transfers also for an evaluation of the intermetallic distance [7].

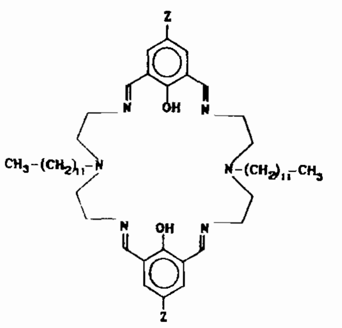
The reported Gd–Gd distance (3.97 Å) for the complexes $[Gd_2(III)(NO_3)_4]\cdot 2H_2O$ is considerably shorter than that estimated for the similar complexes with H_2-**IV**. Moreover in the Eu–Eu complex with H_2-**III**, the lifetime is much shorter than the lifetime reported for the complex with H_2-**IV**. It was suggested that the different Z-substituent may induce a different conformation of the ligand and hence different Ln···Ln distances [7, 8].

It was recently observed that it is possible to prepare Schiff base complexes containing f ions, very soluble in non-coordinating solvents, by adding aliphatic chains to the organic ligand without alteration of the coordination moiety [9–11].

The macroacyclic H_2-**VI** and macrocyclic H_2-**VII** ligands ($Z = Cl^-$, CH_3^-, $(CH_3)_3C$) and related uranyl(VI) UO_2(**VI**), UO_2(**VII**) and lanthanide(III) $Ln(H_2\text{-}\mathbf{VI})(NO_3)_3$ and $Ln(H_2\text{-}\mathbf{VII})(NO_3)_3$ complexes have been prepared and their properties studied [10–12].



H_2-VI

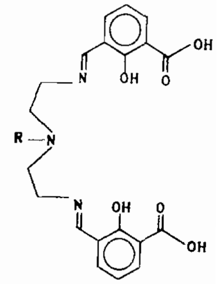


H_2-VII

We have accordingly tried to obtain complexes with 4f ions, soluble, easier to purify and study, by using the compartmental Schiff base H_4L_A obtained by condensation of 3-formylsalicylic acid and 4-*N*-dodecyldiethylenetriamine.

R = -$(CH_2)_{11}$-CH_3 **H_4L_A**

R = -H **H_4L_B**

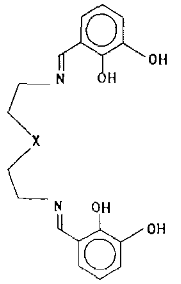


Lanthanide complexes with the similar ligand H_4L_B have also been prepared for an evaluation of the presence of the long aliphatic chain on the physicochemical properties of the complexes.

We had already verified that it was possible to prepare mono- and homo-dinuclear uranyl(VI) complexes with H_4L_B [13, 14] and that Schiff bases with a donor set N_3O_2 coordinate the lanthanide ions, roughly in their equatorial plane [15, 16]. Thus the two coordination chambers, N_3O_2 and O_2O_2 of H_4L_A and H_4L_B seem to be suitable for an easy coordination of 4f ions.

Homo-dinuclear complexes have been obtained by reaction of the preformed ligands with the appropriate lanthanide(III) salt or by template procedure. On the contrary, the preparation of mono- and hence hetero-dinuclear complexes, with the ligand H_4L_A failed. Thus the synthesis of similar ligands, especially designed and synthesized for coordination of the f ions has been undertaken. The potentially heptadentate compartmental ligands have been prepared

X	
NH	H_4L_C
S	H_4L_D
N-$(CH_2)_{11}$-CH_3	H_4L_E



by condensation of 2,3-dihydroxybenzaldehyde with 1,5-diamino-3-X-pentane. Both inner N_2XO_2 and outer O_2O_2 chambers have the correct geometry for allowing the coordination of two f ions. These compartmental ligands form mono-, homo- and heterodinuclear complexes.

In the complexes with the ligands H_4L_A–H_4L_D a short Ln···Ln distance may be proposed; consequently a metal–metal interaction can occur, as recently proposed for the complexes $[Ln_2(III)(NO_3)_4]\cdot 2H_2O$ [8].

The purpose of the present investigation is thus to set up the preparation of mono-, homo- and hetero-dinuclear complexes containing 4f ions H_4L_A–H_4L_D, to study the physicochemical properties (particularly magnetic) of these species and to compare the results with those obtained with similar macrocyclic systems.

Experimental

3-Formylsalicylic acid was prepared according to a literature procedure [17]. 2,3-Dihydroxybenzaldehyde, 1,5-diamino-3-azapentane, 1.5-diamino-3-thiapentane, 4-*N*-dodecyldiethylenetriamine and the lanthanide(III) nitrate or chloride hydrates are commercial products and were used without further purifications. H_4L_B was obtained as a yellow powder by reaction of 3-formylsalicylic acid and 1,5-diamino-3-aza-pentane in a 2:1 molar ratio, in methanol, as reported in the literature [13].

Preparation of the ligands

H_4L_A

To a warm methanolic solution of 3-formylsalicylic acid (332 mg, 2 mmol), 4-*N*-dodecyldiethylenetriamine (271.5 mg, 1 mmol) in ethanol was added. The resulting yellow solution was stirred under reflux for 1 h. The solution was evaporated to dryness under reduced pressure and the yellow residue was treated with 75 ml of ethanol. The pale yellow solid obtained was filtered, washed with ethanol and dried *in vacuo*.

H_4L_D

To a methanolic solution (100 ml) of 2,3-dihydroxybenzaldehyde (276 mg, 2 mmol), 1,5-diamino-3-thiapentane (120 mg, 1 mmol) dissolved in methanol (15 ml) was added. The yellow solution obtained was stirred for 2 h. After this time the solvent was evaporated to dryness and the oil obtained was treated with diethylether and stirred for 2 h and the solid obtained was filtered and dried under an IR lamp.

H_4L_C *and* H_4L_E

They were prepared by the same procedure employed for the synthesis of H_4L_D, using 1,5-diamino-3-azapentane or 4-*N*-dodecyldiethylenetriamine as amine precursors, respectively. They are yellow oils, difficult to purify and characterize.

Preparation of the complexes

$[Ln_2(L_A)(NO_3)_2]\cdot nH_2O$ *(Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb; n = 3–6)*

To a methanolic (50 ml) solution of 3-formylsalicylic acid (166 mg, 1 mmol), 4-*N*-dodecyldiethylenetriamine (142 mg, 0.5 mmol) was added. The yellow solution obtained was stirred under reflux, then LiOH (48 mg, 2 mmol) and the appropriate $Ln(NO_3)_3\cdot xH_2O$ lanthanide salt were added in order. The solution was refluxed for 4 h, then filtered, and reduced in volume under reduced pressure. The solid obtained was filtered, washed with methanol and diethyl ether and dried *in vacuo*.

$[Ln_2(L_A)(Cl)_2]\cdot nH_2O$ *and* $[Ln_2(L_B)(Cl)_2]\cdot nH_2O$ *(Ln = La, Sm; n = 5–8)*

The same procedure employed for the synthesis of the nitrate derivatives was used. $LnCl_3\cdot nH_2O$ lanthanide salts were used instead of the corresponding nitrate salts. Before reducing the volume of the solution, the excess of LiCl formed was filtered off. For the $[Ln_2L_BCl_2]\cdot nH_2O$ complexes, 1,5-diamino-3-azapentane was used instead of 4-*N*-dodecyldiethylenetriamine.

$[Ln(H_4L_C)(NO_3)_3]\cdot nH_2O$ *(Ln = La, Eu, Gd, Tb; n = 1, 2)*

1,5-Diamino-3-azapentane (52 mg, 0.5 mmol) was added to a methanolic (100 ml) solution of 2,3-dihydroxybenzaldehyde (138 mg, 1 mmol). Then the appropriate $Ln(NO_3)_3\cdot xH_2O$ lanthanide salt (0.5 mmol) was added to the resulting yellow solution which became orange in a few minutes. After refluxing for 1 h the solution was partially evaporated and the solid product obtained was filtered, washed with methanol and dried *in vacuo*.

$La(H_4L_E)(NO_3)_3 \cdot 4H_2O$

The same procedure, employed to obtain $La(H_4L_C)(NO_3)_3 \cdot 4H_2O$ was used. 4-*N*-Dodecyldiethylenetriamine (135 mg, 0.1 mmol) was used as facultative polyamine.

$Ln_2(L_C)(NO_3)_2 \cdot nH_2O$ (Ln = Tb, Gd, Eu, La), $La_2(L_D)(NO_3)_2 \cdot 3CH_3OH$ and $La_2(L_E)(NO_3)_2 \cdot 4H_2O$

To a yellow methanolic solution (50 ml) of 2,3-dihydroxybenzaldehyde (138 mg, 1 mmol) and 1,5-diamino-3-azapentene (51.5 mg, 0.5 mmol) or 1,5-diamino-thiapentene (60 mg, 0.5 mmol) or 4-*N*-dodecyldiethylenetriamine (135 mg, 0.5 mmol), LiOH (48 mg, 2 mmol) was added. To the resulting red–brown solution, the appropriate $Ln(NO_3)_3 \cdot 6H_2O$ (1 mmol) in methanol was added and the solution was refluxed for 2 h. The volume of the solution was reduced under reduced pressure, until a brown precipitate was obtained. This was collected by filtration, washed with diethyl ether and dried *in vacuo*.

Ln^1-$Ln^2(L_C)(NO_3)_2 \cdot nH_2O$ (Ln^1-Ln^2 = La–Tb, Gd–Tb, La–Gd, La–Eu, Gd–Tb, Tb–Eu)

To a methanolic solution (100 ml) of 2,3-dihydroxybenzaldehyde (138 mg, 0.5 mmol) 1,5-diamino-3-azapentane (52 mg, 0.5 mmol) was added. The resulting yellow solution became orange by adding the first amount of the appropriate $Ln^1(NO_3)_3 \cdot xH_2O$ lanthanide salt (0.5 mmol) and turned to red by adding LiOH (48 mg, 2 mmol) under reflux. After a few minutes the second amount of $Ln^2(NO_3)_3 \cdot xH_2O$ lanthanide salt (0.5 mmol) was added and a little precipitate was formed. The reflux was continued for 3 h, the solvent was partially evaporated and the solid product was collected by filtration, washed with diethyl ether and dried *in vacuo*.

$LaTbL_D(NO_3)_2 \cdot 2CH_3OH$

The same procedure used in the synthesis of the complexes of the type $Ln^1Ln^2L_C(NO_3)_2 \cdot nH_2O$ was carried out. 1,5-Diamino-3-thiapentane was used instead of 1,5-diamino-3-azapentane.

Physicochemical data

Analytical data for the ligands H_4L_A and H_4L_D and for the prepared complexes are given in Table 1. The correct metal content of the reported complexes was determined by atomic absorption or flame emission, using a Varian AA-275 atomic absorption spectrophotometer. The Ln^1/Ln^2 ratio in the heterobinuclear lanthanide(III) complexes was also established by a new procedure using a SIMS apparatus [18, 19]. In the case of punctual analyses, metal ratios were conveniently determined by the integral counting of X-ray fluorescence radiation from a Philips SEM 505 model scanning electron microscope equipped with an EDAX X-ray energy dispersive spectrometer [20, 21]. Samples, suitable for SEM analysis, were prepared suspending the microcrystalline powders in diethyl ether. Same drops of the resulting suspension were deposited on a graphite plate and after evaporation of the solvent the samples (for taking photographs) were metallized with graphite and gold (in that order) by using a Edward's S150B model sputter coater [20, 21]. The IR spectra were carried out as KBr pellets by using a Perkin-Elmer 580B model infrared spectrophotometer. Magnetic susceptibilities were determined by the Faraday method at room temperature or in the 4.2–300 K temperature range, by using an Oxford Instrument equipped with a helium continuous-flow cryostat, the apparatus being calibrated with $HgCo(NCS)_4$ [22]. Diamagnetic corrections were carried out using Pascal's constants [23].

Results and discussion

It has been recently shown that it is possible to prepare homo- and hetero-dinuclear complexes, by using the large macrocyclic ligands H_2-**III** $\cdots$ H_2-**V**. It was also suggested that these macrocycles, can behave as compartmental, or as binucleating ligands, the two metal ions being held, inside the coordinating cavity, at a metal–metal distance of about 4 or about 8–10 Å.

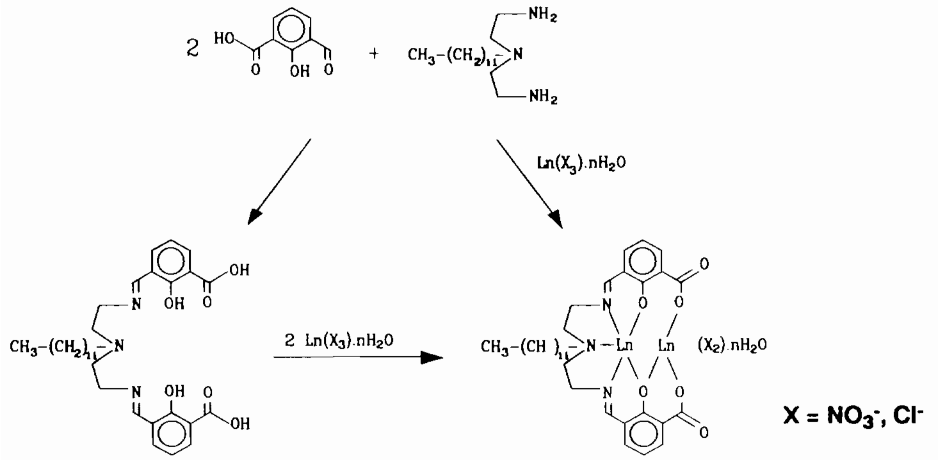
By reaction of 3-formylsalicylic acid and 4-*N*-dodecyldiethylenetriamine in the presence of the appropriate amount of $Ln(NO_3)_3 \cdot xH_2O$ or $LnCl_3 \cdot xH_2O$, homo-dinuclear complexes of the type reported in Scheme 1 have been synthesized.

The long aliphatic chain at the periphery of the coordinating moiety was introduced to enhance the solubility of the complexes in organic solvents which, unfortunately, is not as high as expected. This behaviour can be ascribed to oligo- or polymerization of the complexes through the oxygen atoms of the carboxylic groups. This certainly decreases the solubility of the complexes, making the introduction of the long aliphatic chain useless. In addition this oligomerization can produce unsymmetrical coordination about the lanthanide(III) ions; this causes low symmetry of the complexes as a whole, as evidenced by luminescence data, and makes doubtful any further optical study on the site occupancy of the 4f ions.

The IR spectra of the complexes $Ln_2(L_A)(NO_3)_2$ and $Ln_2(L_A)(Cl)_2$ show similar patterns: the bands associated with the nitrate groups cause only broadenings of the absorption bands of the ligand (a band

TABLE 1. Analytical data for the prepared compounds

Compound	Calc. (%)			Found (%)		
	C	H	N	C	H	N
H_4L_A	66.88	8.11	7.20	66.92	7.75	7.00
H_4L_D	59.79	5.59	7.77	59.54	6.13	7.50
$La_2L_A(NO_3)_2\cdot 6H_2O$	35.80	4.97	6.52	35.87	4.67	6.55
$Pr_2L_A(NO_3)_2\cdot 5H_2O$	36.27	4.84	6.61	37.00	4.46	6.45
$Nd_2L_A(NO_3)_2\cdot 3H_2O$	37.31	4.59	6.80	37.63	4.28	6.71
$Sm_2L_A(NO_3)_2\cdot 6H_2O$	35.05	4.87	6.39	35.26	4.23	6.48
$Eu_2L_A(NO_3)_2\cdot 4H_2O$	36.14	4.64	6.58	36.32	4.56	6.82
$Gd_2L_A(NO_3)_2\cdot 4H_2O$	35.78	4.59	6.52	35.76	4.51	6.74
$Tb_2L_A(NO_3)_2\cdot 4H_2O$	35.67	4.54	6.50	36.34	4.54	6.68
$Dy_2L_A(NO_3)_2\cdot 4H_2O$	35.43	4.58	6.46	35.79	4.28	6.09
$Yb_2L_A(NO_3)_2\cdot 4H_2O$	35.06	4.46	6.33	35.70	3.91	6.21
$La_2L_B(NO_3)_2\cdot 3H_2O\cdot CH_3OH$	28.56	3.08	7.93	29.27	2.82	7.40
$Sm_2L_B(NO_3)_2\cdot H_2O\cdot 3CH_3OH$	29.57	3.35	7.50	30.05	3.10	7.10
$La_2L_ACl_2\cdot 8H_2O$	36.38	5.43	3.98	36.41	5.24	3.58
$Sm_2L_ACl_2\cdot 7H_2O$	36.21	5.21	3.96	36.24	5.21	3.58
$La_2L_BCl_2\cdot 5H_2O$	28.80	3.26	5.04	28.77	3.35	5.63
$Sm_2L_BCl_2\cdot 5H_2O$	28.03	3.17	4.90	27.62	3.46	5.21
$La(H_4L_C)(NO_3)_3\cdot H_2O$	31.50	3.38	12.24	32.06	3.68	12.04
$Eu(H_4L_C)(NO_3)_3\cdot 2H_2O$	30.13	3.51	11.71	31.07	3.40	11.04
$Gd(H_4L_C)(NO_3)_3\cdot H_2O$	30.68	3.29	11.92	30.01	3.54	12.38
$Tb(H_4L_C)(NO_3)_3\cdot H_2O$	30.61	3.02	11.89	29.62	3.32	12.25
$Eu_2L_C(NO_3)_2\cdot H_2O$	27.53	2.44	8.92	27.66	2.66	8.80
$Tb_2L_C(NO_3)_2\cdot 2H_2O$	26.46	2.59	8.57	26.49	2.63	8.53
$LaEuL_C\cdot (NO_3)_2\cdot H_2O$	27.99	2.48	9.07	28.37	2.86	9.01
$EuTbL_C(NO_3)_2\cdot 2H_2O$	26.68	2.61	8.64	26.14	2.59	8.76
$La_2L_D(NO_3)_2\cdot 3CH_3OH$	29.52	3.30	6.56	29.80	3.09	6.59
$LaTbL_D(NO_3)_2\cdot 2CH_3OH$	28.72	2.87	6.65	28.82	3.00	6.48
$La(H_4L_E)(NO_3)_3\cdot 4H_2O$	39.83	5.46	9.29	39.25	5.44	10.07
$La_2(L_E)(NO_3)_2\cdot 4H_2O$	36.71	5.03	7.13	36.59	4.52	7.28



Scheme 1. Synthesis of homo-dinuclear lanthanide(III) complexes $Ln_2(L_A)(X_2)\cdot nH_2O$.

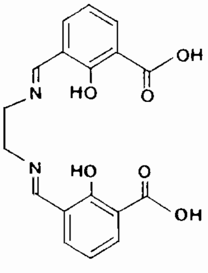
or a shoulder at about 1384 cm^{-1} is also present in the spectra of the nitrato complexes). Thus the assignment of the nitrate coordination behaviour, by comparison with the analogous chloride complexes, is not possible.

In the 1700–1550 cm^{-1} region, three strong bands attributable to C–O, C–N and C–C groups are present.

The free ligand H_4L_A, obtained by condensation of 3-formylsalicylic acid and 4-*N*-dodecyldiethylenetriamine in a 2:1 molar ratio, shows, in its IR spectrum, meaningful peaks at 1686sh, 1663vs, 1613 cm^{-1} due to C=O, C=N and C=C modes, respectively. These absorption bands well parallel those found in H_4L_B (1685vs, 1652 and 1605 cm^{-1}) and in the two forms of the very similar ligand obtained by using 1,5-diamino-thiapentane as polyamine precursor (1698vs, 1660 and 1600 for one form and 1730, 1660 and 1600 cm^{-1} for the other form) [14].

The IR spectra of the complexes with H_4L_B, resemble those recorded for H_4L_A. Three main peaks are present in the range 1650–1557, 1469, and 1318 cm^{-1} and assigned to bidentate nitrate groups. The peak at about 1343 cm^{-1}, due to the ionic NO_3^- group, can be caused by the KBr used for the preparation of the pellets.

H_4L_A easily forms mononuclear complexes with transition metal ions; for instance the copper complex $Cu(H_2L_A)\cdot 2H_2O$ has been prepared by template procedure. For this complex, with the copper very probably in the inner coordination chamber, the νC=O lies at about 1685 cm,$^{-1}$, as already observed for other mononuclear complexes with the similar compartmental ligand H_4-**VIII**, derived by condensation of 3-formylsalicylic acid and ethylenediamine, where the inner occupancy does not affect the νC=O IR band [24].



H_4-VIII

We were successful only in the preparation of mononuclear lanthanum complexes $La(H_4L_A)(NO_3)_3$ and $La(H_2L_A)(NO_3)$, obtained in the absence and in the presence of two equivalents of LiOH, respectively. Here the metal ion occupies the external chamber O_2O_2, where the νC=O is at about 1650 cm^{-1}, as is observed for the analogous mononuclear, O_2O_2, uranyl(VI) complex with H_4-**VIII** [24].

Attempts to extend the preparation of mononuclear compounds to the other lanthanide(III) ions failed; in any case a mixture of complexes was obtained. Thus it was absolutely impossible to prepare hetero-dinuclear complexes in a pure form where non-reproducible or inhomogeneous samples were obtained.

In order to obtain mononuclear but especially hetero-binuclear complexes the preparation of the ligands H_4L_C–H_4L_E and of the related f-containing complexes was carried out, according to reaction Scheme 2.

The change from the ligands H_4L_A or H_4L_B to ligands H_4L_C–H_4L_E was done for two reasons:

(i) to avoid the presence of free C=O groups, hence reducing the possibility of unsymmetrical oligo- or polymeric species with more well defined coordination sites;

(ii) to enlarge the external coordination chamber O_2O_2 in order to accommodate better a lanthanide ion inside it.

Only using 1,5-diamino-3-thiapentane as an amine precursor, an orange–brown solid (H_4L_D) was obtained which is stable in the solid state, for a long period of time, and soluble in the common organic solvents. H_4L_C and H_4L_E, on the contrary are yellow–brown oils, difficult to purify and handle correctly.

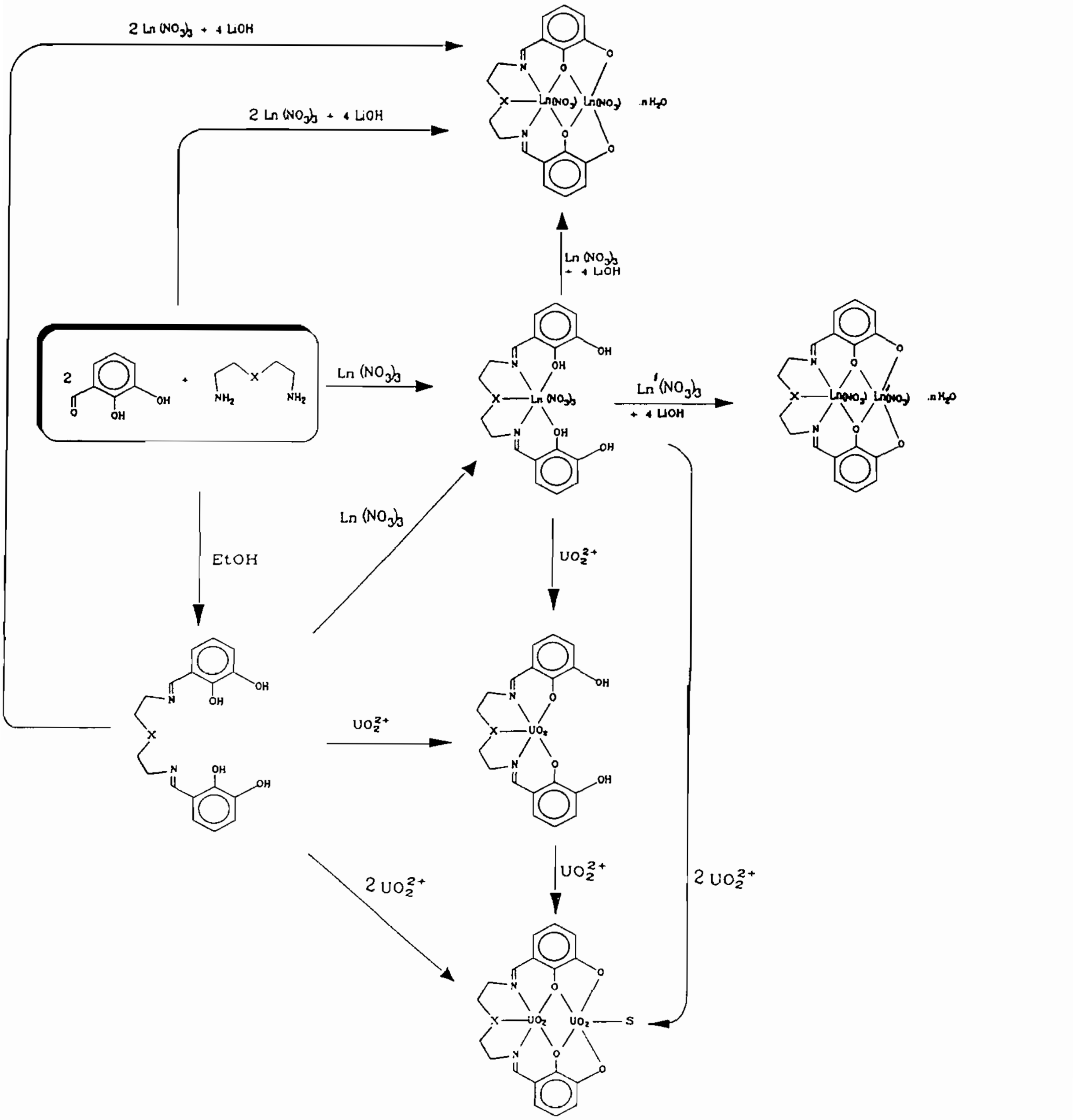
As can be seen in Scheme 2, by using mild conditions, it is possible to obtain mononuclear lanthanide(III) complexes where the Schiff base behaves as a neutral pentadentate ligand.

These mononuclear complexes suffer a transmetallation reaction when treated with uranyl(VI) salts, giving rise to the mononuclear and homo-dinuclear uranyl(VI) complexes already reported [25].

Owing to the failure to grow crystals suitable for X-ray investigations, the inner occupancy of the metal ion cannot be clearly identified in the mononuclear complexes. For instance on going from the mononuclear to the dinuclear terbium(III) complexes, small differences are detectable in their IR spectra; νC=N lies almost at the same frequency (1648 cm^{-1} in the mono and 1646 cm^{-1} in the dinuclear species). A new band, at 1563 cm^{-1}, due to the C–O phenolic groups is present in the dinuclear complex. In addition the complexity of absorptions in the range 1493–1218 cm^{-1}, due to the NO_3 groups, in the mononuclear complex is considerably reduced in the dinuclear complex, where for the same IR range, only three bands at 1468, 1392 and 1274 cm^{-1} are present.

The inner N_3O_2 occupancy in the mononuclear complexes may be suggested also by analogy with the uranyl(VI) mononuclear complex, for which this coordination behaviour was established by X-ray diffractometry [26]. In $UO_2(H_2L_C)\cdot$dmf (dmf=dimethylformamide) the ligand, using the inner coordination chamber, binds equatorially to UO_2^{2+} leading to seven coordinated uranium in a distorted bipyramidal coordination geometry. A dmf molecule is hydrogen bonded to the phenolic oxygens of the ligand (Fig. 1(a)).

The ability of these ligands to act as compartmental dinucleating agents towards f ions has been also



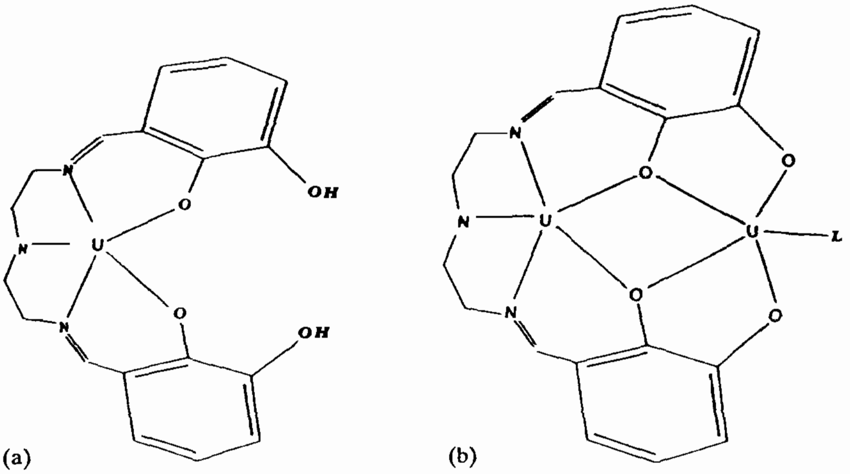
Scheme 2. Synthesis of mononuclear, homo- and hetero-dinuclear f-containing complexes of the ligands H_4L_C–H_4L_E.

verified on the complexes $(UO_2)_2(L_C)(dmso)$ (dmso = dimethyl sulfoxide) and $(UO_2)_2(L_C)(dmf)$ (Fig. 1(b)).

The chelating ligand coordinates the inner UO_2^{2+} as in $UO_2(H_2L_C)\cdot dmf$, while the outer UO_2^{2+} is coordinated by four oxygen atoms of the dinucleating ligand and by the oxygen atom of the solvent molecule.

The homo-dinuclear lanthanide(III) species are conveniently prepared in one step reaction, by template procedure. The hetero-dinuclear complexes must be prepared in two subsequent steps. This is allowed by the easy formation of the mononuclear lanthanide(III) complex. Again the introduction of a long aliphatic chain does not considerably enhance the solubility of the dinuclear complexes derived from the ligand H_4L_E.

The homogeneity and the metal ratio in the hetero-dinuclear complexes have been established by electron microscopy together with X-ray fluorescence analysis [21]. It was observed that the complexes are homogeneous with a 1:1 metal ratio within experimental error; for one complex, $LaTb(L_D)(NO_3)_2\cdot 2CH_3OH$, the S/La/Tb ratio (1\1\1) has been estimated.



(a) (b)

Fig. 1. Schematic representation of the mononuclear $UO_2(H_2L_C)$ (a) and dinuclear $(UO_2)(L_C)(L)$ (b) (L = dmso, dmf) uranyl complexes.

It must be noted that for this complex, prolonged heating can lead to a partial transmetallation reaction. As a final result, the lanthanide/sulfur ratio remains unaffected (2:1) but the lanthanide/terbium ratio is in favour of terbium (1:2) and means that the second ion tends to substitute the lanthanum from its inner coordination chamber. A similar behaviour has been observed for the other hetero-dinuclear species.

Differently from the outer linear UO_2^+ group in the dinuclear $(UO_2)_2(L_C)(S)$ complexes, which reaches its equatorial pentacoordination through the coordination of a solvent molecule (dmso, dmf, H_2O, etc.), the outer lanthanide(III) can reach its coordination saturation through oligomerization. Thus in the prepared complexes with H_4L_C–H_4L_E a dimerization through the phenolic oxygens, in order to fill the coordination sphere about the rare earth metal ion, can be suggested.

This bridging behaviour of the phenolic oxygens is well known and has been recently observed also in the hetero-dinuclear complexes, containing rare earths, $[MLn(L_F)(NO_3)(dmso)]_2$, (H_4F is the potentially hexadentate compartment ligand obtained by condensation of ethylenediamine and 2,3-dihydroxybenzaldehyde in methanol) [27]. Thus the complex $[CuY(L_F)(NO_3)(dmso)]_2$ (Fig. 2) is a tetranuclear asymmetric unit, two eight coordinate yttrium(III) ions being held together by two phenolic oxygen bridges. One bidentate nitrate group and one oxygen of a dimethylsulfoxide molecule complete the coordination sphere about each yttrium(III).

This oligomerization, via the phenolic oxygen of the outer chamber, can be prevented by the addition of anions, i.e. $CuLn(H_2L_F)(NO_3)_3$, which fill the coordination sphere about the lanthanide(III) ion with the consequent formation of monomeric species.

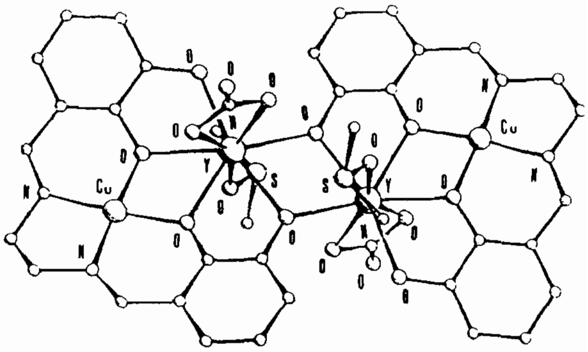


Fig. 2. Schematic representation of the tetranuclear complexes $[CuY(L_F)(NO_3)(dmso)]_2$.

As the Gd(III) ion has an orbital singlet as ground state (^8S) in $[Gd_2(L_A)(NO_3)_2]\cdot 4H_2O$ its magnetic properties are rather straightforward within the isotropic spin Hamiltonian approximation [28, 29]. The temperature dependence of the magnetic susceptibility of the gadolinium derivative in the χT versus T fashion in the range 4.2–300 K is shown in Fig. 3.

It is apparent that the effective magnetic moment decreases on decreasing the temperature passing from 10.97 μ_B at room temperature to 7.96 μ_B at 4.2 K. The room temperature value is slightly lower than the expected one for a couple of non-interacting $S = 7/2$ ions (11.17 μ_B). The decrease in the χT values on lowering the temperature is indicative that states with a lower spin multiplicity are progressively populated at temperatures lower than room temperature. This fact may be indicative that some magnetic interactions are operative between the gadolinium ions in the complex. By using the Hamiltonian $\mathcal{H} = JS_1S_2$, it is possible to derive the expression for

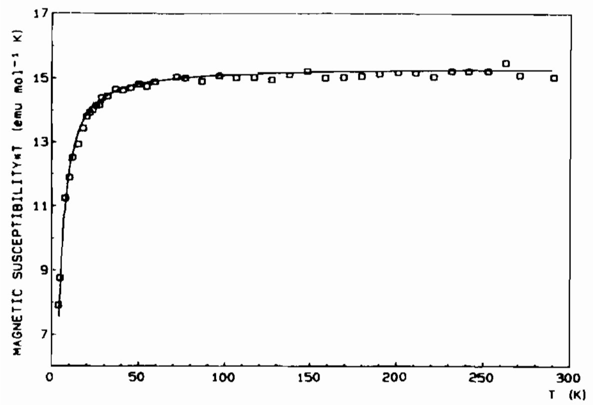


Fig. 3. Temperature dependence of the magnetic susceptibility of [$Gd_2(L_A)(NO_3)\cdot 4H_2O$] in the range 4.2–300 K in the χT vs. T fashion.

the magnetic susceptibility. A least-squares fitting procedure to the experimental data, maintaining the g factor to the fixed value of 1.975, yielded an antiferromagnetic coupling constant $J = 0.211(4)$ cm^{-1} with an agreement factor $R = 0.011$. If a Gd–Gd distance of 3.8 Å is assumed by comparison with similar complexes, a value of 0.032 cm^{-1} for the dipolar interaction is calculated [29]. This value is one order of magnitude lower than the coupling constant derived by the fitting procedure: this fact is indicative that a superexchange mechanism through the bridging atoms is operative in this compound.

In conclusion, it is possible to prepare homo- and hetero-dinuclear lanthanide(III) complexes from suitable compartmental ligands, which contain a large inner coordination chamber to accommodate a 4f ion. It is also possible, by magnetic measurements, from 4.2 K to room temperature to evaluate the type and the extent of magnetic interaction between the two metal ions and hence the metal···metal distance.

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References

1 G. A. Leonard and J. C. Bünzli, personal communication.
2 M. Sakamoto, M. Takagi, T. Ishimori and H. Okawa, *Bull. Chem. Soc. Jpn., 61* (1988) 1613.
3 A. Chisari, A. Musumeci, M. Vidali and A. Seminara, *Inorg. Chim. Acta, 81* (1984) L18–L21.
4 K. K. Abib and D. E. Fenton, *Inorg. Chim. Acta, 109* (1985) L5–L7.
5 I. A. Kahwa, J. Selbin, T. C.-Y. Hsieh and R. A. Laine, *Inorg. Chim. Acta, 118* (1968) 179.
6 I. A. Kahwa, F. R. Fronczek and J. Selbin, *Inorg. Chim. Acta, 126* (1987) 227.
7 P. Guerriero, P. A. Vigato, J.-C. G. Bünzli and E. Moret, *J. Chem. Soc., Dalton Trans.,* (1990) 647.
8 I. A. Kahwa, S. Folkes, D. J. Williams, S. V. Ley, C. A. O'Mahoney and G. L. McPherson, *J. Chem. Soc., Chem. Commun.,* (1989) 1531.
9 R. L. Carlin, *Magnetochemistry,* Springer, Berlin, 1986, p. 237.
10 E. Bullita, P. Guerriero, S. Tamburini and P. A. Vigato, *J. Less-Common Met., 153* (1989) 211.
11 J. C. Dupuy, M. Prevost, P. A. Vigato, P. Guerriero, E. Bullita and S. Tamburini, *Tech. Rep. EEC contract: MA1R.0013 C,* Padua, 1990; E. Bullita, P. Guerriero, S. Tamburini, P. A. Vigato, J. C. Dupuy, M. Prevost, R. Bonora and L. Marchesini, *Mater. Chem. Phys.,* in press.
12 P. A. Vigato, P. Guerriero, S. Tamburini, R. Seraglia and P. Traldi, *Org. Mass Spectrom., 25* (1990) 420.
13 U. Casellato, D. Fregona, S. Sitran, S. Tamburini, P. A. Vigato and P. Zanello, *Inorg. Chim. Acta, 95* (1984) 309.
14 U. Casellato, D. Fregona, S. Sitran, S. Tamburini and P. A. Vigato, *Inorg. Chim. Acta, 110* (1985) 161.
15 J.-C. G. Bunzli, E. Moret, U. Casellato, P. Guerriero and P. A. Vigato, *Inorg. Chim. Acta, 150* (1988) 133.
16 P. Guerriero, U. Casellato, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 129* (1987) 127.
17 J. C. Duff and E J. Bills, *J. Chem. Soc.,* (1932) 1987.
18 S. Daolio, E. Bullita, B. Facchin, P. Guerriero, C. Pagura and P. A. Vigato, *Workshop on the Basic and Applied Aspects of Rare Earths, Venice, Italy, May 26–27, 1988,* p. 25.
19 S. Daolio, B. Facchin, C. Pagura, P. Guerriero, S. Sitran and P. A. Vigato, *Inorg. Chim. Acta, 178* (1990) 131.
20 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 119* (1986) 215.
21 P. Guerriero, P. A. Vigato and B. Burtet-Fabris, *Inorg. Chim. Acta, 164* (1989) 155.
22 C. J. O'Connor, E. Sinn, E. J. Cukauskas and B. S. Deaver, Jr., *Inorg. Chim. Acta, 32* (1979) 29.
23 C. J. O'Connor, in S. J. Lippard (ed,), *Progress in Inorganic Chemistry, Vol. 29,* Wiley, New York, 1982, pp. 208–211.
24 M. Vidali, U. Casellato, P. A. Vigato, L. Doretti and F. Madalosso, *J. Inorg. Nucl. Chem., 39* (1977) 1985.
25 S. Tamburini, P. A. Vigato, P. Guerriero, U. Casellato and A. Aguiari, *Inorg. Chim. Acta, 183* (1991) 81.
26 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *J. Chem. Soc., Dalton Trans.,* (1990) 1533.
27 U. Casellato, P. Guerriero, S. Tamburini, S. Sitran and P. A. Vigato, *J. Chem. Soc., Dalton Trans.,* (1991) 2145.
28 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc., 107* (1985) 8128.
29 C. Benelli, A. Caneschi, A. C. Fabretti, D. Gatteschi and L. Pardi, *Inorg. Chem., 29* (1990) 4153.