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TEMPLATE SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR (La, Yb), HOMOBINUCLEAR (Ce, Eu) AND HETEROBINUCLEAR (La/Sn) COMPLEXES WITH AN ACYCLIC LIPOPHYLIC SCHIFF BASE DERIVED FROM 2,6-DIFORMYL-4-METHYLPHENOL

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Abstract—New lipophylic compounds $LaL(NO_3)\cdot 5H_2O$, $YbL(NO_3)\cdot 2H_2O$, $Ce_2L(NO_3)_2(OH)_2\cdot 6H_2O$, $Eu_2L(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2EtOH$ and $LaSnMe_2Cl_2L(NO_3)\cdot 5H_2O$ [$L = C_{38}H_{55}N_3O_4$] have been synthesized by a template condensation and characterized by using infrared and Mössbauer spectroscopies. In the homopolynuclear compounds, the two compartments in close proximity are both occupied, while for the La/Sn compound the $SnMe_2Cl_2$ was bonded by oxygen atoms out of these compartments; the Mössbauer parameters seemed to indicate a severely distorted *trans* octahedral geometry around the tin atom. For the mononuclear complexes, the metal La or Yb was encapsulated in the inner N_3O_4 compartment.

Recently, the chemistry of polynuclear complexes containing two or more different metal ions has been the subject of much interest, due to the metal selectivity for different sites in polydentate ligands.[1–7] The involvement of compounds containing such centres in catalytic processes has been the primary interest and this is reflected in the growth and development of the metal cluster chemistry. Further stimulus has come from the discovery that many proteins and enzymes require two or more metal ions for their activity and from the need to understand the nature of the active site and intermetallic interplay in these metallo species. The introduction of a lipophylic function into these molecules should produce interesting catalysts or carrier systems.

As part of our programme on polynuclear chelates, we have reported the synthesis of N-2-hexadecyl diethylene triamine trihydrochloride and its template condensation with 2,6-diformyl-4-methylphenol to form mononuclear (La, Yb), homobinuclear (Ce, Eu) and heterobinuclear (La/Sn) complexes of the non-isolated ligand.

EXPERIMENTAL

Starting materials were commercially available and used without further purification. The analytical data are reported in Table 1. Elemental analyses were performed by the analytical laboratory of the Department of Inorganic Chemistry

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Table 1. Elemental analyses

No.	Compound		C(%)	H(%)	N(%)
		Calc	58.5	5.2	19.6
2	$C_{18}H_{19}N_5O_4$	Found	58.5	5.2	18.9
		Calc	68.8	8.7	11.8
3	$C_{34}H_{51}N_5O_4$	Found	69.1	8.8	11.9
		Calc	55.0	11.1	9.6
4	$C_{20}H_{45}N_3 \cdot 3HCl$	Found	54.4	11.1	9.6
		Calc	65.8	4.9	
5	$C_9H_8O_3$	Found	65.8	4.9	
		Calc	50.2	7.2	6.2
6	$LaL(NO_3) \cdot 5H_2O$	Found	50.8	6.8	6.7
		Calc	51.3	6.7	6.3
7	$YbL(NO_3) \cdot 2H_2O$	Found	52.1	6.9	6.2
		Calc	42.6	6.3	5.0
8	$LaSnMe_2Cl_2L(NO_3) \cdot 5H_2O$	Found	42.2	6.2	5.1
		Calc	39.2	6.0	6.0
9	$Ce_2L(NO_3)_2(OH)_2 \cdot 6H_2O$	Found	38.9	5.9	6.1
		Calc	41.8	6.1	5.8
10	$Eu_2L(NO_3)_2(OH)_2 \cdot 2H_2O \cdot 2etOH$	Found	42.0	6.2	5.7

(University of Padua, Italy). Infrared spectra were recorded on a NICOLET 5SXC spectrophotometer as Nujol mulls or using KBr pellets. ^{119}Sn Mössbauer spectra were recorded at 80 K using a constant acceleration drive coupled with a multichannel analyser. The source used was $Ca^{119}SnO_3$ maintained at 295 ± 2 K and isomer shifts were reported with respect to this source. Spectra curves were fitted using conventional least-squares techniques to standard Lorentzian line shapes. The sample was prepared as finely ground powder to avoid orientation effects. The diene derivative was prepared through an improvement of the literature method:[8] instead of refluxing, the mixture was put in an ultrasonic bath to avoid the deterioration of the alkylated long chain. The preparative route is given in Scheme 1.

Preparation of **2**

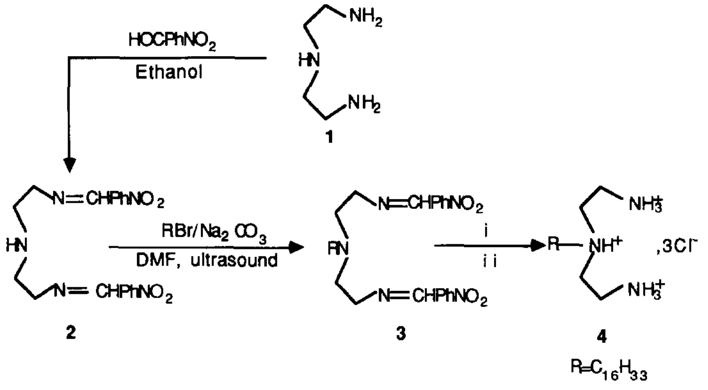
In a 500 cm^3 flask, 30.50 g (200 mmol) of *p*-nitrobenzaldehyde and 250 cm^3 of hot ethanol were introduced; 10.35 g (100 mmol) of **1** were added dropwise while stirring. After 5 min the mixture became yellowish. The solution was heated for 4 h before cooling at room temperature. After 1 h a precipitate was obtained in a good yield. The solid was filtered and washed twice with 150 cm^3 of ethanol and dried *in vacuo*. Exposed to the air, the yellow compound turned slowly to yellow–red. Yield 90%. M.p. = 114.5°C.

Preparation of **3**

66.10 g (178 mmol) of **2** were introduced in a 1 l flask and dissolved with 400 cm^3 of DMF; 72 cm^3 (231 mmol) of bromohexadecane and 21.80 g (224 mmol) of sodium carbonate were added. The mixture was put in a ultrasonic bath for 24 h. When the mixture was cooled at room temperature, a solid was obtained. After filtration, the precipitate was washed three times with hot water to separate the excess of sodium carbonate and sodium bromide. It was then washed with ethanol, ether and water and dried *in vacuo*. Yield 53%. M.p. = 105°C.

Preparation of **4**

51.03 g (86 mmol) of **3** were stirred with HCl 6 M solution. The mixture was put in an ultrasonic bath for 20 h. A white precipitate was obtained and filtered. The precipitate was heated moderately under reflux in methanol for 2 h to dissolve the *p*-nitrobenzaldehyde formed, filtered hot and dried *in vacuo*. Yield 90%. M.p. > 250°C (with decomposition).



Scheme 1. (i) HCl 6 M, ultrasound; (ii) moderate refluxing in MeOH.

Preparation of the dialdehyde (**5**)

2,6-Diformyl-4-methylphenol was prepared, improving the method described in the literature[9] by crystallizing the compound in *n*-hexane. Yield 66%. M.p. = 131°C. ^1H NMR (ppm) 2.84 (3H, s, CH_3); 7.74 (2H, s, aromatic); 10.15 (2H, s, CHO).

Preparation of $LaL(NO_3) \cdot 5H_2O$ (**6**)

0.238 g (2 mmol) of the dialdehyde in 20 cm^3 of ethanol was added, while stirring at room temperature, to 0.4331 g (1 mmol) of $La(NO_3)_3 \cdot 6H_2O$ and 0.0479 g (2 mmol) of LiOH in 20 cm^3 of ethanol. Then an ethanolic solution of **4** (0.4365 g, 1 mmol) and LiOH (0.0718 g, 3 mmol) was added and the mixture was heated under reflux for 1 h. The ethanol was removed and the crude compound was extracted with chloroform to eliminate LiCl and $LiNO_3$ by filtration on celite. The chloroform was removed and the resulting compound dried *in vacuo*. Yield 65%.

Preparation of $YbL(NO_3) \cdot 2H_2O$ (**7**)

This compound was prepared by a similar method to that described above for $LaL(NO_3) \cdot 5H_2O$, while using dichloromethane to extract the complex. Yield 42%.

Preparation of $LaSnMe_2Cl_2L(NO_3) \cdot 5H_2O$ (**8**)

To a solution of 0.9088 g (1 mmol) of $LaL(NO_3) \cdot 5H_2O$ in 30 cm^3 of ethanol was added, dropwise, an ethanolic solution of $SnMe_2Cl_2$ (0.2196 g, 1 mmol) while stirring. This solution was heated under reflux for 2 h and filtered hot. The filtrate was recuperated and then the ethanol was removed; the compound was washed with several portions of hexane and dried *in vacuo*. Yield 70%.

Preparation of $Ce_2L(NO_3)_2(OH)_2 \cdot 6H_2O$ (**9**)

To 0.238 g (2 mmol) of the dialdehyde in ethanol was added, while stirring, 0.434 g (1 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$. Then 0.049 g (2 mmol) of LiOH was added. An ethanolic solution of **4** (0.4365 g, 1 mmol) and LiOH (0.0718 g, 3 mmol) was added slowly using a dropping funnel; when the first drops were added the mixture turned from yellow to deep red. The mixture was then heated under reflux for 1 h before removing the ethanol. The crude compound was extracted by chloroform and filtered on an alumina column. The filtrate was evaporated to dryness and the resulting solid was dried *in vacuo*. Yield 80%.

Preparation of $Eu_2L(NO_3)_2 \cdot (OH)_2 \cdot 2H_2O \cdot 2EtOH$ (**10**)

This compound was prepared by a similar method to that described above for $Ce_2L(NO_3)_2(OH)_2 \cdot 6H_2O$. In this case the colour of the solution turned from yellow to deep yellow. Yield 80%.

RESULTS AND DISCUSSION

Infrared spectra

The most characteristic frequencies of the starting materials (the diene derivative and the dialdehyde) and of the complexes are listed in Table 2.

The absence of the ammonium stretching frequencies (2755–2388 cm^{-1}) in all the spectra of the complexes indicates the formation of the azomethine (C=N) linkage after the template condensation. The characteristic bands of the C=N group were observed in the range 1637–1647 cm^{-1} in agreement with previous assignment[10–12] for a similar series of complexes. For all these complexes,

Table 2. IR spectral data (cm^{-1})[a]

Dien	Attribution	**5**	Attribution	**6**	**7**	**8**	**9**	**10**	Attribution
				3406	3379	3356	3422 L	3427 L	$\nu\mathrm{H_2O}$
				3160	3180	3200			
2750 sh									
2720 sh	$\nu\mathrm{aNH_3^+}$								
2690 s									
2600 sh									
2570 s	$\nu\mathrm{sNH_3^+}$								
2520 s									
2480 sh									
2444 vs	$\nu\mathrm{NH^+}$								
2388 s									
		1682 vs	$\nu(\mathrm{C{=}O})$						
		1645							
	$\delta\mathrm{NH_3^+}$	1603 vs							
2017	+	1457	$\nu(\mathrm{C{=}C}$ ring)						
	$\tau\mathrm{NH_3^+}$	1404							
1606 vs	$\delta\mathrm{aNH_3^+}$								
1531 vs	$\delta\mathrm{sNH_3^+}$								
							1662 sh	1672 sh	$\delta(\mathrm{OH})$
				1645 vs	1637 vs	1647 vs	1641 vs	1639 vs	$\nu(\mathrm{C{=}N})$
				1547 vs	1547 vs	1547 vs	1539 vs	1540 vs	$\nu(\mathrm{C{=}})$
						1534 vs			
1462 s	$\delta\mathrm{CH_2}$								
1377 s									
1348 w	$\omega\mathrm{CH_2}$								
				1311 m	1309 m	1309 m	1309 b	1309 b	$\nu_4(\mathrm{NO_3^-})$ and $\gamma(\mathrm{OH})$
1245 w	$\gamma\mathrm{CH_2}$	1259 s	$\gamma(\mathrm{CH_3})$	1255 sh	1257 m	1255 m	1255 w	1255 sh	$\gamma(\mathrm{CH_2})$
		1215 s		1224 w	1224 m	1224 m	1224 w	1224 w	
		1159 s	$\nu(\mathrm{C{-}OH})$	1168 sh		1168 sh	1168 w	1168 w	
				1153 w	1155 m	1155 sh	1155 sh	1155 sh	$\nu(\mathrm{C{-}O})$
		1076 s	$\delta[\mathrm{C{-}H(ring)}]$	1072 sh	1072 m				
		1044 s	$\delta[\mathrm{C{-}H(CHO)}]$						
1057 m	$\nu\mathrm{aC{-}N}$			1035 m	1040 m	1035 m	1039 m	1041 m	$\nu(\mathrm{C{-}N})$ and $\nu_2(\mathrm{NO_3^-})$
1000 m	$\nu\mathrm{aC{-}C}$			997 w	1005 w	995 m	997	997	$\nu_a(\mathrm{C{-}C})$
980 w	$\nu\mathrm{C{-}N'}$			972 sh	972 sh	972 sh	972	972	$\nu(\mathrm{C{-}N'})$
945 w	$\nu\mathrm{sC{-}C}$	962 s	$\omega(\mathrm{C{-}H})$						
		885 m	δ(ring)						
		870 sh		868 m	866 m	869 m	871 m	868 m	δ(ring)
852 w	$\rho\mathrm{NH_3^+}$								
821 s	$\rho\mathrm{NH_3^+}$			817	819	817	819	817	$\nu_3(\mathrm{NO_3^-})$
						805 sh			$\rho(\mathrm{CH_3})(\mathrm{SnMe_2})$
		808	Terminal $\omega(\mathrm{CH_3})$				800	800	Terminal $\omega(\mathrm{CH_3})$
780		796	$\gamma_a(\mathrm{C{-}H(ring)})$	781 w	779 w	783	782 (Evans hole)	782 (Evans hole)	$\gamma_a[\mathrm{C{-}H(ring)}]$ and $\nu_5(\mathrm{NO_3^-})$
		747							
727 m	$\rho\mathrm{CH_3}$	719 m	$\rho(\mathrm{CH_3})$	723 m	721 m	721 m	721 m	721 m	$\rho(\mathrm{CH_3})$
		625 s	$\gamma_s[\mathrm{C{-}H(ring)}]$	652 w	636 w	650 w			$\gamma_s[\mathrm{C{-}H(ring)}]$
		589 w		569 m	567 w	569 vs			
						557 vs			$\nu_{as}(\mathrm{SnC_2})$
						519 m			$\nu_s(\mathrm{SnC_2})$
500 w	$\tau\mathrm{NH_3^+}$	474	$\gamma[\mathrm{C{-}C(ring)}]$	499 m	501 m	505 m	500 m	510 m	$\gamma[\mathrm{C{=}C(ring)}]$
		436							
						469 wb			$\nu(\mathrm{Sn{=}O})$
						464 wb			
						280 s			$\nu(\mathrm{Sn{-}Cl})$

[a] S, strong; m, medium; w, weak; b, broad; sh, shouldering; vs, very strong.

the spectra showed a broad absorption of medium intensity at 3400–3200 cm^{-1} due to the presence of hydrogen bonded water molecules. The presence of the two subbands was indicative of the presence of two types of water molecules.

Compounds **6**, **7** *and* **8**. On moving from the La and Yb complexes to the binuclear LaSn complex, the infrared spectra showed remarkable analogies, apart from the appearance of a doublet in the spectrum of **8** at 1534 and 1547 cm^{-1} attributed to ν(C=O), whereas it gave a single band in all the other spectra, and some bands due to the organotin group. In particular the C=N stretching laid almost at the same frequencies for both mononuclear and binuclear LaSn complexes, with a small shift to lower frequencies (1637 cm^{-1}) in the Yb compound. This is indicative of a tighter metal bond to the azomethine group while the ν(C—N) stretching at higher frequency (1040 cm^{-1}) suggested that the amide group is more slightly bonded in the Yb complex than in the other two.

As expected, the characteristic band of the C—O group of the dialdehyde observed[13] at 1159 cm^{-1} gave two weak bands at 1168 and 1155 cm^{-1} upon coordination. All these spectral features attest an encapsulation of the La or Yb metal atom in the inner N_3O_4 compartment (Fig. 1).

Consequently, the $SnMe_2Cl_2$ moiety in the binuclear compound was expected to be coordinated out of this compartment via the nitrogen or the oxygen. No band attributable to ν(Sn—N)[14,15] was observed in the range 340–400 cm^{-1} in the spectrum of **8**. Instead, a weak doublet absent in the spectrum of **6** was observed at 469 and 464 cm^{-1} and assigned to the ν(Sn—O) in accordance with established results,[16,17] the presence of two bands due to Sn—O being probably due to two different Sn—O distances (Fig. 2).

The low frequency region 600–200 cm^{-1}, where Sn—C and Sn—Cl vibrations were expected, gave information regarding the stereochemistry of organotin complexes.[18,19] On coordination, the Sn—Cl bond lengthened and consequently lowered the Sn—Cl stretching frequencies compared to 310–330 cm^{-1} in $SnMe_2Cl_2$.[15] Thus the sharp and strong band appearing at 280 cm^{-1} could be assigned to ν(Sn—Cl).

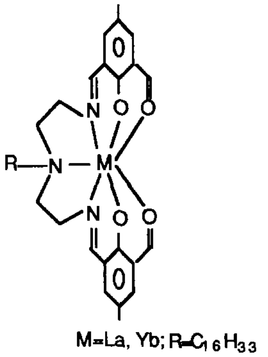


Fig. 1.

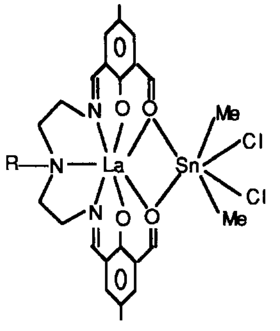


Fig. 2.

The spectrum of **8** showed two SnC_2 bands at 557 and 519 cm^{-1} assignable to asymmetric and symmetric stretching indicative of a non-linear configuration of the C—Sn—C moiety.

Compounds **9** *and* **10**. The spectra of these two complexes were quite similar. They showed significant differences compared to mononuclear and La/Sn binuclear complexes owing to the presence of a broad absorption band between 900 and 400 cm^{-1} with an Evans hole at 782 cm^{-1}.

For strong hydrogen bonds, the Evans effect[20] is well documented and several examples in many different types of systems are known.[21] This arises from the interaction of a broad level ν(O—H) with a narrow skeletal mode and produces sharp transmission windows in the spectrum. In the present case, we have noted a sharp transmission at 782 cm^{-1} corresponding to the absorption bands observed at 781, 779 and 783 cm^{-1} respectively in the spectra of **6**, **7** and **8** and attributed it to the out-of-plane ring bonding. Such a feature would be consistent with a very short and strong hydrogen bond generally found at frequencies below 800 cm^{-1} [22] and consequently to an O···O distance of *ca* 2.4 Å.[23] Unlike the previous observations in complexes containing hydroxide ions,[10,24] there was no sharp band in the region 3000–4000 cm^{-1} attesting coordination with the metal; instead, the large absorption noted above could be reasonably assigned to the hydrogen bonds involving the hydroxide ion. These features are consistent with an uncoordinated hydroxide.[25] Strong hydrogen bonding increases both in-plane and out-of-plane (δOH and γOH) bending frequencies, and in compounds containing C=O groups the δOH mode is strongly mixed with the C=O stretching mode.[26]

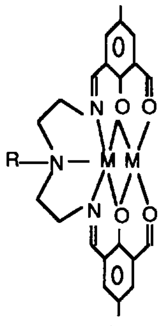
The two shoulders observed at 1662 and 1672 cm^{-1} in the spectra of **9** and **10** are therefore attributed to δOH, and γOH is probably located at 1309 cm^{-1} in the region of $\nu_4(NO_3^-)$, which is abnormally broad compared to **6**, **7** and **8**.

For these two compounds, the Ce and Eu atoms occupy the two inner compartment N_3O_2 and O_4 sites (Fig. 3).

Vibration of the nitrates. The main problem in the assignment of normal modes which appear below 1600 cm^{-1} was the overlapping of nitrate (free and/or bonded) and ligand bands. The spectra were consistent with an assignment of only coordinated (C_{2v} symmetry) bidentate nitrate groups.[27] In addition, the separation between ν_4 and ν_1 (161 cm^{-1}), assuming that ν_1 occurs at 1462 cm^{-1}, also attributed to the -CH_3 rocking, is of the magnitude frequently associated with bidentate nitrate groups.[28] The ν_5 and ν_6 are expected in the range 700–780 cm^{-1} overlapping with the skeletal bands.

Mössbauer spectra

The ^{119}Sn Mössbauer effect parameter of the heterobinuclear La/Sn compound gave a two line spectrum originating from the tin atom in an asymmetric environment. The values of the quadrupole splitting ($\Delta Q = 3.14$ mm s^{-1}) and the isomer shift ($\delta = 1.44$ mm s^{-1}) are consistent with hexa (or penta) coordinated tin.[29,30] It has been shown previously that hexacoordinated tin complexes with two *trans* methyl groups exhibited ΔQ values of *ca* 3.55 mm s^{-1} while bipyramidal trigonal geometries led to ΔQ of *ca* 3 mm s^{-1} or less.[17,31,32] In **8** the decrease of the ΔQ value, with respect to $SnMe_2Cl_2$ ($\Delta Q = 3.55$ mm s^{-1}, $\delta = 1.61$ mm s^{-1}), seemed to indicate a severely distorted *trans* octahedral geometry. This was supported by the infrared results since $\nu_{as}SnC_2$ and $\nu_{as}SnC_2$ were both observed, attesting the existence of a *trans* nonlinear Me_2Sn moiety.



M=Ce, Eu

Fig. 3.

In organotin(IV) compounds, when the other ligands have high electronegativity, the ΔQ is governed by the C—Sn—C bond angle.[33] The value observed here corresponded to a bond angle of about 131°.

In all the compounds the coordination sphere of the lanthanide, in addition to the ligand coordination, is completed with the bidentate nitrate ions and the water molecules.

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