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Complexation of a Schiff base ligand having two coordination sites (N_2O_2 and O_2O_2) with lanthanide ions (Ln = La, Pr): an NMR study

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With the help of spectroscopic data, we have characterized several isolated entities resulting from the reaction of lanthanide ions with a hexadentate Schiff base ligand obtained by reacting *o*-vanillin and 1,2-diaminoethane. This H_2L ligand possesses two coordination sites, an N_2O_2 inner site and an O_2O_2 outer site. In the first isolated complex, formulated as $(H_2L)Pr(NO_3)_3 \cdot H_2O$ **1Pr**, the NMR data confirm that the Pr^{3+} ion is only linked to the ligand by its deprotonated phenol functions while the ligand does exist in a neutral zwitterionic phenolato-iminium form (O^-, NH^+) in agreement with a migration of the protons from the phenolic functions to the imine groups. Deprotonation of the ligand in **1Pr** yields a new and original product, $LPr(NO_3) \cdot H_2O \cdot CH_3OH$ **2Pr** for which spectroscopic results agree with a coordination of the Pr^{3+} ion at the N_2O_2 site. This result, which is surprising in view of the oxophilic character of the lanthanide ions, is also confirmed by comparison with the NMR data of the $LZnPr(NO_3)_3$ complex **3Pr** that retains the Pr^{3+} ion in the O_2O_2 site. Another anionic complex **4Pr**, L_2PrCs, with two ligands linked to the lanthanide centre by their N_2O_2 sites is also isolated. Starting with the mononuclear cationic or anionic entities, **2Pr** or **4Pr**, we have not been able to isolate and characterize genuine homo- or hetero-dinuclear lanthanide complexes.

Introduction

Acyclic compartmental ligands with two differentiated sites afford a straightforward route to heterodinuclear 3d/4f complexes.[1] To obtain a variety of strictly dinuclear complexes associating a 3d element (Cu^{II},[2,3] Ni^{II} high[4] or low spin,[5] VO^{II},[6] Fe^{II},[7]) with a 4f element we have resorted to hexadentate Schiff bases derived from *o*-vanillin and diamines, abbreviated H_2L or H_2L' in the following and represented in Fig. 1. The complexes are prepared according to a two-step process leading first to a mononuclear species (LM) with the 3d ion (M = Cu, Ni, VO, Fe) located in the inner site (N_2O_2) of the ligand. It is then possible to insert the lanthanide ion in the outer site (O_2O_2) to obtain a $LMLnX_3$ complex, X standing for a monoanionic auxiliary ligand. The complexing possibilities of H_2L with 3d and alkali metal ions have also been explored.[8,9] To extend the scope of the coordination abilities of the H_2L ligands, we have performed a study of the H_2L/Ln systems. This study is essentially based on spectroscopic data (^1H and ^{13}C NMR, IR, MS FAB^+) for we have not succeeded in obtaining single crystals of the new complexes. Among Ln ions, the choice of Pr^{3+} is very interesting for it brings a substantial δ variation without an excessive modification of the half-height width for the different signals.

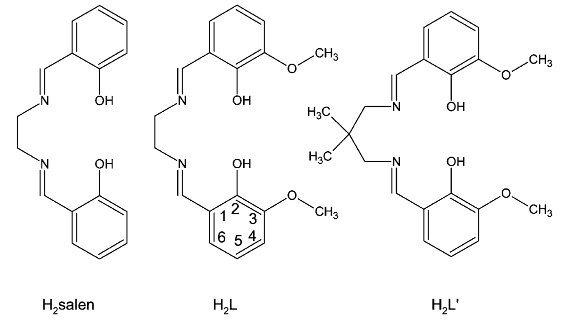

Fig. 1 Schematic representation of the ligands used in this study with the NMR numbering scheme.

Results and discussion

Preparation

Among the various lanthanide complexes of the H_2salen ligand and its derivatives,[10] two types deserve special interest. The first family described since 1968[11] has an overall formula Ln_2salen_3. To date no examples have been structurally characterized but spectroscopic and magnetic arguments[12,13] favour a structure involving a LnO_2Ln bridging core similar to that structurally determined for Gd_2thd_6[14] (thd = 1,1,5,5-tetramethylheptanedionato). The second type of complex is represented by the formula $Ln(H_2L)(NO_3)_3$.[15] A recent study[16] of the parent complex (L = salen) has stressed its unusual structural characteristics: the Schiff base coordinates as a neutral ligand *via* the phenolato oxygen atoms, the nitrogen atoms remaining uncoordinated. The protons move from the phenol functions to the imine groups. Finally each H_2salen molecule adopts an extended configuration and bridges two Ln ions resulting in a polymeric chain. Some of these particular features, *i.e.* coordination restricted to the phenolato oxygen atoms and the presence of an iminium group ($C{=}NH^+$) have been previously observed in three complexes involving dysprosium, neodymium and terbium ions and 4-methoxy-*N*-butyl-2-hydroxybenzaldimine.[17]

Seemingly we have succeeded in obtaining two complexes of this type. Reacting equimolar amounts of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La or Pr) and H_2L in methanol yields a yellow precipitate which, according to analytical data, is best described by the formula $(H_2L)Ln(NO_3)_3(H_2O)$ (abbreviated **1Ln** in the following). In these complexes the lanthanide ion can achieve the usual 9-coordination through two oxygen atoms from H_2L, six

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oxygen atoms from three chelating nitrate ions with one oxygen atom afforded by the water molecule. Spectroscopic results (*cf.* below) are consistent with coordination of the metal *via* the phenolato oxygens only of H_2L and the presence of the ligand in a neutral zwitterionic (O^-, NH^+)$_2$ form. This is also supported by a chemical argument. Addition of triethylamine to a suspension of **1Pr** in methanol first dissolves the initial complex while a new precipitate which was formulated $LPr(NO_3)(H_2O)(CH_3OH)$ (**2Pr**) appears a few minutes later. Charge balance considerations show that the occurrence of one nitrate prescribes that the ligand is doubly deprotonated. Using two nitrato oxygen atoms and two afforded by H_2O and CH_3OH, Pr^{3+} has to bind the four donors (N_2O_2) of the ligand to be 8-coordinated. Lower coordination numbers are unlikely. Spectroscopic data agree with the presence of the N_2O_2 donor set in the coordination sphere of the praseodymium ion. It is interesting to emphasize that this original complex is the first example in which a dideprotonated ligand of the salen type is linked to a Ln^{3+} ion in a 1 : 1 ratio. For the sake of comparison and to complete the description of the coordination chemistry of H_2L or H_2L' we have considered the complexes $LZnLn(NO_3)_3$ (**3Ln**), $L'ZnLn(NO_3)_3$ (**3′Ln**) and L_2LnCs (**4Ln**). In order to prepare the **3Ln** and **3′Ln** complexes, we first reacted Zn^{2+} ions with H_2L (or H_2L') to obtain a mononuclear precursor $LZn{\cdot}2H_2O$ (or $L'Zn{\cdot}2H_2O$) which contains the 3d metal within the inner (N_2O_2) coordination site. The $LZn{\cdot}2H_2O$ complex is able to act as a ligand towards the Ln^{3+} ions through the outer (O_2O_2) site to yield the expected dinuclear species.[2–7] These complexes are very interesting for they are the only ones to accommodate the Ln ion in the outer site. Substitution of the $N–(CH_2)_2–N$ diamino chain by $N–(CH_2)–C(CH_3)_2–CH_2–N$ increases the solubility of the prepared complexes. The reaction involving two molecules of H_2L with one of $Ln(NO_3)_3$ in the presence of CsOH leads to the isolation of **4Ln**. This complex belongs to a known type of sandwich-like species[18] in which a Ln^{3+} ion is linked to two deprotonated ligands *via* their (N_2O_2) chromophores to yield an anionic species $(L_2Ln)^-$. In spite of many attempts, we have not succeeded in obtaining a pure L_3Pr_2 sample. It may be recalled that the analogous derivatives of H_2salen and H_2dsp (*N*,*N*′-disalicylidene-1,2-phenylenediamine) are easily isolated.[11,12] When $Pr(NO_3)_3$ is added to L_2PrCs, the resulting product is not a homo-di- or -tri-nuclear species as expected on the basis of previous results[2–7] but the mononuclear complex **2Pr**. The difficulty in synthesising the homo-di- or -tri-nuclear complexes starting with mononuclear lanthanide species must be due to the large ionic radii of the lanthanide ions. Owing to their sizes the Ln^{3+} ions fastened in the inner N_2O_2 site increase the gap between the two halves of the ligand causing the outer O_2O_2 cavity to become too large to receive and retain a second Ln^{3+} ion. Use of **2Pr** as starting material does not give better results. The entire set of reactions is summarized in Fig. 2.

Characterization

The failure to obtain crystals suitable for a structural study and the low solubility in inert solvents make difficult the characterization of the complexes. The mass spectroscopy (FAB$^+$) has been limited to **2Ln** and **3Ln** complexes while FAB$^-$ has been useful for **4Ln** complexes. The spectra of the La^{3+} and Pr^{3+} species (**2La**, **2Pr**) are simple, each comprising one feature attributable beyond doubt to a $(LLn)^+$ ion (m/z = 465 and 467 for **2La** and **2Pr** respectively). This result gives evidence for the presence of one dideprotonated ligand per metal ion and supports the $LLn(NO_3)$ formulation suggested by the analytical data. For **3Pr** and **3′Pr** the observed isotope patterns of the cationic $[LZn(NO_3)_2]^+$ or $[L'Zn(NO_3)_2]^+$ species match the expected theoretical signals.

The IR spectra obtained from powdered samples of all the complexes offer many similarities. This is the case for the CN stretching vibration which is easily recognized in the 1620–1650 cm^{-1} range. The largest value of 1647 cm^{-1} corresponds to both $(H_2L)Ln(NO_3)_3$ complexes, **1La** and **1Pr**. Very similar values (1642, 1662 cm^{-1}) have been quoted in the literature for the lanthanide complexes of zwitterionic Schiff base ligands.[16,17] Otherwise a value of 1632 cm^{-1} has been attributed to ν(CN) in a complex where the imine groups are not coordinated.[19] The lowest value (1620 cm^{-1}) is reached by **4Pr** which has a sandwich-like structure with a $Pr[(N_2O_2)_2]$ core. Similar values are obtained for $LZn{\cdot}2H_2O$ and various lanthanide complexes in which the metal ion has a mixed (N_2O_2[2–7] or $(N_2O_2)_2$[12]) environment. It has been noted[17] that coordination of a Schiff base ligand to a metal ion through the phenolic oxygen atoms increases the wavelength of ν(CN) with respect to the free ligand value while coordination *via* the phenolic oxygen and the imino nitrogen atoms causes a shift towards lower ν(CN) values. In accordance with this rationale it is expected that ν(CN) would decrease in going from **1Ln** to **2Ln** if the latter species actually possess a $Ln(N_2O_2)$ core; indeed the ν(CN) values decrease from 1647 cm^{-1} for **1Ln** to 1627 cm^{-1} for **2Ln**. Assignments of the nitrate absorptions have been made by comparison with spectra of the free ligands or the zinc complexes. Strong bands appear at 1470 (**3′Pr**), 1456 (**1Pr**, **2Pr**, **3Pr**), 1318 (**1Pr**), 1292 (**2Pr**), 1290 (**3′Pr**), 1278 cm^{-1} (**3Pr**). Weaker bands are present at 1037, 818 cm^{-1} (**1Pr**), 1034, 819 cm^{-1} (**2Pr**), 1038, 815 cm^{-1} (**3Pr**), and 1025, 815 cm^{-1} (**3′Pr**). These splittings are similar to those of other CuLn complexes[2–5] for which the structural determinations have confirmed a η^2-chelation of the nitrate groups.

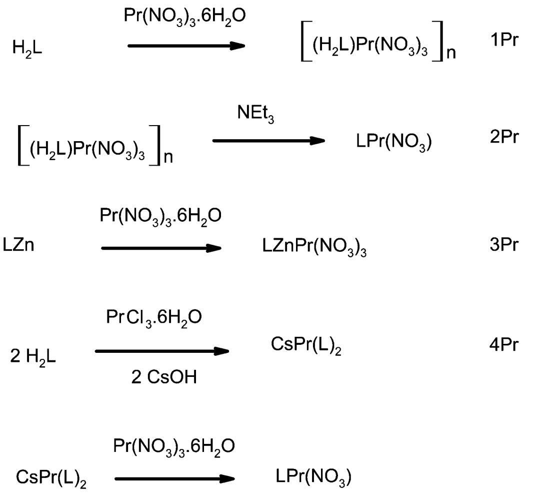

Fig. 2 Summary of the different reactions along with abbreviations of the isolated complexes (solvent molecules are omitted).

To complete the characterization of the complexes we have performed a detailed study of the ^1H and ^{13}C NMR spectra of the lanthanum and praseodymium species. The latter complexes are particularly interesting. Pr^{3+} is expected to induce specific effects which influence the chemical shifts of the neighbouring nuclei but do not significantly affect the relaxation rate and therefore the signal width. Well resolved spectra are obtained in all cases. The chemical shifts (δ) of the ^1H and ^{13}C nuclei along with the intensity ratios (^1H) are reported in Tables 1 and 2. The differences (Δ) between the $\Delta(^1H)$ values of a given proton in the praseodymium and lanthanum complexes are also indicated. Signals coming from water are present in the **1Ln**, **2Ln** and **3Ln** complexes.

Similar δ values are obtained for the free ligand H_2L and the lanthanum complexes of types **1**, **2**, **3** and **4**. Literature data[12,16,20,21] allow a straightforward attribution of the signals. Surprisingly these δ values are little affected in substituting Pr^{3+} for La^{3+} in the **1** complexes. **1Pr** is insoluble in acetone, chloroform, reasonably soluble in nitromethane and very

Table 1 ^1H NMR data (chemical shifts in ppm *vs.* $SiMe_4$) of the different compounds in dmso-d_6 with intensity ratios given in parentheses

	CH_2	CH	CH-4	CH-5	CH-6	OCH_3	OH,NH
H_2L	4.04(4)	8.68(2)	7.12(2)	6.90(2)	7.13(2)	3.87(6)	13.62(2)
1La[a]	4.28(4)	8.67(2)	7.13(2)	6.72(2)	7.17(2)	3.95(6)	14.37(2)
1Pr[a]	4.05(4)	8.72(2)	7.12(2)	6.92(2)	7.12(2)	3.77(6)	13.78(2)
Δ[b]	−0.23	0.05	−0.01	0.20	−0.05	−0.18	
2La	3.87(4)	8.34(2)	6.96(2)	6.48(2)	6.98(2)	3.85(6)	3.17(3)[e]
2Pr	−51.59(4)	34.66(2)	33.40(2) 35.80	27.76(2)	35.80(2) 33.40	23.77(6)	2.51(3)[e]
Δ[b]	−55.46	26.32	26.50 28.80	21.28	28.80 26.50	19.92	
LZn	3.46(4)	8.54(2)	6.89(2)	6.47(2)	6.89(2)	3.84(6)	
3La	3.49(4)	8.63(2)	7.24(2)	6.94(2)	7.38(2)	3.76(6)	
3Pr	7.35(4)	9.80(2)	−6.48(2)	1.41(2)	5.08(2)	−17.93(6)	
Δ[c]	3.89	1.26	−13.37	−5.07	−1.81	−21.77	
L′Zn[d]	3.58(4)	8.28(2)	6.88(2)	6.43(2)	6.88(2)	3.83(6)	
3′Pr	6.70(4)	9.89(2)	−6.00(2)	2.18(2)	5.80(2)	−18.12(6)	
Δ[c]	3.12	1.61	−12.88	−4.25	−1.08	−21.95	
4La	4.16(8)	8.26(4)	6.84(4)	6.19(4)	6.70(4)	3.59(12)	
4Pr	−45.51(8)	3.71(4)	14.30(4)	11.03(4)	9.89(4)	5.02(12)	
Δ[b]	−49.67	−4.55	7.46	4.84	3.19	1.43	

[a] In CD_3NO_2 as solvent. [b] ($\Delta = \delta_{Pr} - \delta_{La}$). [c] ($\Delta = \delta_{3Pr} - \delta_{LZn}$). [d] Resonance of the $C(CH_3)_2$ group: $\delta(CH_3) = 1.09$ ppm. [e] Methanol resonances.

Table 2 ^{13}C data (chemical shifts in ppm *vs.* $SiMe_4$) of the different compounds in dmso-d_6

	CH_2	CH	CH-4	CH-5	CH-6	OCH_3	C-1	C-2	C-3
H_2L	58.5	167.2	114.7	117.9	123.2	55.7	118.4	151.6	148.1
2La[a]	63.3	165.2	111.6	115.5	127.3	55.8	122.2	158.2	151.0
2Pr[a]	−21.7	233.6	161.7	171.9	150.2	84.0	245.6	252.7	261.2
Δ[b],[c]	−80.2	66.4	47.0	54.0	27.0	28.3	≈100	≈100	≈100
3Pr[d]	60.7	174.2	127.5	111.2	106.3	24.0	127.3	134.6	139.7
Δ[b]	2.2	7.0	12.8	−6.7	−16.9	−31.7	8.9	−17.0	−8.4
4Pr	−35.4	142.6	133.7	120.3	129.0	60.8	159.9	221.1	188.5
Δ	93.9	−24.6	19.0	2.4	5.8	5.1	41.5	69.5	40.4
H_2L'	66.7	166.9	114.8	117.9	123.3	55.8	118.4	151.8	148.2
3′Pr[e]	77.4	174.8	127.1	109.9	104.6	20.0	120.9	130.9	131.1
Δ[b]	10.7	7.9	12.3	−8.0	−18.7	−35.8	2.5	−19.9	−17.1

[a] MeOH: 49.5 ppm (**2La**), 32.5 ppm (**2Pr**). [b] ($\Delta = \delta_{Pr} - \delta_{ligand}$). [c] We cannot confirm the *ipso*-C assigments, but whatever their positions, the Δ differences are larger or equal to 100 ppm. [d] In CD_3COCD_3. [e] Resonances of the $C(CH_3)_2$ group: $\delta(C) = 38.6$ ppm; $\delta(CH_3) = 27.4$ ppm.

soluble in dmso. The ^1H spectrum in CD_3NO_2 is very informative. A resonance having a width $\Delta\nu_{1/2}$ of 17 Hz is centered at 13.78 ppm while the signals at 8.72 and 4.05 ppm present a fine structure of pseudo-doublets. Owing to their δ values they are attributed to the HC=N and N–CH_2 nuclei. Selective irradiation of the absorption at 13.78 ppm causes the doublets to merge into singlets, thus showing that the broad signal must be attributed to C=NH^+ groups in agreement with a migration of the protons from the phenolic functions to the imine groups. An outstanding question concerns the absence of specific effects in the praseodymium spectrum. In dmso solution, this is easily explained by the dissociation of the **1Ln** complexes, the H_2L, **1Pr** or **1La** species giving superimposed spectra. In the solid state and in a non-dissociating solvent such as nitromethane, an extended conformation of the diimino chain, which has been structurally established in one instance[16] must increase the flexibility of the molecular network, which results in averaging to nearly zero the paramagnetic shifts.

The other Pr^{3+} complexes show well resolved ^1H and ^{13}C spectra characterized by chemical shifts significantly different from those observed in the free ligand or in their lanthanum homologs. In the case of $LPr(NO_3)(H_2O)(CH_3OH)$ **2Pr**, signal integration allows differentiation of the CH, CH_2 and CH_3 signals. More precise assignments result from a ROESY experiment that confirms the central position of the signal at 27.76 ppm and its interaction with signals centred at 35.8 and 33.4 ppm, so that these three CH signals can be assigned to the phenolic cycle. The remaining signal at 34.66 ppm corresponds to the HC=N imine moiety. Unfortunately, we have no additional information to attribute the 35.8 and 33.4 ppm signals to the CH-6 (or CH-4) and CH-4 (or CH-6) positions. Indeed, if the HMQC-GS experiment gives the δ shifts of the carbon atoms linked to the different hydrogen atoms, the HMQC-LR experiment does not furnish any new information. Indeed, relaxation is so fast on the NMR timescale that any long range information is lost before being registered. The three *ipso*-carbon atoms giving signals at 245.6, 252.7 and 261.2 ppm cannot be unambiguously attributed. However these values differ considerably from those observed for the free ligand. Substituting Pr^{3+} for La^{3+} causes a deshielding (Δ varying from *ca.* 20 to 30 ppm) of all the ^1H signals except the CH_2 nuclei of the diamino chain which are shielded by as much as −55.46 ppm. These effects largely overcome those induced by complexing a diamagnetic ion such as La^{3+}. A better appreciation of these paramagnetic shifts and possible connections with localization of the lanthanide ion in the inner or outer site may be gained from a comparison with complexes **3Pr**, **3′Pr** and **4Pr**.

Previous work dealing with the structural characterization of 3d/4f complexes of compartmental ligands[2–7] shows that the 3d ion has a strong preference for the inner, mixed (N_2O_2) site, while the outer oxygenated site would comply with the oxophilicity of the lanthanide ion. The ^1H spectrum of **3Pr** in dmso displays an unexpected multiplicity which is due to a partial dissociation leading to a mixture of signals attributable to $LZnPr(NO_3)_3$ (80%) and LZn (20%) respectively. Dissociation does not occur in acetone. A complex stable in dmso is obtained by replacing H_2L by H_2L' (*cf.* Fig. 1, complex **3′Pr**). Its ^1H

spectrum is easily analysed from intensity and multiplicity considerations. The cyclic CH signals show fine structures of doublets ($\delta = -6.0$ and 5.8 ppm) and a triplet ($\delta = 2.18$ ppm). Very similar chemical shifts are observed for the more intense set of signals in dmso solutions of **3Pr**. With respect to the mononuclear Zn complex, the dinuclear **3Pr** species is mainly characterized by a shielding of the cyclic CH and methoxy side arms. The effects are important for OCH_3 ($\Delta \approx -21.8$ ppm) and CH-4 ($\Delta \approx -13.3$ ppm) and lower for CH-5 ($\Delta \approx -5$ ppm) and CH-6 ($\Delta \approx -1.8$ ppm). The N–CH_2 and N=CH protons are deshielded by 3.9 and 1.3 ppm respectively. As expected, the influence of the paramagnetic ion appears in the vicinity of the outer site. The most appropriate models for mimicking the effects of placing a Pr^{3+} ion in the inner site seem to be the sandwich-like complexes **4Ln** which offer the lanthanide ion a double N_2O_2 environment.[12] The ^1H and ^{13}C spectra of **4Ln** are simple showing that the two ligands are equivalent and that, within each ligand, the two halves of the molecule also are equivalent. Signal intensities and COSY correlations allow an unambiguous attribution of all the ^1H signals. It may be noted that the cyclic CH resonances show a characteristic doublet–triplet–doublet structure ($J_{HH} = 7.6$ Hz). The presence of a paramagnetic centre in **4Pr** finds expression in shielding effects which are large for CH_2 ($\Delta \approx -50$ ppm) and more reduced for N=CH ($\Delta \approx -5$ ppm). The other protons are deshielded with Δ values ranging from 1.5 to 7.5 ppm. Identification of the ^{13}C resonances are based on HMQS-LR experiments. As a whole the ^{13}C shifts tend to parallel the ^1H shifts and deserve similar comments.

Considering the NMR parameters of the reference complexes **3Ln**, **3′Ln** and **4Ln** we observe that the occupancies of the inner and outer coordination sites are well differentiated by characteristic effects undergone by neighbouring nuclei. The N–CH_2 and O–CH_3 groups do not participate directly in the delocalised electronic system of the ligand and are expected to be little affected by variation of the contact contribution, so that they are considered as valuable probes to indicate the proximity of the paramagnetic centre. Actually the ^1H (and ^{13}C) nuclei of the N–CH_2 groups are strongly shielded in **4Pr** and weakly deshielded in **3Pr**. Conversely shielding of OCH_3 occurs in **3Pr** ($\Delta\ ^1H \approx -21.8$ ppm) while a slight deshielding ($\Delta\ ^1H \approx 1.4$ ppm) is observed for **4Pr**. Interestingly the cyclic CH suffer a shielding varying from −13.4 to −1.8 ppm in **3Pr** and a deshielding of 7.5 to 3.2 ppm in **4Pr**. The original **2Pr** complex displays shifts of higher amplitude. The major effect concerns the CH_2 group with a shielding $\Delta\ ^1H$ of −55.5 ppm. Deshieldings of 20 to 30 ppm are observed for all the other ^1H nuclei. The trends parallel those observed in the case of **4Pr** and suggest an N_2O_2 environment for the lanthanide ion in **2Pr**. Furthermore the behaviour of the cyclic CH and methoxy OCH_3 groups militate against the occurrence of a Pr–(O_2O_2) chromophore in **2Pr**.

A questionable point concerns the HC=N imine groups. Indeed the ^1H and ^{13}C nuclei are deshielded, while shielding effects are expected on the basis of **4Pr** behaviour. A possible explanation results from the structural difference between **2Pr** and **4Pr**. In the latter case the sandwich-like structure places the lanthanide ion in between two N_2O_2 planes whereas in the former complex Pr^{3+} is most probably coplanar with the N_2O_2 donor set. This is also confirmed by the deshielding of the three *ipso*-carbon atoms of **2Pr**. Although we cannot precisely assign these three signals, their deshieldings are greater than or equal to 100 ppm, while they only vary from 40 to 70 ppm in **4Pr**. As expected, dmso solutions of **2Ln** and **4Ln** are 1 : 1 electrolytes.

As stated above, we have been unable to isolate crystals suitable for a structural study. Very recently, the structural determination of the samarium complex made with use of a Schiff base derived from the reaction of 2,2-dimethyl-3,5-hexanedione and 1,3-diaminopropane and containing the bulky bis(trimethylsilyl)amido anion, has confirmed the existence of a Sm(Schiff base)(anion) complex.[22] This is in perfect agreement with our results. Furthermore, with the use of the same Schiff base, the structural characterization of a complex that can be considered as similar to Ln_2salen_3 has been published.[22] The structural determination of the dinuclear neodymium complex confirms the presence of a NdO_2Nd bridge, two ligands being coordinated to the same Nd centre, each participating in μ-O bridging by one of its keto functions. The third ligand is only linked to the second Nd centre without any participation in the bridge. In agreement with these reported results and our spectroscopic data, Fig. 3 gives a schematic representation of the different complexes.

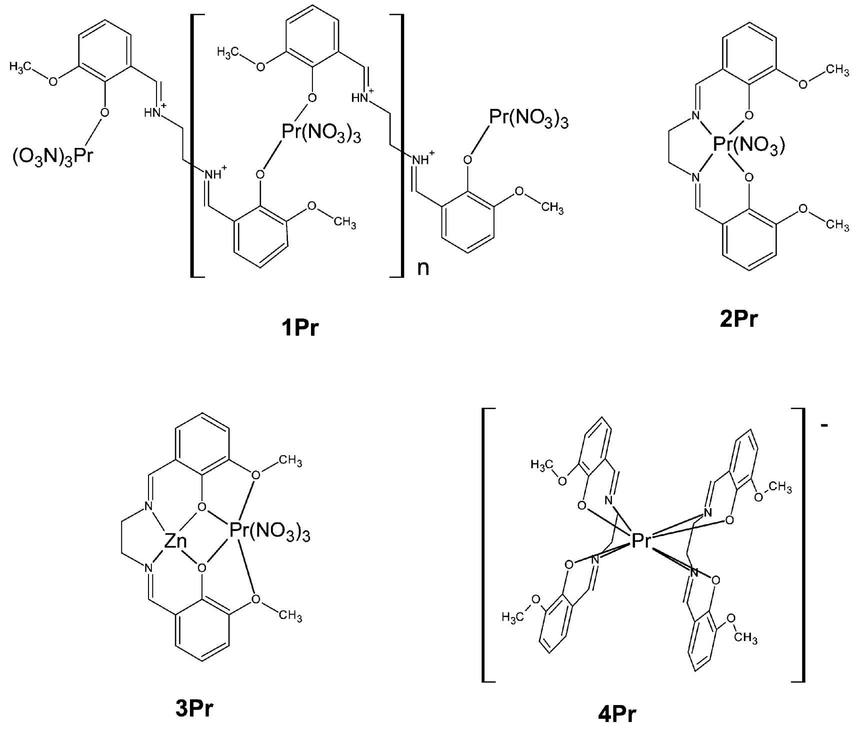

Fig. 3 Schematic representation of the different complexes. Solvent molecules are not included.

Conclusion

NMR allows direct characterization of the ligand as its free or complexed form and determines its protonation state along with the coordination site occupied by the lanthanide centre, in agreement with the IR data. It appears that, in spite of the generally accepted oxophilicity of the Ln^{3+} ions, they do not seem to have a particular affinity for the outer O_2O_2 coordination site of the H_2L or H_2L' ligands, as could have been expected from previous studies concerning the 3d/4f complexes. In the **2Ln** complexes, where the two N_2O_2 and O_2O_2 sites are vacant, the Ln^{3+} ions do prefer to occupy the inner N_2O_2 site. Attempts to add a supplementary Ln^{3+} ion to the outer O_2O_2 site, as in the 3d/4f complexes, have been unsuccessful. We have also observed the preparation and isolation of the type **1** complexes that retain their chain conformation in non-coordinating solvents. These **1Ln** complexes give new examples for coordination of Ln^{3+} ions by the deprotonated oxygen phenolate atoms, without complexing the oxygen atom of the neighbouring methoxy group. This special coordination induces flexibility of the molecular network and results in averaging to nearly zero the paramagnetic shifts in **1Pr**. In dmso, the **1La** and **1Pr** complexes are destroyed, yielding the protonated Schiff base. On the contrary the **2Ln**, **3Ln** and **4Ln** complexes, in which the Ln centres are coordinated to the N_2O_2 site, the O_2O_2 site and to two N_2O_2 sites respectively, retain their coordination in dmso solutions.

Experimental

Physical measurements

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). IR spectra were recorded on KBr discs with a Perkin-Elmer 983 spectrometer. 1-D ^1H NMR spectra were acquired at 250.13 MHz on a Bruker WM250 spectrometer. 1-D ^{13}C spectra using ^1H broadband decoupling $\{^1H\}^{13}C$ and gated ^1H decoupling with selective proton irradiation during acquisition were performed with the Bruker WM250 apparatus working at 62.89 MHz. 2-D ^1H COSY experiments using standard programs and 2-D pulse-field gradient HMQC ^1H–^{13}C correlation using the PFG-HMQC standard program were performed on a Bruker AMX400 spectrometer. Chemical shifts are given in ppm *versus* $SiMe_4$ (^1H and ^{13}C) using $(CD_3)_2SO$, CD_3NO_2 and CD_3COCD_3 as solvents. Mass spectroscopy spectra (FAB^+ and FAB^-) were recorded in dmf as a solvent with a 3-nitrobenzyl alcohol matrix on a Nermag R10–10 spectrometer. Electrical conductivity was measured in dmso at 10^{-3} M concentration.[23]

Preparation of ligands

H_2L was obtained as previously described.[24] H_2L' was prepared in a similar manner to H_2L but as it did not precipitate in methanol, the solvent was removed, giving a syrupy liquid that was diluted in diethyl ether. From the solution the yellow solid that appeared was filtered off and dried. Yield: 94%. Anal: Calc. for $C_{21}H_{26}N_2O_4$: C, 68.1; H, 7.1; N, 7.6. Found: C, 67.8; H, 7.0; N, 7.4%. ^1H NMR: δ 1.04 (s, 6 H, CH_3), 3.59 (s, 4 H, CH_2), 3.89 (s, 6 H, OCH_3), 6.92 (t, $J = 7.8$ Hz, 2 H, CH-5), 7.12–7.17 (m, 4 H, CH-4 and CH-6), 8.64 (s, 2 H, N=CH), 14.02 (s, 2 H, OH). IR (cm^{-1}, KBr disk): 1629, 1474, 1418, 1390, 1270, 1255, 1171, 1081, 973, 776, 734.

Preparation of complexes

$Pr(LH_2)(NO_3)_3{\cdot}H_2O$ 1Pr. $Pr(NO_3)_3{\cdot}5H_2O$ (0.42 g, 1 10^{-3} mol) was added to a suspension of H_2L (0.33g, 1 10^{-3} mol) in methanol (15 ml). After dissolution, a new yellow precipitate appeared quickly. It was filtered off and washed with methanol, diethyl ether and dried. Yield: 0.64 g, 95%. Anal: Calc. for $C_{18}H_{22}N_5O_{14}Pr$: C, 32.1; H, 3.3; N, 10.4. Found: C, 31.9; H, 3.1; N, 10.0%. IR (cm^{-1}, KBr disk): 3436, 1647, 1550, 1500, 1456, 1318, 1232, 1089, 1037, 958, 853, 818, 786, 733, 614, 429.

$La(LH_2)(NO_3)_3{\cdot}H_2O$ 1La. This compound was prepared in a similar way to **1Pr**. Yield: 93%. Anal.: Calc. for $C_{18}H_{22}LaN_5O_{14}$: C, 32.2; H, 3.3; N, 10.4. Found: C, 31.8; H, 3.1; N, 9.9%. IR (cm^{-1}, KBr disk): 3413, 1647, 1549, 1502, 1457, 1320, 1230, 1089, 1037, 957, 853, 819, 786, 732, 613, 421.

$PrL(NO_3){\cdot}H_2O{\cdot}CH_3OH$ 2Pr. $Pr(LH_2)(NO_3)_3{\cdot}H_2O$ (0.67 g, 1 10^{-3} mol) was suspended in methanol (15 ml). Addition of triethylamine (0.25 g, 2.5 10^{-3} mol) gave a yellow solution a few minutes later. After stirring for 3 hours, the precipitate which appeared was filtered off, washed with a few ml of methanol, diethyl ether and dried. Yield: 0.21 g, 36%. Anal: Calc. for $C_{19}H_{24}N_3O_9Pr$: C, 39.4; H, 4.2; N, 7.3. Found: C, 39.1; H, 4.0; N, 7.1%. Mass spectrum (FAB^+): *m*/*z* = 467 (100), $[PrL]^+$. IR (cm^{-1}, KBr disk): 3413, 1627, 1549, 1456, 1292, 1240, 1219, 1080, 1034, 962, 852, 819, 784, 735, 631, 540.

$LaL(NO_3){\cdot}H_2O{\cdot}CH_3OH$ 2La. This compound was prepared in a similar way to **2Pr**. Yield: 43%. Anal.: Calc. for $C_{19}H_{24}LaN_3O_9$: C, 39.5; H, 4.2; N, 7.3. Found: C, 39.2; H, 4.0; N, 7.2%. Mass spectrum (FAB^+): *m*/*z* = 465 (100), $[LaL]^+$. IR (cm^{-1}, KBr disk): 3430, 1627, 1549, 1454, 1290, 1220, 1079, 1034, 957, 851, 819, 783, 735, 633, 542.

$LZn{\cdot}2H_2O$. Addition of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.43 g, 2 10^{-3} mol) to a suspension of H_2L (0.66 g, 2 10^{-3} mol) in methanol (30 ml) gave a yellow solution that was heated for 30 minutes. After cooling, addition of water (60 ml) induced precipitation of a pale yellow powder that was filtered off. The precipitate was suspended in acetone and stirred again for 15 minutes, then filtered off and washed with acetone, diethyl ether and dried. Yield: 0.68 g, 80%. Anal: Calc. for $C_{18}H_{22}N_2O_6Zn$: C, 50.5; H, 5.2; N, 6.6. Found: C, 50.3; H, 5.0; N, 6.7%. IR (cm^{-1}, KBr disk): 3286, 1644, 1546, 1473, 1442, 1317, 1240, 1217, 1084, 973, 854, 725, 638, 423.

$LZnPr(NO_3)_3{\cdot}H_2O$ 3Pr. $Pr(NO_3)_3{\cdot}5H_2O$ (0.42 g, 1 10^{-3} mol) was added to a suspension of $LZn{\cdot}2H_2O$ (0.43g, 1 10^{-3} mol) in acetone (10 ml). After dissolution, a new yellow precipitate appeared quickly. It was filtered off and washed with acetone, diethyl ether and dried. Yield: 0.56 g, 85%. Anal: Calc. for $C_{18}H_{20}N_5O_{14}PrZn$: C, 29.4; H, 2.7; N, 9.5. Found: C, 29.3; H, 2.6; N, 9.0%. Mass spectrum (FAB^+): *m*/*z* = 655 (100), $[LZnPr(NO_3)_2]^+$. IR (cm^{-1}, KBr disk): 3354, 1636, 1557, 1456, 1397, 1278, 1220, 1075, 1038, 954, 849, 815, 784, 736, 638, 509, 449.

$L'Zn$ and $L'ZnPr(NO_3)_3$ were prepared in a similar way.

$L'Zn{\cdot}2H_2O$. Yield: 75%. Anal.: Calc. for $C_{21}H_{28}N_2O_6Zn$: C, 53.7; H, 6.0; N, 6.0. Found: C, 53.5; H, 5.9; N, 5.8%. IR (cm^{-1}, KBr disk): 3304, 1621, 1545, 1471, 1448, 1325, 1242, 1220, 1068, 970, 855, 740, 638, 444.

$L'ZnPr(NO_3)_3{\cdot}H_2O$. Yield: 86%. Anal.: Calc. for $C_{21}H_{26}N_5O_{14}PrZn$: C, 32.3; H, 3.4; N, 9.0. Found: C, 32.2; H, 3.2; N, 8.6%. Mass spectrum (FAB^+): *m*/*z* = 697 (100), $[L'ZnPr(NO_3)_2]^+$. IR (cm^{-1}, KBr disk): 3440, 1626, 1562, 1505, 1470, 1416, 1290, 1226, 1063, 1025, 929, 849, 815, 783, 744, 642, 480.

L_2LaCs and L_2PrCs were prepared according to a slight modification of a method described in the literature.[12] H_2L (0.61 g, 1.86 10^{-3} mol) and CsOH (0.62 g, 3.72 10^{-3} mol) were mixed in methanol (15 ml), giving a yellow solution a few minutes later. Then $PrCl_3{\cdot}6H_2O$ (0.33 g, 0.93 10^{-3} mol) was added at once as a solid. After stirring and refluxing (15 minutes), the white precipitate which appeared was filtered off and washed with water, methanol, diethyl ether and dried. Yield: 0.72 g, 90%. Anal: Calc. for $C_{36}H_{36}CsN_4O_8Pr$: C, 46.7; H, 3.9; N, 6.0. Found: C, 46.0; H, 3.6; N, 5.6%. Mass spectrum (FAB^-): m/z = 793 (100), $[L_2Pr]^-$. IR (cm^{-1}, KBr disk): 1620, 1541, 1466, 1443, 1322, 1220, 1075, 975, 962, 854, 735, 631, 530.

L_2LaCs was obtained in a similar way. Yield: 80%. Anal: Calc. for $C_{36}H_{36}CsLaN_4O_8$: C, 46.8; H, 3.9; N, 6.1. Found: C, 46.2; H, 3.6; N, 5.7%. Mass spectrum (FAB^-): m/z = 791 (100), $[L_2La]^-$. IR (cm^{-1}, KBr disk): 1620, 1541, 1465, 1443, 1322, 1219, 1075, 975, 960, 854, 735, 631, 530.

$LZnLa(NO_3)_3 \cdot H_2O$ 3La. Was prepared as for **3Pr**. Yield: 80%. Anal: Calc. for $C_{18}H_{20}LaN_5O_{14}Zn$: C, 29.4; H, 2.7; N, 9.5. Found: C, 29.5; H, 2.6; N, 9.1%. Mass spectrum (FAB^+): m/z = 653 (100), $[LZnLa(NO_3)_2]^+$. IR (cm^{-1}, KBr disk): 3436, 1634, 1556, 1455, 1397, 1277, 1220, 1074, 1036, 954, 847, 817, 784, 738, 636, 510, 450.

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