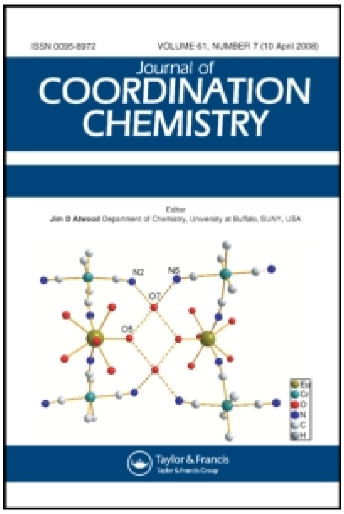

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LANTHANIDE(III) NITRATE ADDUCTS WITH 2,6-DIMETHYL-4H-PYRAN-4-ONE

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The new lanthanide complexes [$Ln(DMP)_3(NO_3)_3$] (Ln = La, Ce, Pr, Nd, Sm, Eu or Gd; DMP = 2,6-dimethyl-4H-pyran-4-one) and [$Ln(DMP)_2(H_2O)_2(NO_3)_3$].$H_2O$ (Ln = La or Ce) have been characterized by spectroscopic (infrared, ^{1}H nmr, ^{13}C nmr) and thermogravimetric data. Moreover the uranyl adducts [$UO_2(DMP)_2(NO_3)_2$] and [$UO_2(DMP)(O_2CMe)_2$] have been isolated. The influence of the solvent on the reaction products is discussed.

Keywords: 2,6-Dimethyl-4H-pyran-4-one, lanthanides, complexes, synthesis, thermal behaviour

INTRODUCTION

Coordination compounds of 2,6-dimethyl-4H-pyran-4-one (DMP) with various metal salts have been reported, in which the ligand acts as donor through the carbonyl oxygen.[1-5] With anhydrous lanthanide(III) chlorides, octahedral complexes of formula [$Ln(DMP)_3Cl_3$] have been generally isolated,[6,7] except for lanthanum, which has been found to form the lower stoichiometry adducts [$La(DMP)_2Cl_3$] and [$La(DMP)(H_2O)Cl_3$]$_n$.[6,8] Recently we characterized several uranyl and lanthanide(III) complexes with a diformylphenol derivatives.[9-12] In particular, 2,6-diformyl-4-methylphenol, H(MDA), and the complexes [$UO_2(MDA)_2(L)$] (L = H_2O, MeOH, EtOH) and [$Ln(MDA)_3$] undergo in alcoholic media partial or total acetalation of one of the formyl groups, leading to formation of 2-dialkylacetal-4-methyl-6-formylphenol and related complexes. With the aim of extending the study to diketoderivatives, we examined the behaviour of diacetylacetone, which is prepared from 2,6-dimethyl-4-pyrone and can form different condensation products in various organic media.[13] Meanwhile we observed that uranyl and lanthanide(III) nitrates form coordination compounds with 2,6-dimethyl-4-pyrone, which are soluble in non-alcoholic media. We thought it then of interest to characterize the related complexes, which can be used as intermediates in the synthesis of diacetylacetone derivatives.

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EXPERIMENTAL

Chemicals

Hydrated lanthanide(III) nitrates (Johnson Matthey), uranyl nitrate and uranyl acetate (Fluka) were used as supplied. 2,6-Dimethyl-4H-pyran-4-one (DMP, $C_7H_8O_2$, Ega-Chemie) was recrystallized from benzene/*n*-pentane. Water content in lanthanide salts was estimated by thermal analysis. Anhydrous lanthanum and cerium nitrates were obtained by heating (*ca* 100°C) the corresponding hydrates under reduced pressure (2h). Solvents were purified and dried as usual.[14] Deuterated solvents were kept over molecular sieves.

Preparation of the compounds

The complexes $[Ln(DMP)_3(NO_3)_3]$ (Ln = Pr, Nd, Sm, Eu or Gd) were prepared in satisfactory yields (70–80%) by adding a benzene solution of DMP to a suspension of the appropriate lanthanide salt in the same solvent (1.0 mmol of $Ln(NO_3)_3.nH_2O$ and 4.0–6.0 mmol of DMP in 30 cm^3 of benzene) with stirring. The reaction was complete within 4 d at room temperature or within 3 h under reflux. (Yields are improved by using anhydrous benzene and by operating under dinitrogen flux.) The solids were separated by centrifugation and washed with anhydrous benzene and *n*-pentane. The crude products were dissolved in anhydrous dichloromethane, in which the hydrated species are insoluble. The resulting crystals were washed with benzene and *n*-pentane and dried *in vacuo*. The complex purity was checked by infrared spectra. When a sharp band was present at 1386 cm^{-1}, the product was washed with anhydrous benzene. A progressive decrease of the band was observed, along with a parallel increase of the absorption at 1477 cm^{-1}. The samples were washed with benzene/*n*-pentane until the infrared spectrum was unchanged.

The preparation of $[La(DMP)_3(NO_3)_3]$ and $[Ce(DMP)_3(NO_3)_3]$ was carried out analogously under strictly anhydrous conditions. The starting nitrates were previously dehydrated. When hydrated lanthanum nitrate was used, the white compound $[La(DMP)_2(H_2O)_2(NO_3)_3].H_2O$, insoluble in dichloromethane, was obtained, whereas hydrated cerium nitrate yielded a mixture of $[Ce(DMP)_2(H_2O)_2(NO_3)_3].H_2O$ and $[Ce(DMP)_3]$, which were separated by their different solubilities in dichloromethane.

The 1:3 adducts were also prepared by reaction of lanthanide nitrate and DMP in anhydrous dichloromethane at molar ratio 1:6. The solution, decanted and evaporated to dryness, yielded an oil which was treated with benzene/*n*-pentane until solidification occurred. On standing in air overnight, the 1:3 lanthanum and cerium adducts release one of the DMP molecules to give the corresponding hydrated complexes, whereas the heavier lanthanide complexes are generally unchanged. The same effect is observed when solid samples are washed with wet solvents.

The compound $[UO_2(DMP)_2(NO_3)_2]$ precipitated gradually from the yellow solution obtained by adding DMP to a suspension of uranyl nitrate (1.0 mmol) in anhydrous benzene (40 cm^3, molar ratio 6:1, reaction time: 3 d at room temperature; 3 h under reflux). The yellow powder was filtered, washed with benzene/*n*-pentane and dried *in vacuo*. It can be recrystallized from dichloromethane/*n*-pentane.

The complex $[UO_2(DMP)(O_2CMe)_2]$ was obtained by adding DMP to a suspension of uranyl acetate in benzene (molar ratio 2:1) with stirring overnight. The yellow powder was filtered and washed with benzene/*n*-pentane.

When DMP and uranyl nitrate were reacted in refluxing methanol (molar ratio 4:1; 3 h) a yellow solution was obtained, which by slow evaporation yielded crystals of $[UO_2(DMP)_2(NO_3)_2]$. Under the same conditions uranyl acetate and DMP (molar ratio 1:4) gave a yellow solution which separated a small amount of a brown unidentified product. Slow evaporation of the filtered solution yielded a yellow powder which was separated by centrifugation and dried *in vacuo*. The solid was then washed with benzene/*n*-pentane. Analysis: found C = 18.6; H = 2.4%. The solid does not contain the acetate group (by nmr spectra in deuterated dimethyl sulfoxide).

Measurements

Infrared spectra were obtained using a Perkin-Elmer 580B spectrophotometer (4000–400 cm^{-1}; KBr pellets). NMR spectra were obtained with a Jeol FX 90 Q spectrometer. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 cm^3 min^{-1}; reference material Al_2O_3).

TABLE I
Analytical data for the complexes (calculated values in parentheses).

Compound	colour	mp (°C)	C%	H%	N%
$[La(DMP)_3(NO_3)_3]$	white	[a]	36.7 (36.2)	3.6 (3.5)	5.9 (6.0)
$[La(DMP)_2(H_2O)_2(NO_3)_3].H_2O$	white		26.4 (26.8)	3.2 (3.5)	6.7 (6.7)
$[Ce(DMP)_3(NO_3)_3]$	beige	150–2	36.6 (36.1)	3.6 (3.5)	5.9 (6.0)
$[Ce(DMP)_2(H_2O)_2(NO_3)_3].H_2O$	beige		26.1 (26.7)	3.2 (3.5)	6.8 (6.7)
$[Pr(DMP)_3(NO_3)_3]$	pale green	157–9	36.0 (36.1)	3.5 (3.5)	5.8 (6.0)
$[Nd(DMP)_3(NO_3)_3]$	pale violet	152–5	36.0 (35.9)	3.4 (3.4)	5.9 (6.0)
$[Sm(DMP)_3(NO_3)_3]$	white	168–9	35.8 (35.6)	3.5 (3.4)	5.9 (5.9)
$[Eu(DMP)_3(NO_3)_3]$	white	169–72	35.3 (35.5)	3.4 (3.4)	5.8 (5.9)
$[Gd(DMP)_3(NO_3)_3]$	white	170–73	35.3 (35.2)	3.4 (3.4)	5.8 (5.9)
$[UO_2(DMP)_2(NO_3)_2]$	yellow	184–7	26.4 (26.2)	2.6 (2.5)	4.2 (4.4)
$[UO_2(DMP)(O_2CMe)_2]$	pale yellow		25.5 (25.8)	2.6 (2.7)	

[a] The solid melts in part at 130–3°C; complete melting is observed at 140–2°C.

RESULTS AND DISCUSSION

The lanthanide(III) nitrate adducts with 2,6-dimethyl-4-pyrone, of general formula $[Ln(DMP)_3(NO_3)_3]$ (Table I) have been prepared in benzene (molar ratio of ligand to metal from 4:1 to 6:1). The preparation of the lanthanum and cerium 1:3 complexes requires anhydrous conditions. Otherwise the species $[Ln(DMP)_2(H_2O)_2(NO_3)_3].H_2O$ (Ln = La or Ce) are obtained, which also are formed when the corresponding 1:3 adducts are either washed with wet solvents or left standing in air. The heavier lanthanide 1:3 adducts are scarcely affected by water. In fact, they have been prepared using hydrated nitrates as reagents. All the 1:3 complexes have been recrystallized from anhydrous dichloromethane, in which the hydrated 1:2 species are nearly insoluble. The reaction of uranyl nitrate and ligand, either in benzene or in methanol, yields the adduct $[UO_2(DMP)_2(NO_3)_2]$, whereas uranyl acetate behaves differently in these solvents. In refluxing benzene the pale yellow 1 : 1 adduct $[UO_2(DMP)(O_2CMe)_2]$ is isolated, whereas in refluxing methanol an orange powder is obtained which does not contain the acetate group. The analytical and spectral data could suggest a $UO_2(OH)_2DMP$ adduct, polymeric through hydroxo bridges.

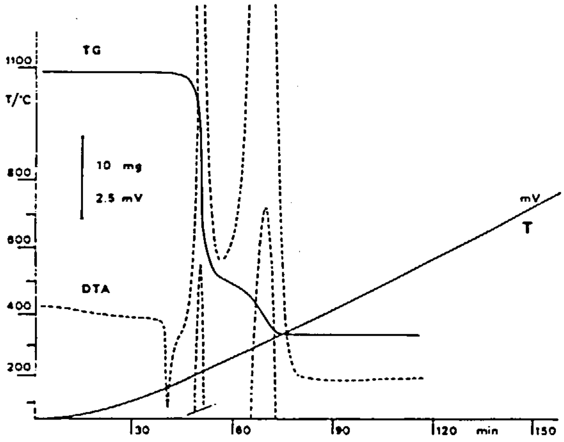

FIGURE 1 Thermograms of $[Ce(DMP)_3(NO_3)_3]$ (41.28 mg).

The thermal behaviour of the 1:3 adducts resembles that of $[Ce(DMP)_3(NO_3)_3]$. As is shown in Fig. 1, degradation immediately follows the melting process (150°C). Two strong exotherms are observed in relation to the successive decomposition steps, the final pyrolysis product being Ce_2O_3 (total weight loss up to 450°C: calcd, 76.5%; found, 76.7%). The thermograms of $[La(DMP)_3(NO_3)_3]$ (Fig. 2) suggest than on heating one ligand molecule is removed from the metal coordination sphere. Two close endotherms are observed, the one at 130°C due probably to melting of unbound DMP, followed by melting of the decomposition mixture (145°C). The weight loss in the first degradation step (19%, 220°C) is close to the calculated value for release of one ligand molecule (17.8%) and suggests formation of a 1:2 adduct as intermediate. The first endotherm in the $[La(DMP)_2(H_2O)_2(NO_3)_3].H_2O$ curves (110°C, Fig. 3) corresponds to evolution of the external water molecule, followed by release of one of the coordinated water molecules (168°C). The experimental weight loss in each step is 2.7%, as against a calculated value of 2.9% (for one H_2O molecule). The sample then decomposes without melting in the 200–700°C temperature interval. The total weight loss is 75.3% (calculated value for La_2O_3 as final product, 74.0%). As regards the uranyl complexes, $[UO_2(DMP)_2(NO_3)_2]$ (Fig. 4) melts at 180°C and decomposes in the 190–550°C temperature interval (total weight loss, 57.9%;

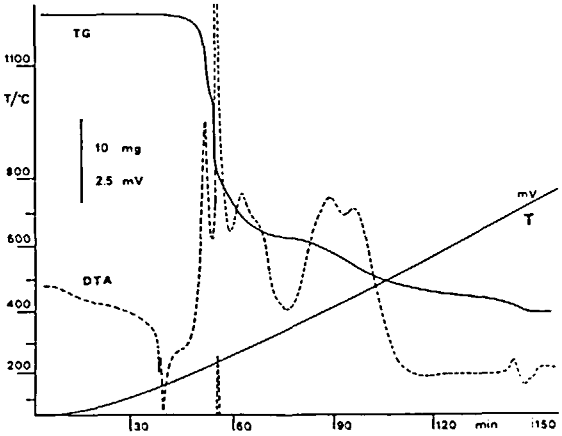

FIGURE 2 Thermograms of [La(DMP)$_3$(NO$_3$)$_3$] (46.00 mg).

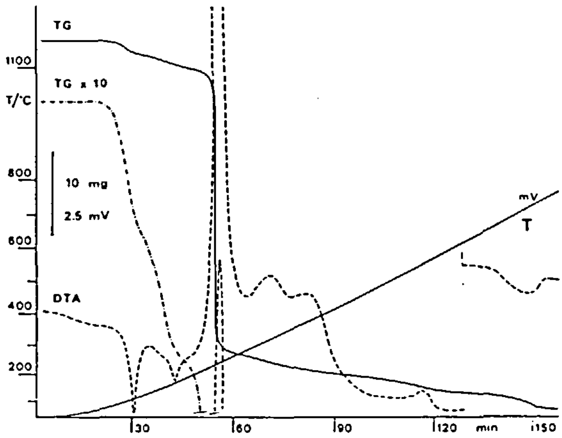

FIGURE 3 Thermograms of [La(DMP)$_2$(H$_2$O)$_2$(NO$_3$)$_3$].H$_2$O (59.76 mg).

calculated weight loss for UO$_2$ as pyrolysis product, 57.9%). Degradation of [UO$_2$(DMP)(O$_2$CMe)$_2$] occurs in the 160–450°C temperature range, the total weight loss being 44.7% (calculated for final UO$_3$, 44.14%). The related DTA curve shows two endothermic peaks at 210°C and 255°C, followed by an exotherm at 395°C.

In the 1700–1600 cm^{-1} range, the infrared spectrum of 2,6-dimethyl-4-pyrone contains two strong absorptions, assigned as ν(C=C) (1669 cm^{-1}) and ν(C=O) (1611 cm^{-1}). The shoulder at 1599 cm^{-1} is due to ring vibrations, as are the bands at 1444 cm^{-1}, 1397 cm^{-1}, 1340 cm^{-1} and 925 cm^{-1}.[15] On coordination the carbonyl group stretching frequency undergoes a low energy shift of the order of 60–80 cm^{-1}, whereas the ring absorptions are nearly unchanged except for the ones at 1669 cm^{-1} and 1599 cm^{-1} (Δν, 20–40 cm^{-1}). Accordingly the [UO$_2$(DMP)$_2$(NO$_3$)$_2$] spectrum (Fig. 5a) shows the ν(C=C) absorption at 1647 cm^{-1}, whereas the carbonyl absorption should contribute to the broad band at 1528 cm^{-1} along with the ν_1 vibration of the bidentate nitrato groups.[16,17]

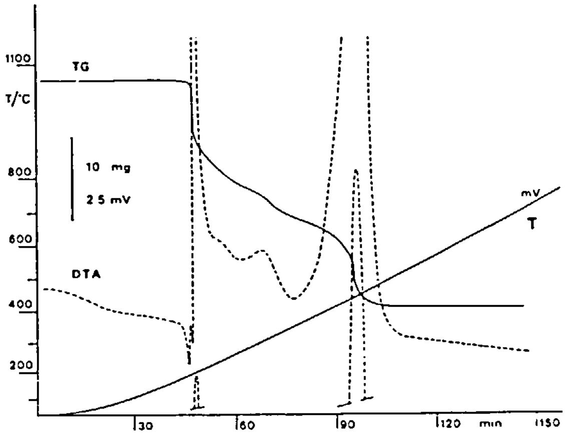

FIGURE 4 Thermograms of [$UO_2(DMP)_2(NO_3)_2$] (47.70 mg).

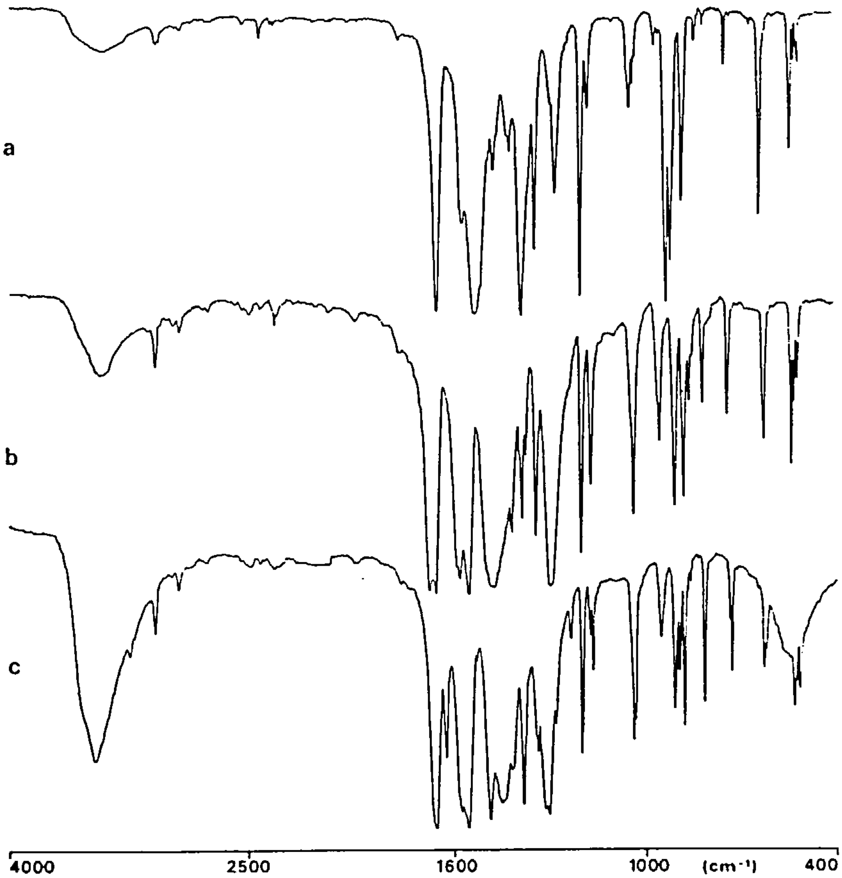

FIGURE 5 Infrared spectra of a, [$UO_2(DMP)_2(NO_3)_2$]; b, [$Pr(DMP)_3(NO_3)_3$]; c, [$La(DMP)_2(H_2O)_2(NO_3)_3$].$H_2O$.

Other significant bidentate nitrate absorptions (ν_4, 1278 cm^{-1}; ν_2, 1033 cm^{-1}) coincide with those observed in various 1:2 uranyl nitrate–carbamic ester adducts.[16] Of the three sharp bands at *ca* 900 cm^{-1}, the two at 915 cm^{-1} and 881 cm^{-1} are ligand absorptions whereas the uranyl group asymmetric stretching gives the absorption at 929 cm^{-1}. The infrared spectra of the lanthanide 1:3 adducts are all similar and coincide with that of [Pr(DMP)$_3$(NO$_3$)$_3$] (Fig. 5b). In this complex the coordinated ligand ν(C=O) is observed at 1550 cm^{-1}, along with two close ν(C=C) absorptions at 1671 cm^{-1} and 1653 cm^{-1}, which suggest a different situation of the coordinated DMP molecules. The nitrato group absorptions (ν_1, 1477 cm^{-1}; ν_4, 1299 cm^{-1}; ν_2, 1034 cm^{-1}; ν_6, 819 cm^{-1}; ν_3, 739 cm^{-1}) coincide in shape and intensity with those observed for various 1 : 3 lanthanide nitrate-sulfoxide adducts, which were found to contain bidentate nitrato groups.[18–21] Other nitrato species can be ruled out on the basis of the absence of either a broad absorption at *ca* 1350 cm^{-1} (ionic nitrate) or a sharp absorption at *ca* 1500 cm^{-1} (monodentate nitrate).[22] As an example, the adducts [Zn(DMP)$_2$(NO$_3$)$_2$] and [Cu(DMP)$_2$(NO$_3$)$_2$] contain monodentate nitrates,[23,24] and consequently give strong bands at 1505 cm^{-1} and 1484 cm^{-1}, respectively.[2] The complex [La(DMP)$_2$(H$_2$O)$_2$(NO$_3$)$_3$].H$_2$O shows, as does the cerium analogue, one absorption for the C=O (1557 cm^{-1}) and C=C (1659 cm^{-1}) vibrations, along with the water absorption at 1626 cm^{-1} (Fig. 5c). Moreover, in the 1400–1500 cm^{-1} range, two nitrato bands are observed (1491 cm^{-1} and 1454 cm^{-1}), which could suggest the presence of coordinated nitrate in both monodentate and bidentate modes. In the [UO$_2$(DMP)(O$_2$CMe)$_2$] spectrum ν(C=C) falls at 1657 cm^{-1} whereas the ligand C=O and acetato CO$_2$ vibrations cause a broad absorption at *ca* 1550 cm^{-1}. The uranyl group asymmetric stretching band is observed at 927 cm^{-1}

TABLE II
^{1}H-nmr data for the complexes[a] (CDCl$_3$; ppm; T = 25°C).

Compound	CH	CH$_3$	other
[La(DMP)$_3$(NO$_3$)$_3$]	6.30	2.27	
[La(DMP)$_2$(H$_2$O)$_2$(NO$_3$)$_3$].H$_2$O[b]	6.19	2.27	1.66[c]
[Ce(DMP)$_3$(NO$_3$)$_3$]	8.70	2.74	
[Pr(DMP)$_3$(NO$_3$)$_3$]	10.78	3.15	
[Nd(DMP)$_3$(NO$_3$)$_3$]	9.28	2.80	
[Sm(DMP)$_3$(NO$_3$)$_3$]	6.87	2.42	
[Eu(DMP)$_3$(NO$_3$)$_3$]	3.63	1.99	
[UO$_2$(DMP)$_2$(NO$_3$)$_2$]	6.83	2.45	
[UO$_2$(DMP)(O$_2$CMe)$_2$]	6.74	2.35	2.90[d]
DMP	6.01	2.21	

[a]The 1:3 complex solutions were 2 × 10^{-2} M; [b]saturated solution; [c]H$_2$O; [d]acetato protons.

The proton nmr spectrum of 2,6-dimethyl-4-pyrone (Table II) contains the singlets due to the methyl (2.21 ppm) and ring CH (6.01 ppm) protons.[25] In the uranyl complex spectra both signals are shifted downfield, the effect being larger for the ring CH resonance (Δppm, *ca* 0.8). The complex [Ln(DMP)$_3$(NO$_3$)$_3$] shows similar also if less marked behaviour, whereas in the cerium, praseodymium, neodymium and samarium analogues the metal paramagnetism causes a larger downfield shift, which is at a maximum for [Pr(DMP)$_3$(NO$_3$)$_3$] (Δ_{CH_3} = 0.94; Δ_{CH} = 4.77 ppm). Conversely, an opposite shift is observed for $[Eu(DMP)_3(NO_3)_3]$, the ring CH signal being 3.63 ppm upfield with respect to free ligand. The paramagnetic influence on the ligand signals follows the trend observed in the $[Ln(MDA)_3]$ (MDA = 2,6-diformyl-4-methylphenolato) series.[12] In fact the ring CH singlet was shifted upfield in $[Eu(MDA)_3]$ (Δppm with respect to HMDA, 6.3) and in the opposite direction for cerium, praseodymium, neodymium and samarium complexes. Also in this series the praseodymium complex showed the larger paramagnetic downfield effect with a Δppm value for the ring CH signal of 4.54. The resonance values reported in Table II refer to 2.10^{-2} M solutions. On diluting, the signals shift progressively towards the corrsponding free ligand values, suggesting partial ligand release to form 1:2 adducts. Excessive broadening causes the spectrum of the gadolinium complex to be uninterpretable. The trend in the ^{13}C nmr spectra (Table III) resembles that observed in the proton NMR spectrum series. In particular, the carbonyl carbon resonance, at 179.0 ppm in DMP, is found upfield in the europium complex (141.8 ppm) and downfield in the other paramagnetic complexes, the praseodymium complex signal being at 213.8 ppm. The downfield shift in $[La(DMP)_3(NO_3)_3]$ and $[UO_2(DMP)_2(NO_3)_2]$, of 12.1 ppm and 15.3 ppm respectively, gives a measure of the complexation effect on the ligand carbonyl group.

TABLE III

^{13}C-nmr data for the complexes[a] ($CDCl_3$; ppm; T = 25°C).

Compound	C=O	C-O-C	CH	CH_3
$[La(DMP)_3(NO_3)_3]$	182.1	169.0	113.7	19.9
$[Ce(DMP)_3(NO_3)_3]$	197.2	169.8	118.2	20.8
$[Pr(DMP)_3(NO_3)_3]$	213.8	170.4	122.9	21.5
$[Nd(DMP)_3(NO_3)_3]$	212.8	169.8	121.4	21.4
$[Sm(DMP)_3(NO_3)_3]$	183.8	169.4	114.2	20.1
$[Eu(DMP)_3(NO_3)_3]$	141.8	168.4	105.0	18.5
$[UO_2(DMP)_2(NO_3)_2]$	185.3	170.6	114.2	20.3
DMP	179.0	164.7	112.7	18.8

[a] The complex concentration was 5×10^{-2} M.

Because the complexes $[UO_2(DMP)(O_2CMe)_2]$ and $[La(DMP)_2(H_2O)_2(NO_3)_3].H_2O$ are scarcely soluble in deuterated chloroform, the nmr spectra were measured in deuterated dimethylsulfoxide. This solvent, which acts as oxygen donor towards these metals, removes either ligand or water from the metal coordination sphere. The ^1H nmr spectrum of $[UO_2(DMP)(O_2CMe)_2]$ contains the free ligand resonances (CH, 6.04 ppm; CH_3, 2.20 ppm) along with the acetato proton singlet (2.34 ppm). The integrated areas of ligand and water (3.40 ppm) proton signals confirm the stoichiometry of $[La(DMP)_2(H_2O)_2(NO_3)_3].H_2O$. The solid obtained by reaction of uranyl acetate and DMP in refluxing methanol is soluble in deuterated dimethylsulfoxide. The proton nmr spectrum contains six water protons for each ligand molecule, the acetato proton signal being absent. On the basis of the analytical, thermogravimetric and spectroscopic data the complex composition should be close to $UO_2(OH)_2.DMP.2H_2O$. The thermograms show an endothermic process (120°C) related to a weight loss of 12.4% due probably to sample dehydration (calculated value for evolution of three water molecules, 11.7%), followed by degradation in the 140–580°C temperature interval. The total weight loss is 38.7%, against a calculated value for final UO_3 of 38.4%. The infrared spectrum shows the ν(C=C) and ν(C=O) absorptions at 1699 cm^{-1} and 1523 cm^{-1} respectively and the water band at 1647 cm^{-1}. The presence of two bands assignable to uranyl group asymmetric stretching (914 cm^{-1} and 924 cm^{-1}) could suggest a polymeric arrangement.

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