Studies on the 1-methylpiperazine adducts of lanthanide tris-6,6,7,7,8,8,8-heptaflùoro-2,2-dimethyl-3,5-octanedionates

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Abstract

Adducts of the type $[Ln(fod)_3(L)_2]$, where Ln = La, Ce, Pr, Sm, Eu, Tb, Er, Yb and Y; Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione; and L = 1-methylpiperazine, have been prepared and characterised by elemental analyses, IR and NMR spectra. 1-Methylpiperazine is coordinated through its NH group.

Introduction

The lanthanide chelates of fluorinated 1,3-diketones undergo stronger interaction with nucleophiles than similar non-fluorinated chelates [1, 2] and are much superior shift reagents [3–5]. This effect is due to the strongly electronegative fluoroalkyl groups which increase the residual acidity on the metal. In view of our continued interest in the coordination chemistry of f-metal systems, the synthesis and characterisation of mixed ligand complexes of the formula $[Ln(fod)_3(L)_2]$, where Ln = La, Ce, Pr, Sm, Eu, Tb, Er, Yb and Y; Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione; and L = 1-methylpiperazine, are reported in this communication.

Results and discussion

The adducts, which were prepared by recrystallization of the chelates, are air-stable crystalline solids. They are soluble in most organic solvents and insoluble in water. They melt to clear liquids over the temperature range 65–130 °C (Table 1). Due to the volatile nature of the compounds, metal analyses had to be performed via EDTA titration. The chelates, which separate as hydrated species, were used as such. They were prepared by a method much simpler than one reported earlier [6].

The IR spectra of the chelates, 1-methylpiperazine and adducts have been compared in order to characterise the adducts. The absence of absorption peaks near 1700 cm^{-1} in the spectra of all the adducts indicates that the

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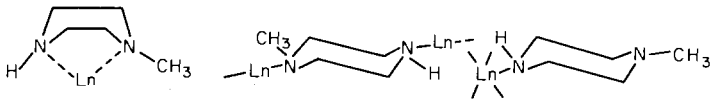
TABLE 1

Elemental analyses, colours, yields and melting points of compounds of the formula $[Ln(fod)_3(L)_2]$

Empirical formula of product	Colour	Yield (%)	M.p. (°C)	Analysis (%)							
				Ln		C		H		N	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_{40}H_{57}F_{21}N_4O_6La$	white	80	90	11.32	11.20	39.11	39.08	4.64	4.60	4.56	4.32
$C_{40}H_{57}F_{21}N_4O_6Ce$	yellow	70	65	11.40	10.90	39.08	39.21	4.64	4.53	4.56	4.35
$C_{40}H_{57}F_{21}N_4O_6Pr$	green	85	110	11.47	11.10	39.05	39.11	4.63	4.59	4.55	4.39
$C_{40}H_{57}F_{21}N_4O_6Sm$	white	87	102	12.13	12.20	38.76	38.93	4.60	4.57	4.52	4.47
$C_{40}H_{57}F_{21}N_4O_6Eu$	green	86	130	12.25	12.75	38.71	38.67	4.59	4.56	4.51	4.49
$C_{40}H_{57}F_{21}N_4O_6Tb$	white	85	127	12.74	12.72	38.49	39.11	4.57	4.43	4.49	4.54
$C_{40}H_{57}F_{21}N_4O_6Er$	pink	85	96	13.32	13.01	38.24	38.34	4.54	4.32	4.46	4.36
$C_{40}H_{57}F_{21}N_4O_6Yb$	white	87	93	13.71	13.50	38.06	38.71	4.52	4.45	4.44	4.61
$C_{40}H_{57}F_{21}N_4O_6Y$	white	89	123	7.55	7.89	40.78	39.98	4.84	4.31	4.75	4.91

diketone bonds in its enol form with all the six oxygen atoms of the fod ligand bonded directly to the lanthanide ion [7, 8]. The other important peaks are at 1620–1540 cm^{-1} (C=O stretching mode), 1540–1400 cm^{-1} (C=C stretching mode coupled slightly with the CH in-plane bending mode), 1579–1445 cm^{-1} (C–F stretching mode of the fluoroalkyl groups) and 1000–850 cm^{-1} (C–F deformation mode of the fluoroalkyl group) [9–11].

The ligand L which exists in a chair form in the free state can coordinate (a) in the boat form [12, 13] as a bidentate chelating ligand, (b) in the chair form as a bidentate ligand giving polymeric species [14] or (c) in the chair form acting as a monodentate ligand coordinating only through NH or NCH_3 nitrogen [15]. In the present compounds, the ligand L coordinates through the NH nitrogen only giving monomeric eight-coordinate species.



(a) (b) (c)

The NH stretch which appears at 3262 cm^{-1} in the free ligand [16] shifts to *c.* 3400 cm^{-1} in the adducts. The deformation mode of the *N*-alkyl group would be expected to give an absorption band of reasonably strong intensity and this has been found to be of great help in identifying whether this ligand coordinates only through NH or NCH_3, or through both [17]. The band due to this mode which appears at 1360 cm^{-1} in the IR spectra (KBr) of all the present adducts is identical in shape, position and intensity to that found for the free ligand. The non-coordination of NCH_3 nitrogen is thus indicated.

This argument seems amply justified in the light of steric and electronic considerations. Due to the presence of three bulky fluorodiketones, the space around the lanthanide metal ion is insufficient for coordination of the NCH_3 nitrogen. The highly electronegative fluorocarbon ligands produce a lanthanide metal ion which is more positive than the one in the case of non-fluorinated diketones. This justifies the stoichiometry $[Ln(fod)_3(L)_2]$ for the present compounds in contrast to that obtained with lanthanide acetylacetonates using the same ligand. Dimeric compounds having bridging 1-methylpiperazine were obtained in that case [18]. Coordination through NH nitrogen is also supported by the shifts in the positions of the NH bending and rocking modes which appear at *c.* 1600 and 520 cm^{-1}, respectively, in the spectra of the adducts. In the free ligand these bands appear at 1620 and 540 cm^{-1}, respectively [16]. The LnO and LnN stretches appear at *c.* 390 and 360 cm^{-1} [19].

The NH coordination of the ligand is also indicated from NMR spectral studies (Table 2). The NH proton undergoes a maximum shift while the resonance due to the NCH_3 group undergoes almost negligible shift [20]. The protons nearest to the nitrogen through which coordination occurs are shifted to a greater extent than those which are further away. The shifts are greater in the spectra of the paramagnetic adducts as compared to the

TABLE 2

NMR spectral data for compounds studied[a] (δ ppm)

	1-Methylpiperazine			t-Butyl
	NH	CH_2	CH_3	
free ligand	1.71	2.83	2.26	–
La	3.24	2.48	2.30	1.06
Ce	11.93	−5.02	−2.68	0.80
Pr	−5.80	−1.70	3.40	−0.54
Sm	8.04	2.02, 1.80		0.996
Eu	5.50	−1.00	3.30	1.52
Yb	7.40	broad signal		1.26

[a]Broad spectra were obtained in the cases of Tb, Er and Y.

diamagnetic, indicating considerable delocalisation of the unpaired electron density into the aromatic ligand. The shift is predominantly of a pseudo-contact origin, since the g tensor is anisotropic [21]. The t-butyl resonance undergoes a shift from its position in the free ligand (1.05 ppm) on adduct formation. The methine resonance, which appears at 6.15 ppm in Hfod, is shifted to such an extent on coordination that it goes off-scale [22]; it was nowhere to be found between −21 to +22 ppm.

One of the objects of this study was to examine the adducts as potential shift reagents. The adducts have been tested with cholesterol as the substrate. From the negligible shifts produced, it is clear that these adducts are unsuitable for general use as NMR shift reagents [23].

Experimental

The ^1H NMR spectra in $CDCl_3$ and in a mixture of $CDCl_3$ and CCl_4 were obtained on Hitachi R-1500 and Bruker 500 FT NMR machines with TMS as an internal standard. Elemental analyses were carried out using a Carlo Erba Strumentazione (Italy) Elemental Analyser, model 1106. The IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. Metals were estimated by standard EDTA titration using xylenol orange as indicator [24].

Materials

Hfod and 1-methylpiperazine were obtained from Aldrich Chemical Co., USA.

Synthesis

For preparing the chelates, Hfod (3.17–3.85 g, 10.7×10^{-3}–13.0×10^{-3} mol) dissolved in NH_3 solution (3.33 cm^3, 2.0 M) was added to a solution of the hydrated nitrate (1 g, 2.14×10^{-3}–2.60×10^{-3} mol) in nitric acid (2.40 cm^3, 2.8 M). The pH of the mixture was increased by dropwise addition

of NH_3 solution. Although the product precipitates out under these conditions, it redissolves immediately. Addition of NH_3 was continued until a pH value of *c.* 6 was attained. At this point, the chelates separated out completely and did not redissolve. They were filtered through a Buchner funnel, washed three to four times with 5 cm^3 portions of distilled water and dried in air to give free-flowing products. The adducts were prepared by recrystallising the chelates (0.5 g) in 4–5 cm^3 of the base in a watch glass. The solids which separated over 20–25 h were subjected to vacuum treatment with hot water until no smell of piperazine was noticeable from the products. Melting points were reported uncorrected.

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