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SHORT COMMUNICATION

Studies in Fluorinated 1,3-Diketones and related compounds Part IX[a]. Synthesis of some New Tris (1,3-Diketonato) Lanthanide Complexes

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It is well recognised that paramagnetic lanthanide complexes act as n.m.r. shift reagents [1,2]. The chelates of fluorinated 1,3-diketones undergo stronger interaction with nucleophiles than similar non-fluorinated chelates [3-5], thereby, producing larger shifts [6]. This has been ascribed to the increased acidity of the fluorinated chelates owing to a decrease in the basicity of fluorinated 1,3-diketones and their higher solubility in non-polar solvents. The ability to produce chemical shifts of such fluorinated chelates, therefore, continues to be of use for spectral clarification and for location of functionality.

In this communication, the synthesis and characterization of nineteen fluorinated lanthanide tris-1,3-diketonates is reported. In the i.r. spectra, the absence of absorption peaks near 1700 cm^{-1}, in the spectra of all the lanthanide tris chelates, can be taken as an evidence for all six oxygen atoms of β-diketones being bonded directly to the lanthanide ion. The chemical analyses also support their hexa co-ordination. Other important peaks are at 1620 - 1540 cm^{-1} ($\mathrm{C} \overset{---}{\text{———}} \mathrm{O}$ stretching mode), 1540 - 1400 cm^{-1} ($\mathrm{C} \overset{---}{\text{———}} \mathrm{C}$ stretching mode coupled slightly with the C-H in-plane bending mode), 1579 - 1445 cm^{-1} (C-F stretching mode of perfluoroalkyl groups) 1000 - 850 cm^{-1} (C-F deformation mode of perfluoroalkyl groups). The shift of C=O absorption to higher frequency indicates that chelation is stabilized due to the benzenoid resonance effect in which the lanthanide (III) back donates its f electrons to the ligand [7,8] .

In the ^{1}H n.m.r. spectra, the disappearance of enolic proton ($=\overset{|}{C}-OH$) resonance provides further strong evidence for co-ordination of the β-diketonato anion to the lanthanide ion. In all ^{1}H n.m.r. spectra, a sharp signal is observed at δ (6.2 - 6.4) ppm which is due to methine proton (=CH-) of the γ-position of the chelated ring. Aromatic protons show sharp signals between δ (6.4-7.9) ppm.

Experimental Section

I.r. spectra were recorded on a Perkin-Elmer-337 spectrometer in nujol mull; ^{1}H n.m.r. spectra by a Perkin-Elmer RB-12 spectrometer in COCl$_3$ or CO$_3$COCO$_3$ solutions with TMS as an internal standard. Melting points are uncorrected.

Materials

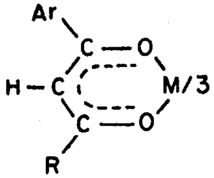
4-Fluorobenzene, 4-methoxy-3-fluorobenzene [9], 4-fluoroacetophenone and 4-methoxy-3-fluoroacetophenone [10] were prepared.

The general method of the preparation of fluorinated 1,3-diketones, used as ligands for preparing these complexes, has been reported earlier by Joshi et al. [11]

Preparation of lanthanide tris 1,3-diketonates

The β-diketonato enolate anion was prepared by dissolving the corresponding β-diketone in methanol and adding, dropwise a calculated amount of 2% methanolic sodium hydroxide solution. The appropriate lanthanide chloride (0.004 mole), dissolved in a minimal amount of methanol, was added dropwise to a methanolic solution of the β-diketonato enolate anion (0.012 mole) The complex was precipitated by slow addition of a ten fold excess of water to the resulting methanolic solution. The precipitated lanthanide tris chelates were crystallized from dichloromethane or benzene. Finally, the chelates were dried in vacuum, over phosphorus pentaoxide, for 24 hrs.

The complexes prepared are recorded in table-1 together with their analytical data.



Where Ar = Fluoroaryl group

R = CH_3, CF_3, C_2H_5, C_2F_5, $\underline{n}$-C_3F_7

M = La^{3+} Pr^{3+} Sm^{3+} Eu^{3+} Ho^{3+}

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a Part VIII. K.C. Joshi, V.N. Pathak and S. Bhargava, J. Fluorine Chem., 9 (1977) 387.

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TABLE 1

Analytical and characteristic data of lanthanide tris 1,3-diketonates (Fig. 1)

Sl. No.	M	Substituent in Ar	R'	M.P. °C	Yield %	Molecular Formula	C%		H%		F%	
							Cal.	Found	Cal.	Found	Cal.	Found
1	Eu	4-F	CH_3	128	86	$C_{30}H_{24}F_3O_6Eu$	52.25	51.98	3.48	3.40	-	-
2	Eu	4-F	CF_3	140	86	$C_{30}H_{15}F_{12}O_6Eu$	-	-	-	-	26.79	26.68
3	Eu	4-F	C_2H_5	147	85	$C_{33}H_{30}F_3O_6Eu$	54.17	54.00	4.10	4.00	-	-
4	Eu	4-F	C_2F_5	160	88	$C_{33}H_{15}F_{18}O_6Eu$	39.56	39.48	1.49	1.40	34.16	34.00
5	Eu	4-F	$\underline{n}$-C_3F_7	240	85	$C_{36}H_{15}F_{24}O_6Eu$	37.53	37.48	1.30	1.26	39.61	39.58
6	Eu	3-F,4-OMe	CH_3	160	83	$C_{33}H_{30}F_3O_9Eu$	50.83	50.00	3.85	3.75	-	-
7	Eu	3-F,4-OMe	CF_3	204	79	$C_{33}H_{21}F_{12}O_9Eu$	-	-	-	-	24.23	24.00
8	Pr	4-F	CF_3	180	84	$C_{30}H_{15}F_{12}O_6Pr$	-	-	-	-	27.14	27.10
9	Pr	4-F	C_2F_5	275	86	$C_{33}H_{15}F_{18}O_6Pr$	-	-	-	-	34.54	34.00
10	Pr	4-F	$\underline{n}$-C_3F_7	168	80	$C_{36}H_{15}F_{24}O_6Pr$	-	-	-	-	41.30	41.30
11	Sm	4-F	CF_3	168	78	$C_{30}H_{15}F_{12}O_6Sm$	42.40	42.00	1.76	1.74	-	-

12	Sm	4-F	C_2F_5	296	75	$C_{33}H_{15}F_{18}O_6Sm$	39.63	39.59	1.50	1.48	34.23	34.00
13	Sm	4-F	C_3F_7	278	79	$C_{36}H_{15}F_{24}O_6Sm$	-	-	-	-	39.68	39.59
14	Sm	3-F,4-OMe	CF_3	178	82	$C_{33}H_{21}F_{12}O_9Sm$	42.17	42.00	1.76	1.74	-	-
15	Ho	4-F	CF_3	170	85	$C_{30}H_{15}F_{12}O_6Ho$	-	-	-	-	26.39	26.20
16	Ho	4-F	C_2F_5	194	86	$C_{33}H_{15}F_{18}O_6Ho$	-	-	-	-	33.73	33.69
17	La	4-F	CF_3	121	83	$C_{30}H_{15}F_{12}O_6La$	-	-	-	-	27.20	27.00
18	La	4-F	C_2F_5	151	86	$C_{33}H_{15}F_{18}O_6La$	-	-	-	-	34.61	34.50
19	La	3-F,4-OMe	CF_3	138	87	$C_{33}H_{21}F_{12}O_9La$	-	-	-	-	24.57	24.49