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STUDIES IN FLUORINATED β-DIKETONES AND RELATED COMPOUNDS PART VIII[a] PREPARATION OF SOME NEW PIPERIDINIUM TETRAKIS RARE EARTH 1,3-DIKETONATES AND THEIR FLUORESCENCE AND INFRARED SPECTRAL STUDIES

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SUMMARY

Some new piperidinium tetrakis rare earth complexes of fluorinated 1,3-diketones, have been prepared and characterised. Most of these complexes have been examined for their fluorescence properties at room temperature. I.R. spectral studies have also been made with special consideration to the four ligand structures. The effect of substituent groups on C$\overset{\cdots}{=}$O and C$\overset{\cdots}{=}$C stretching frequencies has also been discussed.

INTRODUCTION

The chemistry of rare earth complexes of 1,3-diketones has assumed considerable importance due to their practical use as potential laser materials [1-3]. Lempicki et al. [4] and Schimitschek [5] have reported the first laser action from europium benzoylacetonate, at 6130 Å. Nugent et al. [6] have shown that laser emission arises only from the tetrakis europium-1,3-diketonates and tris europium-1,3-diketonates do not lase at all. This has been supported by a number of other workers as well [7-11].

Riedel and Charles [12] have prepared a series of tetrakis europium-1,3-diketonates and discussed the effect of various substituents(R') on laser emission which is significant when R' is a trifluoromethyl group (CF_3). Joshi et al. [13] have recently reported thirty-three new tetrakis rare earth complexes of the type (Fig. 1), and have also discussed the fluorescence spectra of some of these compounds.

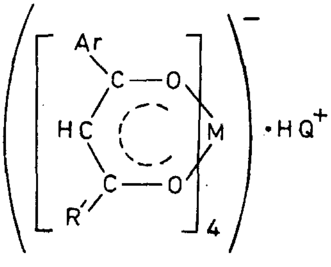
We now report the synthesis of some new piperidinium tetrakis rare earth-1,3-diketonates, most of which contain a $-CF_3$ or $-C_2F_5$ side chain. I.R. spectral data have been recorded in table II and discussed with special consideration to the four ligand structure of these complexes. Most of these compounds have been examined for their fluorescence spectra.

EXPERIMENTAL

Preparation of ligands

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. [30] .

Preparation of piperidinium salts of tetrakis rare earth 1,3-diketonates



(Fig. 1)

Where Ar = fluoroaryl group

R' = aryl, alkyl or perfluoroalkyl group

M = Eu^{3+}, Sm^{3+}, Tb^{3+} or Gd^{3+}

Q = piperidine

The tetrakis chelates of 1,3-diketones have been prepared by the method of Melby et al.[27] and Charles et al. [11]. To a hot solution of appropriate fluorinated 1,3-diketone(0.018 mole) in 95% ethanol (60 ml) and 1.53 g of piperidine, was added an appropriate rare earth chloride (0.004 mole) solution in water (20 ml). The mixture was heated for 1-2 hours, cooled and kept overnight. The solid which appeared was filtered off, washed with 70% ethanol, water and air dired at room temperature. These chelates were recrystallized from benzene-hexane. All the tetrakis rare earth chelates of 1,3-diketones are recorded in table-1 with their analytical data.

Elemental Analysis

Microanalyses for C, H and F were performed by Australian Micro Analytical Service, CSIRO, Melbourne, Australia.

Recording of infrared absorption spectra

The I.R. spectra of tetrakis rare earth chelates of 1,3-diketones were recorded using a Perkin-Elmer infrared spectrophotometer (Model No.337).

Recording of absorption spectra

These were taken on a Cary Model 14 recording spectrophotometer at room temperature.

Recording of luminescence spectra

These were taken at room temperature in methanol solution using a Perkin-Elmer MPF-2A fluorescence spectrophotometer equipped with a R-106 photomultiplier tube (S-19 cathode response).

TABLE 1

Analytical and characteristic data of piperidinium tetrakis rare earth-1,3-diketonates (Fig.1)

Sl. No.	M	Substituent in Ar	R'	M.P. °C.	Molecular Formula	C% Cal.	C% Found	H% Cal.	H% Found	F% Cal.	F% Found
1	Tb	2,5-DiF	CF_3	115	$C_{45}H_{28}F_{20}O_8NTb$	-	-	-	-	30.61	30.91
2	Tb	4-F,3-Cl	CF_3	142	$C_{45}H_{28}F_{16}Cl_4O_8NTb$	34.26	34.18	2.14	2.78	-	-
3	Gd	3-F,4-OMe	CF_3	107	$C_{49}H_{40}F_{16}O_{12}NGd$	45.37	45.13	3.10	3.52	-	-
4	Eu	2,5-DiF	Me	208	$C_{45}H_{40}F_8O_8NEu$	36.49	35.90	3.26	3.16	-	-
5	Eu	2,5-DiF	CF_3	121	$C_{45}H_{28}F_{20}O_8NEu$	-	-	-	-	38.40	38.21
6	Eu	4-F	C_2F_5	dec. 250	$C_{49}H_{32}F_{24}O_8NEu$	-	-	-	-	29.30	29.11
7	Eu	2,5-DiF	C_2F_5	113	$C_{49}H_{28}F_{28}O_8NEu$	-	-	-	-	36.86	36.62
8	Eu	3-F,4-OMe	C_2F_5	dec. 241	$C_{53}H_{40}F_{24}O_{12}NEu$	-	-	-	-	27.13	26.91
9	Eu	3-F,4-OMe	C_6H_5	130	$C_{69}H_{60}F_4O_{12}NEu$	62.46	61.98	4.50	4.25	-	-
10	Sm	2,5-DiF	CF_3	330	$C_{45}H_{28}F_{20}O_8NEu$	-	-	-	-	30.52	30.25

TABLE II

Infrared spectral data of piperidinium tetrakis rare earth 1,3-diketonates (Fig.1)

(only important absorption bands between 1800-600 cm^{-1} are listed in this table;values in cm^{-1})

A= C⩦O stret.; B= C⩦C stret.+C-H in-plane bend.; C= CH_3 symmetrical deform.+C-H bend.; D= C⩦O stret. +C-H bend.+CH_3 symmetrical bend.; E= C-H in-plane bend; F= C-C_6H_5 stret. +C-R' stret.; G= CF_3 stret.+ CF_3 bend.; H= C-F stret.; I = $(CH_2)_n$ rock. mode (n > 4); J= C-H out-of-plane deform. + M-O stretching.

S.N.*	A	B	C	D	E	F	G	H	I	J
2	1600vs	1502vs	1467vs 1410sh	1380vs	1200w	930m	1115s 790m	1065vs 1040s**	725s	-
3	1620vs 1590vs+	1535vs 1490vs	1470vs 1420vs	1380vs 1320vs	1205vs	970s 905s	1300vs 802s	1074vs 1030w**	711vs	635vs
4	1600s 1580s+	1508s 1490vs	1452vs 1420sh	1375vs	1234s	945m	-	1070m 1005m**	745s 720m	655w -
5	1595vs 1620vs	1495vs 1525vs	1460vs 1420sh	1370vs	1250sh 1230sh	960m 900w	1295vs,1140s 790m	1110s 1025s**	719m	655w
6	1625vs 1600vs	1540vs 1503vs	1490s 1460vs	1335s	1210vs	940s	1309s 795s	1080s 1018vs**	718w	640vw
7	1602vs 1575s+	1500s	1452vs 1410s	1370s 1320s	1200s	950w	1281vs 1130s 790s	1070m 1008s**	730s	640sh
8	1602vs 1575s+	1500vs	1452vs 1405sh	1375vs 1320s	1200s	950w	1280vs 789vs	1070s 1015s**	730m	-
9	1595vs	1495vs	1460vs 1420sh	1370vs	1250sh 1230sh	960m 900w	-	1060m 1025s**	719m	655w
10	1620sh	1525w	1452vs 1410sh	1375vs	1205vs	-	1310s 1140s 790m	1020w**	725s	-

*These serial numbers correspond to the serial number of table 1.; + May be due to phenyl ring stretching mode. **. These are mixed with the phenylC-H in-plane bending vibrations.

Abbreviations: s=strong; vs= very strong; w= weak; sh= shoulder; m= medium; vw = very weak.

RESULTS AND DISCUSSION

I.R. Spectra

In our interpretation of I.R. spectra (Table II), we have made assignments which agree with the observations of Pinchas et al.[14], Behnke and Nakamoto[15], and Liang et al. [16]. The C$\equiv$O stretching frequencies of those tetrakis rare earth complexes, which have both Ar and R' as phenyl groups (Compound No.9), shift towards lower region due to mesomeric interaction [17,18]. Whereas in those complexes in which R' is a perfluoroalkyl group (Compound Nos. 1-8 and 10), these frequencies shift towards the higher region due to strong negative inductive effect[16].

The most important feature of the spectra of tetrakis chelates is the appearance of a single band around 720 cm^{-1} which is attributed to the piperidinium portion of the molecule and is due to the rocking mode of the $-(CH_2)_n-$ group, $n > 4$ [19]. The disappearance of the absorption band near 1700 cm^{-1}, in these complexes, can be taken as an evidence of all eight oxygen atoms of 1,3-diketones being bonded directly to the rare earth ion[20] with dodecahedral special arrangement[21]. Another characteristic band of tetrakis rare earth chelates has been observed between 1420-1400 cm^{-1}, which is absent in tris chelates [22].

Fluorescence Spectra

It has previously been reported that all piperidinium tetrakis rare earth chelates of 1,3-diketones exhibit molecular band emission at low temperatures, consisting of both fluorescence and phosphorescence characteristic of the chelating agent [13]. We have interpretated our present room temperature results after considering the observations of Ricke and Allison [23], Nugent et al.[6]and Riedel and Charles [12].

The piperidinium tetrakis europium-1,3-diketonates (Compound Nos. 5 & 7) show very strong red fluorescence at room temperature on exposure to U.V. radiation, and the spectra observed are typical of europium chelates [10]. In all other compounds the emissions are considerably weaker. (This same result is observed for the powders.) In europium complexes (Compound Nos. 4, 5, 7 and 9), the $^5D_0 \longrightarrow {}^7F_0$ transitions are observed near 5800 Å. Analysis of $^5D_0 \longrightarrow {}^7F_0$ emissions has been shown to be of value in determining the number of different europium containing species (α and /or β) contributing to the observed fluorescence[11,13,24,25] . The transitions $^5D_0 \longrightarrow {}^7F_1$ occur in the region 5910-5900 Å. All the europium chelates exhibit $^5D_0 \longrightarrow {}^7F_2$ transitions at approximately 6140 Å. From the emission spectra, this transition is the strongest (approximately 90%) amongst all transitions. The $^5D_1 \longrightarrow {}^7F_1$ transition has been observed in the 5400-5350 Å region. In the cases of compounds 5 and 7 the overlapping of $^5D_1 \longrightarrow {}^7F_1$ (5360-5350 Å) with $^5D_1 \longrightarrow {}^7F_3$, $^5D_1 \longrightarrow {}^7F_4$ and $^5D_2 \longrightarrow {}^7F_4$ around 5340 Å is also possible.

In the terbium chelate, (Compound No.1), the observed fluorescence at 6150, 5910 Å, and in the gadolinium chelate (Compound No.3) emissions at 6150, 5910, 5800 and 5370 Å, appear to be due to impurities of Eu^{3+} ion present in the original rare earth oxide at less than 0.1%. Similar results have been observed by Brown and Shepherd earlier [26]. The terbium complex (Compound No.1) showed fluorescence at 5800 Å (overlapped with the transition of Eu^{3+}) and 5440 Å due to Tb^{3+} ion involving $^5D_4 \longrightarrow {}^7F_4$ and $^5D_4 \longrightarrow {}^7F_5$.

TABLE III

Luminescence results of some piperidinium tetrakis rare earth-1,3-diketonates (Fig.1)
(Values in Å unit)

Transitions	Compounds Nos.*						
	1	3	4	5	7	9	10
$^5D_0$ —— $^7F_0$	5800	5800	5790	5800	5800	5800	6400
$^5D_0$ —— $^7F_1$	5910	5910	5900	5910	5910	5910	5980
$^5D_0$ —— $^7F_2$	6150	6150	6140	6150	6140	6140	5640
$^5D_1$ —— $^7F_1$	5440	5370	5370	5390	5400	5360	-

* Compound Nos. are according to S. No. of Table-1.

transitions respectively. In the **samarium** complex, (**Compound** No. 10) the fluorescence at 5640 Å is due to $^4F_{3/2} \longrightarrow {}^6H_{7/2}$ (Calc. at 5622.4 Å, wave length; 17786 cm^{-1}, wave number); at 5980 Å, is ascribed to $^4G_{3/2} \longrightarrow {}^6H_{9/2}$ (Calc. at 5995 Å, wave length; 16680 cm^{-1}, wave number) and the observed line at 6460 Å may possibly be due to $^4G_{5/2} \longrightarrow {}^6H_{9/2}$ (Calc. at 6422.6 Å, wave length; 15570 cm^{-1}, wave number). The line emission in the **samarium** chelate is very faint but distinct from europium line emission.

Our observations confirm that fluorine substitution increases fluorescence intensity owing to decreased vibrational energy [13]. The enhanced intensity in compounds No.5 and 7 may be partly explained as due to the strong **negative** inductive effect of the perfluoroalkyl group and increasing covalent nature of the europium - oxygen bond. The latter is known to increase the efficiency of the intramolecular transfer from the triplet state to the Eu^{3+} ion[27-29].

The U.V. absorption spectra (Compound Nos. 1,3-5,7,9 and 10) reveal two maxima. The first maximum in the region of 3250-3570 Å (log ϵ 3.94-4.98) is a bathochromic shift of the β-diketone anion absorption due to coordinated chelate ion formation. This clearly indicates that all four β-diketone molecules are used in chelate formation with the metal ion. The second maximum in the region of 2440-2600 Å (log ϵ 3.67-4.48) may be due to free 1,3-diketone anion whose formation in solution is ascribed to ionisation of the original tetrakis chelates as follows [9] :

$$(L)_4MHP \rightleftharpoons L_3M + L^-HP^+$$

Where L = ligand M = rare earth metal.HP^+ = piperidinium ion.

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