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Monothio-β-diketonates of Lanthanides. 2. 3-Mercapto-1,3-diphenylprop-2-en-1-one Chelates of Lanthanides

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Lanthanide complexes derived from sulfur donors are expected to be weak because of the large ionic radii of the metal ions and the lower electronegativity of the donors. Dutt et al.[1] first indicated the formation of lanthanide chelates of monothiobenzoylacetone in solution. Subsequently, Brown et al.[2] and Siddall et al.[3] isolated both tris- and tetrakis(dialkyldithiocarbamates) of lanthanides through careful choice of the reaction conditions. Characterization of the tetrakis chelates of dialkyl dithiophosphinates has been made quite recently by Pinkerton.[4] We have investigated the solvent extraction behavior[5] of Nd(III) with monothiothenoyltrifluoroacetone (HSTTA) and the synergistic extraction[6] with some neutral donors. These studies have established that the species extracted in the organic phase have the composition $Nd(STTA)_3$ and $Nd(STTA)_3A_n$ ($n = 1$, dipyridyl; $n = 2$, tri-*n*-octylphosphine oxide, tri *n*-butyl phosphate). Also it has been shown that although $Nd(STTA)_3$ is much less stable than $Nd(TTA)_3$, the mixed formation constants ($\beta_{3,n}$) of $Nd(STTA)_3A_n$ are greater than the corresponding TTA complexes (HTTA = thenoyltrifluoroacetone). Here we wish to report the facile preparation of a series of tetrakis, tris, and mixed tetrakis complexes of 3-mercapto-1,3-diphenylprop-2-en-1-one (monothiodibenzoylmethane, HSDBM) of lanthanides.

Experimental Section

Materials. Hydrated lanthanide perchlorate crystals were prepared from the lanthanide oxides (99.9% pure, supplied by Johnson Matthey). HSDBM was prepared by a modification[7] of the procedure adopted by Chaston et al.[8]

Preparation of Lanthanide Chelates. (i) $Ln(SDBM)_3{\cdot}H_2O$. To a stirred ethanolic solution (30 ml) containing 1 mmol of the hydrated lanthanide perchlorate and 3 mmol of HSDBM, 3 ml of 1 M sodium hydroxide solution was added during a period of 30 min. The solution was filtered, and on removal of the solvent under reduced pressure a glassy mass was obtained. This was thoroughly stirred with petroleum ether (bp 40–60 °C), and the solvent was decanted off. On repetition of this operation for several times a solid mass free of HSDBM (since the ligand is highly soluble in petroleum ether) was obtained. The product was extracted with minimum volumes of chloroform (any unreacted lanthanide perchlorate and sodium perchlorate formed was thus removed) and filtered, and the filtrate was concentrated under reduced pressure. On cooling, a crystalline product in ~60% yield was obtained.

(ii) $Q[Ln(SDBM)_4]$ (Q = Quaternary Ammonium Ions of Piperidine, Morpholine, and Pyrrolidine). To a stirred ethanolic solution containing 1 mmol of the hydrated lanthanide perchlorate and 4.2 mmol of HSDBM, an ethanolic solution of heterocyclic base (4.2 mmol) was added slowly. The mixture was stirred for 30 min, was cooled in an ice chest for 3 h, and was then filtered through a glass frit. The compound was washed successively with water, with a small volume of ethanol, and freely with petroleum ether. The product (0.5 g) was dissolved in 20 ml of a 1:1 acetone–methanol mixture, the mixture was filtered, and the filtrate was concentrated to ca. 8 ml. On cooling (below 0 °C), shining needle-shaped crystals deposited. Alternatively, 0.5 g of the compound was dissolved in benzene, the mixture was filtered and cooled to 10 °C, and the compound was precipitated by slow addition of petroleum ether (bp 40–60 °C); yield ~65%.

(iii) $Ln(SDBM)_3A_n$ (A = 2,2′-Dipyridyl, *o*-Phenanthroline, $n = 1$; Pyridine *N*-Oxide, $n = 2$). An ethanolic solution of the hydrated lanthanide perchlorate (1 mmol) was slowly added into a stirred ethanolic solution containing 3 mmol of HSDBM, 1 mmol of dipyridyl (*o*-phenanthroline) or 2 mmol of pyridine *N*-oxide, and 3 ml of 1 M sodium hydroxide solution. The mixture was stirred additionally for 30 min, cooled, and then filtered. The product was washed with petroleum ether, water, and cold ethanol. The crude compound was recrystallized from a benzene–petroleum ether mixture; yield ~70%.

Analysis. C and H analyses were carried out in the Microanalytical Laboratory of this institute and CDRI, Lucknow, India. Sulfur was gravimetrically estimated as $BaSO_4$. Lanthanides were volumetrically determined by EDTA titration using xylenol orange as the indicator.

Physical Measurements. Conductivity measurements of the compounds (ca. 1×10^{-3} M solutions in acetone) were carried out with a Philips PR 9500 conductivity bridge. Molecular weights of the compounds in chloroform and benzene were determined in a Mechrolab vapor-phase osmometer. Ir spectra (in Nujol mull) were recorded in the range 4000–250 cm^{-1} in a Perkin-Elmer 421 infrared spectrophotometer. Visible spectra of the Nd(III) compounds were recorded in a Spectro MOM 201 spectrophotometer in the concentration range 8×10^{-3}–1×10^{-2} M in acetone, chloroform, and benzene against the appropriate concentration of the ligand solution as blank. The oscillator strength (P) was determined using the relation

$$P = 4.31 \times 10^{-9} \left[\frac{9n}{(n+2)^2}\right] \epsilon_i(\nu)\, d\nu$$

where n is the refractive index of the medium, ϵ is the molar extinction coefficient, and ν is the energy of transition in wavenumber. The area of a band was measured by a planimeter. X-ray powder patterns were obtained with a Philips PW 1008 x-ray diffraction unit, using a 114.6-mm Debye camera and Cu Kα radiation filtered through nickel.

Results and Discussion

Table I summarizes the analytical and characterization data of a few representative types of lanthanide chelates. Satisfactory analytical data were obtained for other lanthanide complexes. The compounds in general are fairly soluble in acetone, chloroform, and benzene and moderately soluble in methanol and ethanol. The pyrrolidinium compounds have appreciable solubility only in chloroform. The compounds are nonhygroscopic, are stable in air, and remain unchanged in composition for an indefinite period. Molecular weight determinations carried out in chloroform and benzene indicate that $Q[Ln(SDBM)_4]$ type compounds remain undissociated in these solvents (Table I), whereas their molar conductances in acetone are consistent with 1:1 electrolytes. Similar observations have been reported[9] for a large number of lanthanide tetrakis(pivaloyltrifluoroacetonates) having different counterations. Powder diffraction data of $(pipH)[Nd(SDBM)_4]$ and $(pipH)[Nd(DBM)_4]$ reveal they are not isomorphous. The tetrakis chelates of Eu(III) in chloroform fluoresce on exposure to a mercury lamp.

Infrared spectra of SDBM chelates have the overall features expected from the work of Livingstone and co-workers[10] and Uhlemann et al.[11] However, some of their band assignments appear doubtful in the light of normal-coordinate analysis

Table I. Analytical and Characterization Data for 3-Mercapto-1,3-diphenylprop-2-en-1-one Complexes of Lanthanides

Compd	Color	Mp,[a] °C	% M		% C		% H		% S		Mol wt[b]		Molar conductance,[b] Ω^{-1} cm^2 mol^{-1}
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Nd(SDBM)_3 \cdot H_2O$	Brown	78–80	16.40	16.23	61.42	61.11	3.98	4.12	10.91	10.61	879	894	
$[Nd(SDBM)_4]$-(morpH)	Yellow	120–125	12.14	12.01	64.66	64.38	4.54	4.74	10.77	10.52	1188	1141	126
$[Nd(SDBM)_4]$-(pyrrolH)	Orange-yellow	134–136	12.30	12.41	65.51	65.78	4.60	4.49			1172	1167	112
$[Eu(SDBM)_4]$-(pipH)	Orange-yellow	128–130	12.72	12.47	65.32	65.85	4.70	4.75			1194	1158	124
$Nd(SDBM)_3$-(phen)	Deep yellow	135–138	13.86	13.98	65.69	65.25	3.93	4.18			1041	1062	
$Nd(SDBM)_3$(bpy)	Yellow	120–123	14.83	14.52	64.60	64.62	4.00	4.05	9.36	9.06	1017	1023	
$Nd(SDBM)_3$-(*N*-pyO)$_2$	Yellow	141-146	13.72	13.81	62.78	62.91	4.09	3.93	9.13	8.98	1051	1067	

[a] Melting points uncorrected. [b] Extensive molecular weight determinations of $Q[Ln(SDBM)_4]$ chelates in chloroform and benzene and conductivity measurements in acetone gave similar results.

Table II. Characteristic Infrared Bands (cm^{-1}) in SDBM Chelates of Europium

$Q[Eu(SDBM)_4]$			$Eu(SDBM)_3A_n$			$Eu(SDBM)_3 \cdot H_2O$	Band assignments
morpH	pipH	pyrrolH	bpy	phen	*N*-pyO		
						3500	ν(O-H)
3350	3360	3360					$\nu(\equiv N^+-H)$
					1620		Ring def in *N*-pyO
1592	1592	1590	1590	1592	1592	1592	Phenyl ring vib
1582	1582	1580	1582	1582	1580	1580	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ + other vib
1550	1520	1535	1525	1520	1530	1540	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1490	1492	1492	1495	1490	1495	1490	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ + phenyl ring vib
1255	1258	1255	1260	1258	1260	1260	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ + other skel modes of vib
					1225		ν(N–O) in *N*-pyO
720	720	720	720	720	722	722	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
					455		ν(Eu–O) from *N*-pyO
425	432	430	425	425	430		ν(Eu–O)
312	315	310	315		300	315	ν(Eu–S)

carried out for monothioacetylacetonates by Siimann et al.[12] and Martin et al.[13] Table II shows a few characteristic bands along with their assignments. The variation of metal ions affects slightly the metal–oxygen and the metal–sulfur stretching frequencies.

Table III. Oscillator Strength for the Hypersensitive Transition in Neodymium Complexes in Different Solvents

Compd	10^6P		
	Acetone	Chloroform	Benzene
$[Nd(SDBM)_4](pipH)$	140.5	49.7	48.9
$[Nd(SDBM)_4](morpH)$	133.2	45.4	43.6
$[Nd(SDBM)_4](pyrrolH)$		52.3	
$Nd(SDBM)_3(phen)$	85.9	59.9	
$Nd(SDBM)_3(bpy)$	57.4		29.3
$Nd(SDBM)_3 \cdot H_2O$	98.6	21.6	18.7
$[Nd(DBM)_4](pipH)$	95.4	51.0	

Electronic spectra of the Nd(III) chelates have been examined in three different solvents, viz., acetone, chloroform, and benzene, with respect to the band intensities and band shifts compared to those of the aquometal ion. A comparison of the oscillator strengths for several transitions in different Nd(III) compounds in these solvents revealed that, except for the hypersensitive transition, the oscillator strengths for the other transitions in these compounds remain practically the same as in the aquoneodymium(III) ion. This is in accordance with the Judd–Oflet theory.[14] Table III compares the oscillator strengths for the hypersensitive transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}$) in these compounds in the solvents mentioned. In may be noted that the gradation of hypersensitivity in acetone is $Q[Nd(SDBM)_4] > Nd(SDBM)_3 \cdot H_2O \sim Q[Nd(DBM)_4] > Nd(SDBM)_3(phen) > Nd(SDBM)_3(bpy)$. The same order however is not maintained in chloroform and benzene. It is possible to explain the above sequence by invoking the difference in covalent interactions in the Nd–S, Nd–O, and Nd–N bonds. Sulfur being a softer donor than oxygen and nitrogen would lead us to expect a greater deal of covalency in its bonding. The replacement of oxygen by sulfur and the variance in the number of ligands attached to the central metal (from 4 to 3) would result in some changes in the extent of overlap and, therefore, in the degree of covalency of these bonds.[15] This explanation is in keeping with the mechanisms proposed by Choppin et al.[16] and Peacock et al.[17] and receives support from the observations that hypersensitivity depends on polarizability of the ligands.[17] Table III also shows that for any particular solvent, the hypersensitivity in the tetrakis chelates is independent of the Q cations, and in each case the sequence (with respect to the solvent medium) is acetone > chloroform ~ benzene. This trend can be rationalized by recalling that in acetone the compounds dissociate as 1:1 electrolytes but in chloroform and benzene they remain undissociated. It appears to be likely that the dissociation of a complex is associated with the change of its symmetry. Indeed, Bauer et al.[18] have shown that, among the various possible geometries in tetrakis(β-diketonates) of Eu(III), interconversion energies of several of these geometries require little expenditure of energies, and the size of the quaternary ammonium cations and their spatial requirements have definite influence over the specific geometries of these compounds. Of course, in the present context this explanation is quite tentative due to the lack of our knowledge about the structure of the complex species in solution. However, the fact which needs to be emphasized here is the extreme hypersensitivities of

Q[Nd(SDBM)$_4$] chelates in acetone which appear to be highest for any Nd(III) complex in solution reported in the literature.

The nephelauxetic parameter in Sinha's scale[18] was evaluated for the Nd(III) complexes in the three solvents. In general, the bands undergo red shifts with respect to the aquo ion by more than 200 cm^{-1}. The δ values (average for the different J levels) which are in the range 1.2–1.7% do not bear any definite relationship in the compounds with respect to the solvents.

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Registry No. Nd(SDBM)$_3$·H$_2$O, 59654-74-9; [Nd(SDBM)$_4$](morpH), 59654-76-1; [Nd(SDBM)$_4$](pyrrolH), 59654-77-2; [Eu(SDBM)$_4$](pipH), 59654-79-4; Nd(SDBM)$_3$(phen), 58798-42-8; Nd(SDBM)$_3$(bpy), 59654-80-7; Nd(SDBM)$_3$(*N*-pyO)$_2$, 59654-81-8; [Eu(SDBM)$_4$](morpH), 59654-82-9; [Eu(SDBM)$_4$](pyrrolH), 59654-83-0; Eu(SDBM)$_3$(bpy), 59654-84-1; Eu(SDBM)$_3$(phen), 59654-85-2; Eu(SDBM)$_3$(*N*-pyO)$_2$, 59654-86-3; Eu(SDBM)$_3$·H$_2$O, 59654-87-4; [Nd(SDBM)$_4$](pipH), 59654-88-5; [Nd(DBM)$_4$](pipH), 56702-55-7.

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The Electronic Structure of Tetrakis(methyl isocyanide)platinum(II). A Model for the Electronic Structure of Strong Ligand Field d^8 D_{4h} Molecules

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In recent years the electrical properties of one-dimensional inorganic[1-6] and organic[5-8] complexes based on partially oxidized tetracyanoplatinate and 7,7,8,8-tetracyano-*p*-quinodimethane complexes have received considerable attention. The electronic structure of the tetracyanoplatinate(II) anion has been used as a model for calculations and interpretation of the solid state electronic energy band structure for the highly conducting K$_2$Pt(CN)$_4$X$_{0.30}$·3H$_2$O (X = Cl, Br) complex[2,9-12] and as a model for d^8 D_{4h} strong ligand field complexes. Several molecular orbital descriptions for Pt(CN)$_4^{2-}$ have appeared recently which differ in the level ordering for the metal d$_{z^2}$-like molecular orbital[9,10,13-15] which forms the conducting band in the solid.[12] Recent Xα scattered wave molecular orbital calculations suggest that the d orbitals are ordered as d_{xy} (b_{2g}) > d_{xz}, d_{yz} (e_g) > d_{z^2} (a_{1g}) with an unfilled $d_{x^2-y^2}$ (b_{1g}) orbital at much higher energy.[9,10,13] Results of other molecular orbital calculations also place the unfilled $d_{x^2-y^2}$ at higher energy but order the filled d orbitals as d_{z^2} > d_{xz}, d_{yz} > d_{xy}.[14-16] The excited state levels for strong ligand field d^8 D_{4h} platinum complexes are also subject to question.[17]

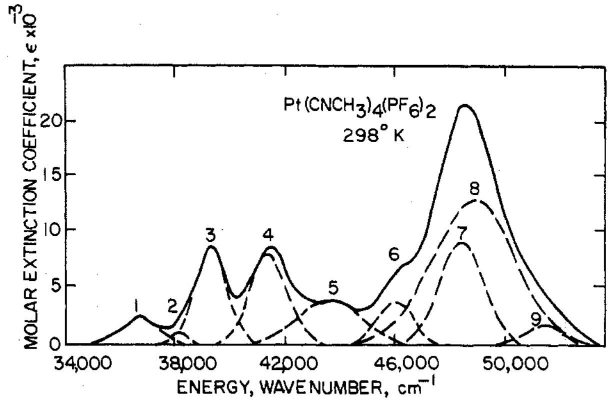

Figure 1. Deconvoluted electronic absorption spectrum of Pt(CNCH$_3$)$_4$(PF$_6$)$_2$ in acetonitrile at room temperature.

Table I. The Electronic Absorption Spectral Parameters for Pt(CNCH$_3$)$_4$(PF$_6$)$_2$[a]

Band	Wavenumber, λ_{max}, cm^{-1}	Molar extinction ϵ, l./(mol cm)[b]	Oscillator strength[c]
1	36 730	2360	0.015
2	38 165	955	0.0028
3	39 320	8310	0.042
4	41 435	7890	0.048
5	43 635	3830	0.039
6	46 085	3850	0.021
7	48 460	9110	0.064
8	48 920	12800	0.169
9	51 490	1540	0.010

[a] The hexafluorophosphate anion does not exhibit an absorption below 52 000 cm^{-1}. [b] In acetonitrile. [c] Energy maxima accurate to ±10 cm^{-1}, ϵ and f accurate to ±10%. Oscillator strengths calculated by $f = 4.32 \times 10^{-9} F \int \epsilon \, d\nu$, $F = 9n/(n^2 + 2)^2 = 0.843$: A. Rubinowicz, *Rep. Prog. Phys.*, **12**, 233 (1948–1949).

In order to understand more fully the properties of these highly conducting complexes we have previously investigated the electronic absorption spectra of Pt(CN)$_4^{2-}$,[17] and now report our results for Pt(CNCH$_3$)$_4^{2+}$,[18] **1**, and a unified state diagram for both complexes.

Results and Discussion

Using computer curve resolving techniques,[17] the room temperature acetonitrile solution spectrum of **1**[19] was deconvoluted into nine Gaussian components (Figure 1, Table I) corresponding to a minimum number of bands to achieve the best fit. This spectrum resembles the deconvoluted absorption spectrum of the tetracyanoplatinate anion, **2**,[17,20] and since the spectrum of **1** is better resolved than **2** it may also serve as a useful model for understanding the electronic structure of d^8 D_{4h} square-planar complexes with strong field ligands.[21] The nine Gaussian bands for **1** are blue shifted with respect to the bands of similar oscillator strength for **2**, due in part to the 4+ charge difference which stabilizes the system