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Some Lanthanide Complexes of Semicarbazone and Thiosemicarbazone Derived from Fluorenone

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A new series of lanthanide chloride complexes with the ligands fluorenone semicarbazone (FSC) and fluorenone thiosemicarbazone (FTSC) of composition $[LnLCl_2(H_2O)_2]$ (Ln = La, PR, Nd, Sm, Gd) were synthesised and characterized by microanalytical, spectral, magnetic and conductivity data. These ligands act as monovalent bidentate and bond through carbonyl oxygen/thiocarbonyl sulfur and the azomethine nitrogen atom.

INTRODUCTION

The chemistry of transition metal compounds with the semicarbazones and thiosemicarbazones have received considerable attention in recent years. Metal complexes of these ligands have been known for their pharmacological applications[1]. Significant antitubercular[2], fungicidal[3] and antiviral[4] activities have been reported for thiosemicarbazides and their derivatives. Perusal of the literature reveals that comparatively less work has been done on the complexes of semicarbazones and thiosemicarbazones with lanthanides. In continuation of our earlier work[5–9], in this paper we have described preparation and characterization of a new series of lanthanide chloride complexes with the ligands fluorenone semicarbazone and fluorenone thiosemicarbazone.

RESULTS AND DISCUSSION

The complexes were analyzed for metal, sulfur and halogens by standard methods[10] and carbon, hydrogen and nitrogen by microanalytical methods. The complexes are insoluble in water and common non-coordinating solvents but are soluble in the coordinating solvents like dimethyl formamide. All complexes are colored and nonhygroscopic. The analytical date for the complexes (Table 1) indicate that they possess general formula $[Ln(L)Cl_2(H_2O)_2]$; (Ln = La, Pr, Nd, Sm, Gd and L = FTSC, FSC). The low conductance value of these complexes in nitrobenzene and DMF shows its non-electrolytic nature.

The magnetic data indicate that all the complexes, except those of lanthanum are paramagnetic as expected on the basis of their J values. The observed magnetic moments of the present complexes show little deviation from the Van Vleck value[11] which suggests that the 4f electrons, which are well shielded by the $5s^2$, $5p^6$ octet, play only a small part in the bonding.

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TABLE 1

MICRO ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF LANTHANIDE COMPLEXES OF FLUORENONE SEMICARBAZONE AND FLUORENONE THIOSEMICARBAZONE

Chelate	Metal %	Carbon %	Hydrogen %	Nitrogen %	Sulfur %	Halogen %	Conductance $ohm^{-1}\ cm^{-1}\ mol^{-1}$	Magnetic Susceptibility B.M.
$[La(FTSC)Cl_2(H_2O)_2]$	27.44 (27.88)	33.53 (33.75)	2.80 (2.83)	8.16 (8.44)	6.41 (6.44)	13.92 (14.23)	7.0	D
$[Pr(FTSC)Cl_2(H_2O)_2]$	28.21 (28.17)	33.57 (33.62)	2.89 (2.82)	8.43 (8.40)	6.34 (6.40)	14.09 (14.80)	2.4	3.2
$[Nd(FTSC)Cl_2(H_2O)_2]$	28.16 (28.65)	33.17 (33.39)	2.80 (2.80)	8.34 (8.34)	6.21 (6.37)	13.72 (14.08)	3.1	3.3
$[Sm(FTSC)Cl_2(H_2O)_2]$	29.21 (29.50)	33.01 (32.99)	2.80 (2.77)	8.29 (8.25)	6.40 (6.29)	13.73 (13.91)	5.9	1.84
$[Gd(FTSC)Cl_2(H_2O)_2]$	30.10 (30.44)	32.19 (32.55)	2.59 (2.73)	8.00 (8.13)	6.38 (6.27)	13.73 (13.73)	2.3	7.85
$[La(FSC)Cl_2(H_2O)_2]$	28.79 (28.81)	34.83 (34.88)	2.93 (2.93)	8.61 (8.72)	—	14.71 (14.70)	7.6	D
$[Pr(FSC)Cl_2(H_2O)_2]$	29.10 (29.11)	34.71 (34.73)	2.90 (2.91)	8.59 (8.68)	—	14.63 (14.65)	4.3	3.1
$[Nd(FSC)Cl_2(H_2O)_2]$	29.53 (29.59)	34.48 (34.49)	2.90 (2.89)	8.43 (8.62)	—	14.10 (14.55)	8.0	3.2
$[Sm(FSC)Cl_2(H_2O)_2]$	30.41 (30.46)	34.07 (34.07)	2.81 (2.86)	8.44 (8.51)	—	14.13 (14.36)	9.1	1.83
$[Gd(FSC)Cl_2(H_2O)_2]$	33.62 (33.60)	31.43 (31.42)	2.85 (2.82)	8.10 (8.40)	—	14.30 (14.17)	1.1	7.83

These complexes are stable in air. An indirect indication of the coordination of the water molecule was obtained by heating the complexes at 100°C in vacuo. No loss in weight was observed which strongly supports the contention that the water molecule is coordinated to the metal ion and is not just a part of the crystal lattice.

The infrared spectroscopic results provide support for the molecular constitution of these complexes (Table 2). The bands at *ca.* 1630 and 1400–50 cm^{-1} in the spectra of the ligand FSC, decreased and modified bands were observed at lower frequencies which supports that the metal coordinates through N of C=N and oxygen of the enolic OH[12]. The bands around 1000 cm^{-1} due to C–O, as marked in the spectra of ligand and complexes, were also supported by Goel *et al.*[13] Low frequency bands at 520 and 430 cm^{-1} were assigned to ν(M–N) and ν(M–O) respectively. The broad bands in the region 3400 cm^{-1} were assigned to coordinated water molecule[14]. Thus FSC behaves as a monovalent bidentate ligand in the lanthanide chloride complexes, coordinating through the carbonyl oxygen and nitrogen of the azomethine group forming a five membered ring.

TABLE 2

SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF METAL CHELATES OF FLUORENONE SEMICARBAZONE AND FLUORENONE THIOSEMICARBAZONE

Compound	ν(C=N)	ν(C–S)	ν(C–O)	ν(M–S)	ν(M–O)	ν(M–N)
FTSC	1650 m	—	—	—	—	—
FSC	1630 m	—	—	—	—	—
$[\text{La(FTSC)Cl}_2(\text{H}_2\text{O})_2]$	1615 w	660 m	—	315 w	—	430 m
$[\text{Pr(FTSC)Cl}_2(\text{H}_2\text{O})_2]$	1620 w	655 m	—	320 w	—	425 m
$[\text{Nd(FTSC)Cl}_2(\text{H}_2\text{O})_2]$	1610 w	650 m	—	320 w	—	435 w
$[\text{Sm(FTSC)Cl}_2(\text{H}_2\text{O})_2]$	1615 w	650 m	—	330 w	—	435 w
$[\text{Gd(FTSC)Cl}_2(\text{H}_2\text{O})_2]$	1620 w	665 m	—	330 w	—	440 w
$[\text{La(FSC)Cl}_2(\text{H}_2\text{O})_2]$	1620 w	—	1010 w	—	425 m	510 w
$[\text{Pr(FSC)Cl}_2(\text{H}_2\text{O})_2]$	1600 m	—	1020 w	—	420 m	525 w
$[\text{Nd(FSC)Cl}_2(\text{H}_2\text{O})_2]$	1600 m	—	1015 w	—	410 m	510 w
$[\text{Sm(FSC)Cl}_2(\text{H}_2\text{O})_2]$	1610 m	—	1020 w	—	430 m	525 m
$[\text{Gd(FSC)Cl}_2(\text{H}_2\text{O})_2]$	1600 m	—	1020 w	—	430 m	520 w

The broad bands of medium intensities due to ν(OH) around 3500 cm^{-1} in the IR spectra of all the FTSC complexes indicate the presence of water molecules in them[15]. The ligand band at 1640 cm^{-1} due to azomethine stretch is shifted to lower wave numbers by about 10–15 cm^{-1} in the spectra of the complexes. This supports the coordination through the terminal hydrazine nitrogen[16]. The band at 850 cm^{-1} which appears in the ligand spectrum may be attributed to pure ν(C=S). In the spectra of chelates this band disappears and a new band appears around 660 cm^{-1} (C–S region). The large shift of this band to lower frequencies in these complexes is the strongest evidence for coordination through the sulfur atom of NH–C=S group after enolisation to N=S–SH and deprotonation[12, 17]. The medium intensity bands at 420–440 and 310–330 cm^{-1} may be assigned to ν(M–N) and ν(M–S) respectively.

All the absorptions due to the f-f transition of the lanthanide ions in the visible region are obscured in the present complexes by the strong absorption of the ligands and by the strong charge transfer band. Hence the electronic spectra are not very helpful in investigations of the transitions involving f electrons of the lanthanide ions.

EXPERIMENTAL

The chlorides of lanthanum(III), praseodymium(III), neodymium(III), samarium(III) and gadolinium(III) were prepared by dissolving respective nitrates or oxides in 80% HCl and crystallizing out the chlorides by evaporating the soltutions on a steam bath. Fluorenone semicarbazone and fluorenone thiosemicarbazone were prepared as reported earlier[18]. The purity of the compounds was checked by elemental analysis and TLC.

General Methods for the Synthesis of the Complexes

Lanthanide(III) chloride (0.004 mol) were dissolved in 20 ml of 80% methanol, and it was added dropwise to a refluxing solution of the ligand (0.004 mol) in methanol. The mixture was then refluxed on a steam bath for 2 h. The resulting yellow solution was treated with dilute ammonia (pH 4–5) solution with stirring. The precipitated complex was separated by filtration, washed with methanol and dried in vacuum over phosphorus(V) oxide.

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