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Studies on Some Azine Complexes of Lanthanum(III) and Samarium(III)

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Synopsis. Pentacoordinated lanthanum(III) and samarium(III) complexes of salicylaldehydeazine and 2-hydroxy-1-naphthaldehydeazine have been synthesized and characterized by elemental analysis, molecular weight determinations, conductance, and magnetic measurements as well as infrared, ultraviolet spectral, and X-ray powder diffraction studies. Their pyrolytic behaviour has also been discussed.

Although, the azine complexes of d-block elements have been extensively studied,[1,2] similar investigations on f-block elements appear to be limited.[3] In view of this, it was considered worthwhile to study the chelating behaviour of azines towards lanthanum(III) and samarium(III) and the results are presented in this paper.

Experimental

All the chemicals used were of analytical grade. Adequate precautions were taken to exclude moisture throughout the experimental work. The triisopropoxylanthanum(III) or -samarium(III)[4] and azines[1,3] were prepared by the literature methods.

The analytical methods and the techniques of physical measurements are the same as reported in our previous communications.[5,6]

Synthesis of Azine Complexes of Lanthanum(III) or Samarium(III): The mixture of triisopropoxylanthanum(III) or -samarium(III) with the stoichiometric amount of azine was heated under reflux for about 8—24 h in benzene medium. The liberated 2-propanol was fractionated azeotropically and then estimated to ascertain the progress of the reaction. On its completion, the excess of the solvent was stripped off under reduced pressure and the residue washed several times with hexane. Finally, the resulting products were dried under vacuum at 50—60 °C/0.5 mmHg† for ≈3 h.

The azinatolanthanum(III) or samarium(III) *t*-butoxides were prepared by refluxing the benzene solution of freshly prepared azinatolanthanum(III) or -samarium(III) isopropoxide with an excess of *t*-butyl alcohol for ≈30 h with continuous removal of benzene-2-propanol azeotrope. After completion of the reaction, the products were isolated by removing the solvent under reduced pressure and subsequent drying.

The analytical data and characteristics of the resulting compounds are recorded in Table 1.

Results and Discussion

These complexes have been synthesized as shown by the following equations:

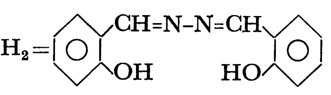
$$(OC_3H_7{}^i)_3Ln + azH_2 \longrightarrow (OC_3H_7{}^i)Ln(az) + 2i\text{-}C_3H_7OH$$

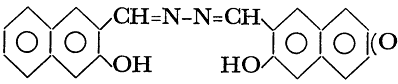
$$2(OC_3H_7{}^i)_3Ln + 3azH_2 \longrightarrow Ln_2(az)_3 + 6i\text{-}C_3H_7OH$$

$$(OC_3H_7{}^i)_3Ln + 2azH_2 \longrightarrow Ln(az)(azH) + 3i\text{-}C_3H_7OH$$

$$(OC_3H_7{}^i)Ln(az) + \underset{\text{(in excess)}}{t\text{-}C_4H_9OH} \longrightarrow (OC_4H_9{}^t)Ln(az) + i\text{-}C_3H_7OH$$

[where Ln = La(III) or Sm(III);

azH_2 =

($sazH_2$)or


($OnazH_2$)].

The resulting complexes, $(OC_3H_7{}^i)Ln$(saz or Onaz), Ln_2(saz or Onaz)$_3$, Ln(saz or Onaz) (sazH or OnazH), and $(OC_4H_9{}^t)Ln$(saz or Onaz) are yellow to reddish brown coloured, nonvolatile solids and decompose without melting when heated above 200 °C. These are insoluble or sparingly soluble in common organic solvents but soluble in DMF or DMSO and in which these behave as nonelectrolytes ($\mu < 20\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$). The alkoxy derivatives, (OR)Ln(az) [where R = Pr^i or Bu^t] are highly moisture sensitive. The azinatolanthanum(III) or -samarium(III) isopropoxides are dimeric, where as the rest of the derivatives are monomeric in nature.

The broad absorption band in the region, 3400—3050 cm^{-1}, due to the hydrogen bonded OH or NH group in the IR spectra of azines disappears in ($OC_3H_7{}^i$ or $OC_4H_9{}^t$)Ln(az) and $Ln_2(az)_3$ complexes indicating the deprotonation of the phenolic protons. However, the characteristic band of νOH/νNH is observed at almost the same position in the spectra of Ln(az)(azH) complexes indicating thereby that at least one hydroxyl group of the two ligand moieties does not take part in coordination.

On the other hand, a strong band at 1610±10 cm^{-1} in the spectra of ligands due to the azomethine (>C=N–)groups splits at 1605±5 and 1580±5 cm^{-1} in the spectra of lanthanum(III) and samarium(III) complexes indicating two different environments around both the azomethine groups of the ligand moiety in the complexes and which is probably due to the coordination of only one unsaturated nitrogen of the ligand to the lanthanoid atom.

The medium to weak intensity bands at 650±10 and 375±10 cm^{-1} in the spectra of azinatolanthanoid complexes may be tentatively assigned to the ring deformation coupled with ν Ln–O and C–H out of plane deformation[7] and ν Ln–N respectively.[8,9]

A bathochromic shift in the transitions of >C=N– chromophore at ≈350 and 425 nm [335 and 415 nm in 2-hydroxy-1-naphthaldehydeazine] in the ultraviolet spectra of lanthanoid complexes probably indicates the formation of Ln–N bond.

The magnetic susceptibilities of these complexes measured at room temperature (35±1 °C) show that the azinatolanthanum(III) complexes are diamagnetic (X_g values-0.34 to -0.92×10^{-6} c.g.s.), whereas the azinatosamarium(III) complexes are paramagnetic (μ $\text{eff}_{\text{exp}} = 1.25$—1.57 BM) in nature.

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† 1 mmHg≈133.322 Pa.

Table 1. Physical characteristics and analytical data of azinatolanthanum(III) and -samarium(III) complexes

Compound, state, and colour	D.P.[a] θ_d/°C	Found(Calcd) (%) La/Sm	Found(Calcd) (%) C	Found(Calcd) (%) H	Found(Calcd) (%) N	Molecular weight Found (Calcd)
1	2	3	4	5	6	7
$(\mathrm{OC_3H_7}{}^i)\mathrm{La(saz)}$ Yellow solid	310—12	31.95 (31.84)	47.00 (46.80)	3.85 (3.93)	6.61 (6.42)	920.15 (436.25)
$\mathrm{La_2(saz)_3}$ Yellow solid	275—77	27.81 (27.99)	50.74 (50.82)	3.10 (3.05)	8.62 (8.47)	964.86 (992.57)
La(saz)(sazH) Dark yellow solid	260—62	22.71 (22.54)	54.71 (54.55)	3.50 (3.43)	9.27 (9.09)	651.73 (616.42)
$(\mathrm{OC_4H_9}{}^t)\mathrm{La(saz)}$ Dark yellow solid	225—27	30.74 (30.85)	48.16 (48.01)	4.18 (4.25)	6.37 (6.22)	486.72 (450.28)
$(\mathrm{OC_3H_7}{}^i)\mathrm{Sm(saz)}$ Light orange solid	304—06	33.73 (33.57)	45.78 (45.60)	3.91 (3.83)	6.47 (6.26)	925.92 (447.68)
$\mathrm{Sm_2(saz)_3}$ Dark yellow solid	276—77	29.45 (29.63)	49.68 (49.71)	3.02 (2.98)	8.43 (8.28)	1054.11 (1015.43)
Sm(saz)(sazH) Dark yellow solid	200—02	24.15 (23.94)	53.70 (53.56)	3.42 (3.37)	9.15 (8.92)	661.23 (627.85)
$(\mathrm{OC_4H_9}{}^t)\mathrm{Sm(saz)}$ Dark yellow solid	265—67	32.71 (32.56)	46.66 (46.82)	4.19 (4.15)	5.95 (6.07)	437.25 (461.71)
$(\mathrm{OC_3H_7}{}^i)\mathrm{La(Onaz)}$ Light reddish brown solid	339—40	26.09 (25.90)	55.83 (55.98)	4.01 (3.95)	5.35 (5.22)	1037.77 (536.38)
$\mathrm{La_2(Onaz)_3}$ Red solid	280—82	21.33 (21.49)	61.52 (61.31)	3.21 (3.27)	6.72 (6.50)	1241.31 (1292.96)
La(Onaz)(OnazH) Reddish brown solid	260—62	17.19 (17.01)	64.89 (64.71)	3.62 (3.58)	7.01 (6.86)	783.49 (816.68)
$(\mathrm{OC_4H_9}{}^t)\mathrm{La(Onaz)}$ Dark brown solid	240—42	25.36 (25.24)	56.53 (56.74)	4.25 (4.21)	5.20 (5.09)	528.11 (550.41)
$(\mathrm{OC_3H_7}{}^i)\mathrm{Sm(Onaz)}$ Reddish brown solid	291—93	27.34 (27.45)	54.97 (54.82)	3.91 (3.86)	5.01 (5.12)	1057.27 (547.81)
$\mathrm{Sm_2(Onaz)_3}$ Red solid	275—77	23.02 (22.85)	60.10 (60.24)	3.16 (3.22)	6.58 (6.39)	1364.10 (1315.82)
Sm(Onaz)(OnazH) Red solid	219—21	18.34 (18.15)	64.00 (63.81)	3.60 (3.53)	6.58 (6.76)	862.83 (828.11)
$(\mathrm{OC_4H_9}{}^t)\mathrm{Sm(Onaz)}$ Red solid	233—35	26.89 (26.75)	55.73 (55.59)	4.07 (4.13)	5.11 (4.98)	593.91 (561.84)

a) D. P.: Decomposition temperature.

Attempts to grow crystals of suitable size for X-ray crystal diffraction studies remained unsuccessful. However, the X-ray powder diffraction patterns have been recorded and these indicate that the compounds $(\mathrm{OC_3H_7}{}^i)\mathrm{Sm(saz)}$, $\mathrm{Sm_2(saz)_3}$, and Sm(saz)(sazH) belong to the orthorhombic symmetry having the molecular unit cell parameters a,b,c (in Å) and Z as 12.64, 16.37, 14.71, and 4; 12.61, 15.63, 30.46, and 4; 6.70, 15.24, 18.28, and 2, respectively.

The comparative thermal stability of the complexes, $(\mathrm{OC_3H_7}{}^i)\mathrm{Sm(saz)}$, $\mathrm{Sm_2(saz)_3}$, and Sm(saz)(sazH) on the basis of IPDT values (549.2, 537.0, and 507.4, respectively) has been evaluated from the pyrolytic curves plotted in the percentage residual weight against the temperature. The activation energy E_A (K· Cal) and order of reaction $n[E_A$, n: 5.72, 1; 4.35, 1; 4.12, 1, respectively] have also been determined with the help of Freeman and Carroll's method.[10] The following order of thermal stability of the complexes has been noted:

$$(\mathrm{OC_3H_7}{}^i)\mathrm{Sm(saz)} > \mathrm{Sm_2(saz)_3} > \mathrm{Sm(saz)(sazH)}.$$

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