

NOTE

Synthesis and Physicochemical Studies of Iodide Complexes of Lanthanides and Yttrium with 4-Aminoantipyrine

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A new series of the iodide complexes of lanthanides and yttrium with 4-aminoantipyrine (AAP) of the composition $[\text{Ln}(\text{AAP})_4\text{I}_2]$ (where $\text{Ln}=\text{La, Pr, Nd, Sm}$ and Gd) and $[\text{Ln}(\text{AAP})_3\text{I}_3]$ (where $\text{Ln}=\text{Y}$ and Dy) were prepared and characterized by elemental, conductance, spectral (IR and electronic) and thermogravimetric analysis. AAP acts as a neutral monodentate ligand coordinating through the carbonyl oxygen. Only one of the iodines in the complexes of La, Pr, Nd, Sm and Gd is not coordinated. TG studies indicate a three stage decomposition with the formation of metal oxides above 520°C in static air and a two-stage decomposition with the formation of metal iodides above 720°C.

Iodide ion is known to act both as a ligand and as a counter anion in the complexes of lanthanides and yttrium¹. In continuation of our studies on iodide complexes of lanthanides and yttrium^{1,2}, a series of complexes of iodides of lanthanides and yttrium with 4-aminoantipyrine (AAP) were synthesized and characterized.

The complexes of La, Pr, Nd, Sm and Gd were prepared as follows: 2 mmol of methanolic solution of the lanthanide iodide was added to 10 ml of methanolic solution of AAP, refluxed for 2 hrs, cooled, concentrated and the resulting black viscous mass was washed several times with hot benzene to remove the excess ligand. The separated complex was recrystallised by dissolving it in the minimum amount of acetone and stirring vigorously with the addition of diethyl-ether. The complex was dried under reduced pressure over P_2O_{10} . 8 mmol of AAP was used for the preparation of the complexes of Dy and Y, the procedure being the same as above.

The complexes were analysed for their metal and iodide contents by the conventional methods^{3,4}. Molar conductance of the complexes in nitrobenzene, acetonitrile and methanol (*ca.* 10^{-3} M solution) was measured using an ELICO type M82T conductivity bridge with dip type cell (type CC-03) and platinum electrodes (cell constant= 1.4 cm^{-1}). Infrared spectra were recorded in the range $4000\text{--}200 \text{ cm}^{-1}$ on a Perkin-Elmer 283 IR spectrophotometer using KBr disc technique. Electronic spectra

in acetonitrile (ca. 10^{-3} M) were recorded in the range 200–850 nm on a Shimadzu UV-200S spectrophotometer. Thermogravimetric studies of the complexes in static air were carried out on a DuPont 2000 thermobalance and in nitrogen on a null point type Delta series TGA-7 thermobalance.

The complexes are yellow solids with slight hygroscopic nature. These are soluble in polar solvents like acetone, acetonitrile, methanol and ethanol and insoluble in solvents of low polarity like benzene and carbon tetrachloride.

The molar conductance values (Table 1) of the complexes in nitrobenzene⁵ show 1 : 1 electrolytic behaviour for the complexes of La, Pr, Nd,

TABLE
ANALYTICAL AND CONDUCTANCE DATA OF IODIDE
COMPLEXES OF LANTHANIDES AND YTTRIUM

Complex	% Metal Found (Calcd.)	% Iodide (Calcd.)	Molar conductance (ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$)		
			$\text{C}_6\text{H}_5\text{NO}_2$	CH_3CN	CH_3OH
[La(AAP) ₄ I ₂]I	10.34 (10.43)	28.19 (28.58)	29.51	187.34	168.19
[Pr(AAP) ₄ I ₂]I	10.38 (10.56)	28.47 (28.54)	29.54	195.43	193.90
[Nd(AAP) ₄ I ₂]I	10.70 (10.78)	28.14 (28.47)	26.15	174.50	169.00
[Sm(AAP) ₄ I ₂]I	11.00 (11.10)	28.21 (28.34)	29.98	176.78	172.95
[Gd(AAP) ₄ I ₂]I	11.32 (11.65)	28.11 (28.20)	29.90	176.77	170.13
[Dy(AAP) ₃ I ₃]	14.24 (14.10)	33.14 (33.04)	5.28	133.03	106.97
[Y(AAP) ₃ I ₃]	8.23 (8.24)	35.20 (35.31)	5.56	133.74	107.88

Sm and Gd and nonelectrolytic behaviour for the complexes of Dy and Y. Hence the complexes may be formulated as $[\text{Ln}(\text{AAP})_4\text{I}_2]\text{I}$ (where Ln = La, Pr, Nd, Sm and Gd) and $[\text{Ln}(\text{AAP})_3\text{I}_3]$ (where Ln = Dy and Y). The complexes dissociate in acetonitrile giving values slightly higher than

those expected for 1 : 1 electrolytes². But in the more polar solvent methanol the complexes of La, Pr, Nd, Sm and Gd show 1 : 2 electrolytic behaviour whereas the complexes of Dy and Y show 1 : 1 electrolytic behaviour showing that one of the coordinated iodine is replaced by methanol molecule².

The infrared spectra show that the carbonyl stretching band observed at 1640 cm^{-1} in AAP is shifted to lower frequency (about 1610 cm^{-1}) in the complexes indicating that the carbonyl oxygen is coordinated. The $\nu_{(\text{N-H})}$ frequency is found as medium bands at 3430 and 3320 cm^{-1} in AAP (one H-bonded and the other free). In the complexes these two bands merge together to appear as a broad band at $3320\text{--}3300\text{ cm}^{-1}$. Since the N-H region of the spectra does not practically undergo any change on complexation, the amino nitrogen is not coordinated. Hence AAP acts as a neutral monodentate ligand and a coordination number of six may be assigned to the rare earth ion in the present complexes.

The electronic spectrum of AAP in acetonitrile shows a strong band at 38.46 kK which is attributed to $\pi \rightarrow \pi^*$ transition. This band is slightly blue shifted to 40.00 kK in the complexes. The complexes of La, Pr, Sm, Gd, Dy and Y show no significant band due to f-f transition. The complex of Nd shows the hypersensitive ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$, ${}^2\text{G}_{7/2}$ band at $16,949\text{ kK}$. The Sinha covalency parameter calculated for the Nd complex ($\delta=0.1899$) suggests weak covalent character of the metal-ligand bond⁶. The shape of the hypersensitive band of Nd (III) in $[\text{Nd}(\text{AAP})_4\text{I}_2]\text{I}$ is similar to those of six coordinated complexes reported by Karrakar⁷ which is in conformity with conductance and infrared spectral data.

Thermogravimetric analysis of the complexes indicate that the nature of decomposition and the final residue obtained differ considerably in the two atmospheres, viz., static air and nitrogen, studied. In static air the decomposition takes place in three stages forming a final residue of the corresponding metal oxide at about 520°C . But in nitrogen atmosphere a two stage decomposition is reported with the formation of metal iodide above 720°C .

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