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Dysprosium and Holmium Complexes of *N*-(2-Pyridyl)salicylideneamine

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Synopsis. Dysprosium and holmium isopropoxides react with monofunctional bidentate Schiff base, *N*-(2-pyridyl)salicylideneamine, in 1:1, 1:2, and 1:3 molar ratios in benzene to yield complexes of the types $\mathrm{Ln(OPr^i)_2(sap)}$, $\mathrm{Ln(OPr^i)(sap)_2}$, and $\mathrm{Ln(sap)_3}$ (where Ln=Dy or Ho and $\mathrm{sap^-}$ is the anion of the Schiff base sapH). Probable structures for these complexes are proposed on the basis of molecular weight and IR spectroscopic data. Reports on metal complexes derived from Schiff bases have aroused considerable interest in the field of coordination chemistry, and have been extensively studied.$^{1-4)}$ A literature survey reveals that no work has been done on Dy(III) and Ho(III) complexes of heterocyclic Schiff base, *N*-(2-pyridyl)salicylideneamine. However, complexes of this Schiff base with d-transition elements$^{5,6)}$ have been reported. The present paper deals with the synthesis of Dy(III) and Ho(III) complexes of *N*-(2-pyridyl)salicylideneamine and their characterization by infrared spectra.

Experimental

Dy(III) and Ho(III) isopropoxides were prepared from the respective trichlorides by sodium alkoxide method.$^{7)}$ The Schiff base was prepared by usual method.$^{6)}$ The reactions of Dy(III) and Ho(III) isopropoxides with the Schiff base in different molar ratios (1:1, 1:2, and 1:3) were carried out in refluxing benzene and the 2-propanol liberated in these reactions was collected azeotropically and estimated by oxidation method.$^{8)}$ For brevity the reactions and their analyses have been summarized in Table 1. The lanthanoid content was determined by ignition to sesquioxide. Nitrogen was estimated by the Kjeldahl method. Molecular weights were determined in refluxing benzene by Cottrell's method.$^{9)}$ IR spectra were recorded in the 4000—200 $\mathrm{cm^{-1}}$ range on a Perkin-Elmer 621 instrument using KBr pellets and as mulls in Nujol.

Results and Discussion

The reactions of Dy(III) and Ho(III) isopropoxides with the Schiff base in 1:1, 1:2, and 1:3 molar ratios in anhydrous benzene liberated one, two and three moles of 2-propanol respectively and resulted in the formation of the corresponding mono-, bis-, and tris-Schiff base derivatives of Dy and Ho.

Diisopropoxy-mono(Schiff base) derivatives are orange-red solids, soluble in benzene and they decompose at temperature ≈150 °C whereas monoisopropoxy-bis(Schiff base) derivatives are benzene insoluble orange coloured solids. Tris(Schiff base) derivatives are isolated as dark yellow powders, insoluble in benzene but fairly soluble in *N*,*N*-dimethylformamide.

The molecular weights of diisopropoxy-mono(Schiff base) derivatives of Dy(III) and Ho(III) in boiling benzene indicate them to be essentially trimeric involving the most probable structure of the type (I).

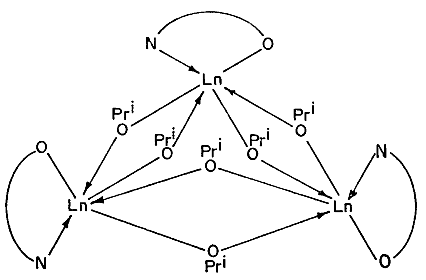
The products $\mathrm{Ln(OPr^i)(sap)_2}$ were found to be insoluble in benzene. The insolubility of these derivatives in common organic solvents prevented determination of molecular weights which could have otherwise useful information about their structures. On serric grounds it can be said that this Schiff base cannot form monomeric structures. With the help of previous work on similar type of derivatives,$^{10-12)}$ we suggest that these complexes may be present in dimeric form (II) where two metal octahedra are bridged through isopropoxide oxygen bridges. The probability of other structures having lanthanoid atom with more than six coordination number, however, cannot be ruled out since lanthanoids have tendency to show coordination number more than six.$^{13)}$

The tris(Schiff base) derivatives of Dy(III) and Ho(III) are also insoluble in benzene and common organic solvents. The insolubility in common noncoordinating solvents and high melting or decomposition temperature (≈260 °C) indicate their associated or polymeric nature. A polymeric structure has also

Table 1. Reactions of dysprosium and holmium isopropoxides with Schiff base (sapH)

Reactants (Molar ratio) (g)	Refluxing time h	Product and colour	2-Propanol in azeotrope (g) Found(Calcd)	Found(Calcd) (%) Ln	N	Decomposition temp °C
$\mathrm{Dy(OPr^i)_3+sapH}$ (1:1) 1.6626+0.9700	5	$\mathrm{Dy(OPr^i)_2(sap)}$ Orange red	0.2896 (0.2940)	33.95 (34.00)	5.43 (5.86)	160
$\mathrm{Dy(OPr^i)_3+sapH}$ (1:2) 1.5202+1.7524	8	$\mathrm{Dy(OPr^i)(sap)_2}$ Orange	0.5284 (0.5377)	26.17 (26.77)	9.00 (9.09)	282
$\mathrm{Dy(OPr^i)_3+sapH}$ (1:3) 1.0006+1.7512	10	$\mathrm{Dy(sap)_3}$ Dark yellow	0.5296 (0.5309)	20.89 (21.54)	10.95 (11.14)	260
$\mathrm{Ho(OPr^i)_3+sapH}$ (1:1) 1.3458+0.7795	5	$\mathrm{Ho(OPr^i)_2(sap)}$ Orange red	0.2368 (0.2363)	34.05 (34.33)	5.83 (5.83)	148
$\mathrm{Ho(OPr^i)_3+sapH}$ (1:2) 1.2772+1.4796	8	$\mathrm{Ho(OPr^i)(sap)_2}$ Orange	0.4452 (0.4485)	26.59 (26.66)	8.95 (9.05)	285
$\mathrm{Ho(OPr^i)_3+sapH}$ (1:3) 1.2592+2.1880	10	$\mathrm{Ho(sap)_3}$ Dark yellow	0.6539 (0.6633)	21.43 (21.79)	11.00 (11.10)	260

sapH = $\mathrm{C_{12}H_{10}N_2O}$



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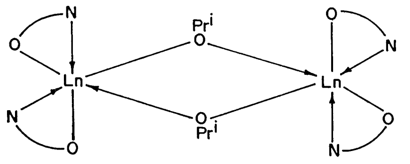

II

Ln= Dy or Ho $\left(^{O}_{N}\right.$ = anion of Schiff base SAPH.

been suggested for tris(salicylideneamino)triethylenetetramine complexes of lanthanoids on the basis of their practically insoluble nature in any available solvents.[14)]

The IR spectrum of ligand exhibited a broad band around 2990—2800 cm^{-1} due to O–H stretching vibration, shifted to lower frequency as a result of intramolecular hydrogen bonding OH···N. The disappearance of this band (ν O–H) in the complexes suggests the participation of OH group of Schiff base in bound formation.

A strong band is observed at 1610 cm^{-1} in the free ligand. This is a characteristic absorption band of the azomethine (>C=N–) group. This band (ν C=N) in the spectra of all the complexes appears at almost the same position and remain unaffected on complexation. Since these bands are associated with –C=N– stretching frequencies, this is consistent with observation of Sarma and Bailar[15)] that indicate coordination through the nitrogen atom of azomethine group. However, some workers have reported a shift of ν C=N frequency either to higher[16)] or to lower[17)] wave number on complexation.

The phenolic C–O stretching vibration in free ligand is observed at 1280 cm^{-1}. This band in complexes is slightly shifted to higher frequency ($\approx$1295 cm^{-1}) indicating the bonding of the ligand to the metal atom through phenolic oxygen. The higher ν C–O in complexes may be ascribed to delocalization of electron density from the oxygen atom to the metal resulting in greater ionic character of the C–O bond and a consequent increase in the C–O vibration frequency. A similar observation was observed by Kovacic for Cu(II) complexes of salicylidene–anilines.[18)]

The mono and diisopropoxy derivatives of Schiff base show characteristic frequencies of isopropyl group at $\approx$1385, 1160, 1150, and 1000 cm^{-1}.[19)] The medium strong band at $\approx$1385 and 1000 cm^{-1} may be assigned to the *gem*-dimethyl structure and bridged C–O stretching vibrations respectively. The value of C–O stretching vibration in mono- and diisopropoxy derivatives of Dy(III) and Ho(III) *ca.* $\approx$1000 cm^{-1} agrees with C–O vibration of bridging alkoxy group.[20)]

The coordination of pyridine molecule to metal is known to cause an upward shift of the four principal bands of pyridine between 1600 and 1430 cm^{-1}, which corresponds to ν C=C and ν C=N vibrations.[21)] In our case no appreciable shift was observed in these bands. This suggests that pyridine nitrogen is not involved in coordination.

The medium and weak bands between 700—200 cm^{-1} are observed in these complexes. These bands are assigned to ν M–O and ν M–N vibrations. No significant differences among the IR spectra were observed for the mono-, bis-, and tris-Schiff base complexes in this region. The bands at $\approx$660, 535, 505, and 460 cm^{-1} are due to metal-oxygen vibrations[22)] whereas the bands observed in the region 400—200 cm^{-1} are assigned to metal-nitrogen vibrations.[23)]

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