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COMPLEXES OF 4-AMINOANTIPYRINE WITH LANTHANIDE THIOCYANATES

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ABSTRACT

Complexes of lanthanide thiocyanates with 4-amino antipyrine have been synthesized for the first time. Unlike other lanthanide complexes, these complexes are quite novel in that the lanthanide ions themselves fall into two groups (the lighter ones and the heavier ones) as regards their coordinating ability. The complexes have been characterized using various physico-chemical techniques such as conductivity measurements, infrared spectroscopy, and thermal analysis (TG, DTG and DTA).

INTRODUCTION

In earlier communications, we have reported on the preparation and characterization of complexes of 4-aminoantipyrine (*aap*) with lanthanide perchlorates¹ and nitrates² with the compositions $[\text{Ln } aap_6] (\text{ClO}_4)_3$ and $[\text{Ln } aap_3 (\text{NO}_3)_3]$ respectively. (Ln = La, Pr, Nd, Sm, Gd, Dy or Y). Similar complexes of *aap* with lanthanide thiocyanates are being reported here.

EXPERIMENTAL

4-Aminoantipyrine used was of Analar grade (BDH). Lanthanide oxides (99.9%) obtained from M/s. Indian Rare Earths Ltd., Udyogamandal, Kerala, were used as such. Ammonium thiocyanate used was from E. Merck (Germany). All solvents used were purified by standard methods³.

Preparation of the complexes

The lanthanide oxides were converted into the corresponding nitrates by the methods described earlier². All the complexes were prepared by the general procedure given below.

Lanthanide nitrate (1g, 2.3 mmol) and *aap* (1.5 mmol) were separately dissolved in minimum amount of cold water (0–5° C) and then mixed together. Any precipitate formed was filtered off. To the clear solution was added, dropwise, a cold (0–5° C) saturated solution of ammonium thiocyanate. The pasty mass which separated out was washed well with cold (0–5°

C) water. The mass was then dissolved in minimum amount of acetone and reprecipitated by addition of benzene or petroleum ether. The solid thus obtained was dried in vacuum over phosphorus (V) oxide.

The lanthanide content was determined gravimetrically by the oxalate-oxide method⁴ and the thiocyanate content by the Volhard's procedure⁵.

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-1 Thermobalance (heating rate: 5°/min; atmosphere: static air; chart speed: 40 cm per hour).

I.R. spectra were run on a Perkin-Elmer 237 i.r. spectrophotometer. KBr pellet technique was used. Conductance measurements were made at room temperature (28 ± 2° C) using a Philips GM 4249 conductivity bridge with dip type cell and Pt black electrode (cell constant = 0.7511 cm⁻¹).

RESULTS AND DISCUSSION

The complexes are extremely hygroscopic, freely soluble in polar solvents and only sparingly soluble in non-polar solvents. The analytical data (Table I) suggest that they have the general formula $\text{Ln } aap_3 (\text{CNS})_3 \cdot 4\text{H}_2\text{O}$.

Thermogravimetric studies show that the complexes are stable upto ~ 100° C. All the four water molecules are lost between 100 and 200° C. X-ray powder diffraction data of the ultimate thermal decomposition residues showed that they were Ln₂O₃ in the case of La, Nd, Sm, Gd, Dy and Y; Pr₆O₁₁ in the case of Pr.

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TABLE I
Analytical data of lanthanide aap thiocyanate complexes

Complex	Found (%)				Calculated (%)			
	Metal	Thiocyanate	C	H	Metal	Thiocyanate	C	H
[La (aap) ₃ (CNS) ₃] 4H ₂ O	13.88	17.00	44.35	4.70	13.96	17.47	44.48	4.73
[Pr (aap) ₃ (CNS) ₃] 4H ₂ O	13.94	17.60	44.38	4.68	14.14	17.46	44.36	4.71
[Nd (aap) ₃ (CNS) ₃] 4H ₂ O	14.19	17.59	43.00	4.72	14.43	17.40	43.20	4.70
[Sm (aap) ₃ (CNS) ₃] 4H ₂ O	14.84	17.15	42.79	4.63	14.94	17.30	42.96	4.67
[Gd (aap) ₃ (CNS) ₃] 4H ₂ O	15.60	17.35	42.69	4.60	15.49	17.14	42.66	4.64
[Dy (aap) ₃ (CNS) ₃] 4H ₂ O	15.70	16.86	42.50	4.65	15.97	17.10	42.46	4.62
[Y (aap) ₃ (CNS) ₃] 4H ₂ O	9.45	18.25	45.71	4.85	9.41	18.42	45.74	4.97

The compounds show non-electrolytic behaviour in nitrobenzene. However, they are roughly 1:1 electrolytes in acetonitrile and met. anol, which may be due to the partial dissociation, induced by the polar solvents. All the complexes (except those of La and Y) were found to be paramagnetic.

The chief i.r. bands and their assignments are presented in Table II. The $\nu(\text{C}=\text{O})$ frequency in the free ligand occurs at $\sim 1650 \text{ cm}^{-1}$ with a shoulder at 1690 cm^{-1} . In all the complexes this band undergoes a shift and is found at 1620 cm^{-1} . This indicates coordination through the carbonyl oxygen.

The $\nu(\text{N}-\text{H})$ frequency occurs as medium intense bands at 3490 and 3380 cm^{-1} in the spectrum of the free ligand. It is here that a significant difference is observed between the lighter lanthanides on the one hand and the heavier ones (and Y) on the other. In the spectra of La, Pr, Nd and Sm complexes, these two bands merge together, and along with the O-H stretching vibration, it appears as a very broad, medium intense band with maximum at 3400 cm^{-1} . However, in the case of the Gd, Dy and Y complexes, the broad medium intense band has its maximum at 3200 cm^{-1} with a shoulder at 3400 cm^{-1} and extending upto 3600 cm^{-1} . This shoulder is attributed to the $\nu(\text{O}-\text{H})$ vibration. The considerable shift of the N-H band (from $3490-3380 \text{ cm}^{-1}$ to 3200 cm^{-1}) indicates co-ordination of the amino-N to the metal atom. Similar shifts have been observed in other cases of amino N coordination⁶. In the spectra of lighter lanthanides (La, Pr, Nd, Sm), the N-H region does not

practically undergo any change on complexation; it is therefore inferred that in these complexes the amino group is not participating in coordination.

The $\delta(\text{O}-\text{H})$ and $\nu(\text{C}=\text{O})$ overlap and occur as a single band at $\sim 1620 \text{ cm}^{-1}$ in all the complexes. As the ligand has bands in the $880-650 \text{ cm}^{-1}$ region, it is difficult to locate any bands due to coordinated water⁷ and as such no conclusion is drawn regarding the nature of binding of the four water molecules.

In the lanthanide aap thiocyanate complexes, the C-N stretching vibration occurs as a very strong band at $2100-2110 \text{ cm}^{-1}$. A comparison with $\nu(\text{C}-\text{N})$ of complexes, in which N-bonding has been proved by X-ray analysis, such as $\text{BaZn}(\text{NCS})_4$ [$\nu(\text{C}-\text{N})$ at 2101 cm^{-1}] indicates N-bonding in the present complexes also. On the basis of earlier assignments regarding the nature of bonding of the thiocyanate ion^{12,13} it may tentatively be suggested that the bonding in lanthanide aap thiocyanates is $\text{Ln} \leftarrow \text{NCS}$.

Assuming that the water molecules do not play any significant role in coordination, it may be concluded that in the aap complexes of lanthanide thiocyanates, the lighter lanthanides (La, Pr, Nd and Sm) show a liganey of 6 and the heavier lanthanides (Gd and Dy) and Y show a liganey of 9. Amino-N coordination was not observed in the aap complexes of the lanthanide nitrates or perchlorates. The exceptional behaviour in the case of the aap complexes of Gd, Dy and Y thiocyanates could be rationalised by two considerations: (i) the stronger complex-forming tendencies of Gd, Dy and Y ions which would induce the ligand

TABLE II
Infrared frequencies of aap and its lanthanide thiocyanate complexes

aap (L)	(LaL ₃ Y') 4H ₂ O	(PrL ₃ Y' ₃) 4H ₂ O	(NdL ₃ Y' ₃) 4H ₂ O	(SmL ₃ Y' ₃) 4H ₂ O	(GdL ₃ Y' ₃) 4H ₂ O	(DyL ₃ Y' ₃) 4H ₂ O	(YL ₃ Y' ₃) 4H ₂ O	Tentative assignments
3490m								
3380m	3400m (br)	3400m (br)	3400m (br)	3400m (br)	3400sh	3400sh	3400sh	^ν (N-H) of amino group
					3200m (br)	3200m (br)	3200m (br)	
	2110vs	2100vs	2100vs	2100vs	2100vs	2100vs	2100vs	^ν (C-N) of thiocyanate group
1690sh								
1650vs	1630vs	1620vs	1620vs	1620vs	1620vs	1620vs	1620vs	^ν (C=O)
1600vs	1590vs	1580vs	1580vs	1580vs	1580vs	1580vs	1580vs	Pyrazolone ring stretching
1510s	1505m	1500m	1500m	1500s	1500s	1500s	1500m	Ring stretching
1460m	1480w	1460w	1460w	1460w	1460w	1460w	1460w	of 5-membered ring + phenyl ring
	1405w	1400w	1390w	1400m	1400m	1400m	1390s	
1360s	1340m	1330m	1320m	1330m	1330m	1330m	1330m	^δ (CH ₃)
1290m								
1240m								
1210m								
775s	780s	775s	780s	780s	780s	780s	775s	^π C-H) of monosubstituted benzene
720m	710s	705s	705s	705s	705s	705s	705s	(out of plane)

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder, L = aap; Y' = CNS.

to utilize its second donor site at the amino-N and (ii) the smaller size and the linear shape of the thiocyanate ligand which would provide no steric hindrance to counteract the above tendency, unlike in the case of the bulkier nitrate and perchlorate ligands. Variations of coordination number in lanthanide complexes are largely decided by the spatial accommodation of the ligands rather than by their bonding characteristics and exhibition of higher coordination is the rule and not the exception for many lanthanide complexes¹⁵.

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