Inorganica Chimica Acta, 110 (1985) 211–213

Lanthanide Nitrate Complexes of 4-N-(2′-Hydroxy-1′-naphthylidene)-aminoantipyrine

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Received April 2, 1985

Abstract

Lanthanide nitrates form with 4-N-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP) complexes of the type [Ln(HNAAP)$_2$(NO$_3$)$_3$] (where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y). The IR spectra of these complexes show that HNAAP acts as a bidentate neutral ligand and nitrate group is coordinated monodentately. The electronic spectra of the Nd complex show reasonable covalency in the metal–ligand bond. The magnetic moments of these complexes are in better agreement with the Van Vleck values. All these complexes are thermally stable up to ~200 °C.

Introduction

In continuation of our previous work on complexes of lanthanide nitrates with pyrazol-5-ones [1–3], a new series of lanthanide nitrate complexes of the ligand 4-N-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP) has been reported. HNAAP would be expected to be a monovalent terdentate ligand, the carbonyl oxygen, the azomethine nitrogen and the deprotonated phenolic oxygen being the potential donor sites. The resulting complexes are of physiological as well as industrial importance.

Experimental

The nitrates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y were prepared by dissolving the respective oxides in 50% nitric acid and crystallising the salts by evaporating the solution on a steam bath. The ligand, HNAAP, was prepared from 4-aminoantipyrine and 2-hydroxy-1-naphthaldehyde by the method reported earlier [4].

The complexes were prepared as follows. Solutions of the nitrate of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho or Y (2 mmol) and HNAAP (6 mmol) in hot dry acetone were mixed and the resulting solution was refluxed on a steam bath for about 1 h. It was concentrated to obtain a viscous black mass which was washed several times with hot benzene to remove the excess ligand. The separated solid complex was recrystallised by dissolving it in the minimum amount of dry acetone and stirring vigorously with dry diethylether. It was dried under vacuum over phosphorus(V) oxide.

These complexes were analysed for metal, carbon, nitrogen and hydrogen by the conventional methods [1, 5]. The physical methods used in the present investigation were the same as described earlier [2].

Results and Discussion

Analytical data (Table I) of the complexes indicate that they have the composition Ln(HNAAP)$_2$-

TABLE 1. Analytical[a] and Conductance Data of Lanthanide Nitrate Complexes of HNAAP.

Complex	Metal %	Carbon %	Hydrogen %	Nitrogen %	Molar conductance[b] in nitrobenzene
[La(HNAAP)$_2$(NO$_3$)$_3$]	13.63(13.37)	50.12(50.82)	3.61(3.66)	12.18(12.13)	6.34
[Pr(HNAAP)$_2$(NO$_3$)$_3$]	13.71(13.54)	49.78(50.72)	3.58(3.65)	11.97(12.10)	6.30
[Nd(HNAAP)$_2$(NO$_3$)$_3$]	13.60(13.82)	49.13(50.56)	3.68(3.64)	11.91(12.06)	6.48
[Sm(HNAAP)$_2$(NO$_3$)$_3$]	14.52(14.31)	49.98(50.27)	3.67(3.62)	12.18(12.00)	6.98
[Gd(HNAAP)$_2$(NO$_3$)$_3$]	15.02(14.87)	50.01(49.94)	3.51(3.59)	12.01(11.92)	6.31
[Tb(HNAAP)$_2$(NO$_3$)$_3$]	14.87(15.02)	49.35(49.86)	3.49(3.59)	11.78(11.90)	7.66
[Dy(HNAAP)$_2$(NO$_3$)$_3$]	15.22(15.29)	48.97(49.69)	3.59(3.58)	12.03(11.86)	6.91
[Ho(HNAAP)$_2$(NO$_3$)$_3$]	15.33(15.49)	49.12(49.58)	3.61(3.57)	11.78(11.83)	7.15
[Y(HNAAP)$_2$(NO$_3$)$_3$]	8.85(8.99)	52.97(53.39)	3.78(3.84)	12.87(12.74)	6.17

[a] Calculated values in parentheses. [b] ~10^{-3} M solutions used; ohm^{-1} cm^2 mol^{-1}.

0020-1693/85/$3.30

TABLE II. Infrared Spectral Data[a] (in cm^{-1}), Magnetic Moments and Thermal Decomposition Data of Lanthanide Nitrate Complexes of HNAAP.

Complex	$\nu_{(C=O)}$	$\nu_{(C=N)}$	$\nu_{4(NO_3)}$	$\nu_{1(NO_3)}$	$\nu_{2(NO_3)}$	μ_{eff} (BM)	Decomposition temperature from TG (°C)
$[La(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1030m	–	200
$[Pr(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1030m	3.53	200
$[Nd(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1030m	3.46	200
$[Sm(HNAAP)_2(NO_3)_3]$	1605vs	1575vs	1455vs	1300vs	1025m	1.58	200
$[Gd(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1460vs	1300vs	1025m	8.09	220
$[Tb(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1025m	9.73	220
$[Dy(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1025m	10.65	220
$[Ho(HNAAP)_2(NO_3)_3]$	1610vs	1575vs	1455vs	1300vs	1025m	10.73	200
$[Y(HNAAP)_2(NO_3)_3]$	1605vs	1575vs	1455vs	1300vs	1025m	–	200

[a] Abbreviations: vs = very strong; m = medium.

$(NO_3)_3$. They are grey non-hygroscopic solids soluble in polar solvents such as acetone, acetonitrile, methanol and ethanol and insoluble in less polar solvents such as benzene, carbon tetrachloride and chloroform. The molar conductance values of the complexes in nitrobenzene (Table I) indicate that they behave as non-electrolytes [6]. Hence these complexes may be formulated as $[Ln(HNAAP)_2(NO_3)_3]$.

The IR spectra of all the complexes (Table II) indicate that the HNAAP bind the metal through carbonyl oxygen and azomethine nitrogen: the C=O and C=N bond stretching frequencies of the complexes are considerably lower (~30 and ~15 cm^{-1}, respectively) than the corresponding ones (around 1635 and 1590 cm^{-1}, respectively) of the free ligand [2, 3, 7–9]. The phenolic OH and C–O stretching vibrations (around 3440 and 1310 cm^{-1}, respectiely) of HNAAP are not shifted appreciably in the complexes showing that the phenolic oxygen is not involved in coordination [10, 11]. Thus HNAAP acts as a neutral bidentate ligand in these complexes coordinating through the carbonyl oxygen and azomethine nitrogen forming a 5-membered chelate ring. The IR spectra (Table II) also show the presence of unidentate nitrate groups in accordance with the literature [3, 12]. Thus, a coordination number of seven may be assigned to these complexes.

All the complexes show a very broad band with absorption maximum around 22.50 kK in the visible region which may be assigned to the ligand to metal charge transfer transition. This charge transfer band is so strong that most of the f–f bands of the lanthanide ions are masked in these complexes. However, in the Nd complex the following f–f bands are observed, the tentative assignments of which are given in brackets: 17.17 kK ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$); 13.12 kK ($^4I_{9/2} \rightarrow {}^4F_{7/2}$); 12.54 kK ($^4I_{9/2} \rightarrow {}^2H_{9/2}$). An appreciable red-shift is observed in these f–f bands compared to the aquo ion [13, 14]. The Sinha covalency parameter (δ = 1.530) calculated for the Nd complex indicates considerable covalency in the metal–ligand bond [14].

The observed magnetic moments (Table II) of the complexes agree closely with the Van Vleck values [15] which show that the 4f electrons are not involved in bonding in these complexes.

The thermogravimetric analysis (TG) of the complexes (Table II) shows that the complexes are stable up to ~200 °C. They undergo thermal decomposition in 3 stages as denoted by 3 well-defined DTG peaks around 265–305, 325–410 and 430–470 °C. The decomposition of these complexes is complete in the range 480–560 °C forming the respective stable lanthanide oxides.

Acknowledgements

The author thanks Prof. Dr. C. G. R. Nair, Prof. Dr. C. P. Prabhakaran and Dr. P. Indrasenan for helpful discussions and Prof. Dr. C. P. Joshua for providing the necessary facilities in the Department of Chemistry, University of Kerala.

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