Asian Journal of Chemistry Vol. 6, No. 3 (1994), 601–605

Studies on Lanthanide (III) Complexes with N-Substituted Thioureas

S.A. KALYANI and A.S.R. MURTY*
Department of Chemistry,
Karnatak University, Dharwad-580 003, India.

Lanthanide (III) complexes of N-thioureas of the type $[MX_{3-m}nL]\ X_m2H_2O$ [M = Sm(III), Eu(III), Dy(III) and Y(III); X = NO_3^-, Cl^-; L=*m*-chlorophenyl thiourea (*m*-Clptu), *p*-chlorophenyl thiourea (*p*-Clptu), *m*-hydroxy phenyl thiourea (*m*-OHptu); m = 0, 1 and n = 3, 4] have been synthesized and characterized by elemental analysis, conductivity, magnetic moment, IR and visible spectra and thermal studies. All complexes are nonelectrolytes except $[Sm(NO_3)_2(m\text{–}OHptu)_4]\ NO_3\cdot 2H_2O$ which is 1 : 1 electrolyte. Barring Y(III) complexes, all others exhibit paramagnetism. While IR spectral data unequivocally suggest S bonding of ligands, results from visible spectra evaluate the extent of covalency.

INTRODUCTION

The majority of the lanthanide complexes involve nitrogen and oxygen containing ligands and a few reports are available on the sulphur ligated complexes of the lanthanide ion. This is probably due to the large ionic radii of the lanthanides (III) and small electronegativity of S atom which result in the formation of weak complexes. Although work has been done on Ln(III) complexes derived from thiourea[1] by other investigators and N-thiourea[2] by our school, the detailed spectroscopic study of Ln(III) thioureas has not been done till now. So we report here a systematic study of lanthanides with N-substituted thioureas.

EXPERIMENTAL

Lanthanide(III) oxides were procured from Koch-Light Laboratories, England and Indian Rare earths Ltd, Alwaye. Reagent grade chemicals were used to prepare ligands and complexes. N-thioureas *i.e.*, *m*-chlorophenyl theourea, *p*-chlorophenyl thiourea and *m*-hydroxy phenyl theourea have been synthesized adopting methods from published literature.[3, 4]

Hydrated lanthanide(III) chlorides or nitrates were obtained by dissolving the oxide in the corresponding dilute acid and evaporating the excess acid. A mixture of $LnCl_3\cdot nH_2O$ or $Ln(NO_3)_3\cdot nH_2O$ (0.001M) and the corresponding ligand

---

For correspondence and present address:
Retired Professor, 3-29-14/6, Krishnanagar, 7th Lane,
Guntur-522 002, (Andhra Pradesh), India.

(0.003 M) was dissolved in absolute ethanol (*ca* 50 cm^3). The mixture was refluxed for 18 to 25 h. until turbidy appeared. After concentration, the mass was extracted with petroleum ether (*ca.* 50 cm^3, 40–60°C). It was filtered and washed successively with a 1 : 1 mixture of ethanol and pet-ether and pet-ether alone. The complex was dried in *vacuo* over P_2O_5.

The metal content of the complex was estimated as oxinate[5] gravimetrically. Determination of **N** by Kjeldahl's method, **S** as barium sulphate and **X** as silver halide were carried out in accordance with the standard methods.[6] The data are presented in Table 1.

TABLE 1
PHYSICAL AND ANALYTICAL DATA FOR THE COMPLEXES

Sl. No.	Complex	% Found (Calcd.)				μ_{eff} (BM)
		M	N	S	Cl/Br	
I	$[Sm(NO_3)_3(m\text{-}Clptu)_4]2H_2O$	13.41 (13.44)	13.79 (13.77)	11.45 (11.46)	12.63 (12.67)	1.76
II	$[EuCl_3(m\text{-}Clptu)_4]2H_2O$	14.59 (14.60)	10.72 (10.76)	12.29 (12.32)	23.88 (23.84)	3.55
III	$[DyCl_3(m\text{-}Clptu)_4]2H_2O$	15.42 (15.45)	10.69 (10.66)	12.29 (12.20)	23.58 (23.60)	10.33
IV	$[Y(NO_3)_3(m\text{-}Clptu)_3]2H_2O$	10.18 (10.21)	14.45 (14.47)	11.06 (11.04)	12.24 (12.21)	—
V	$[EuCl_3(p\text{-}Clptu)_4]2H_2O$	14.60 (14.60)	10.73 (10.76)	12.31 (12.32)	23.86 (23.84)	3.63
VI	$[DyCl_3(p\text{-}Clptu)_4]2H_2O$	15.48 (15.45)	10.59 (10.66)	12.23 (12.30)	23.61 (23.60)	9.82
VII	$[Sm(NO_3)_3(o\text{-}MeOptu)_3]2H_2O$	16.39 (16.36)	13.75 (13.72)	10.36 (10.46)	—	1.76
VIII	$[Y(NO_3)_3(o\text{-}MeOptu)_3]2H_2O$	10.29 (10.37)	14.74 (14.70)	11.15 (11.21)	—	—
IX	$[Sm(NO_3)_3(p\text{-}Brptu)_3]2H_2O$	14.11 (14.11)	11.88 (11.83)	8.96 (8.97)	23.52 (23.49)	1.54
X	$[Y(NO_3)_3(p\text{-}Brptu)_3]2H_2O$	8.90 (8.85)	12.56 (12.55)	9.57 (9.58)	23.88 (23.87)	—
XI	$[Sm(NO_3)_2(m\text{-}OHptu)_4]NO_3\ 2H_2O$	14.38 (14.39)	14.73 (14.74)	12.21 (12.26)	—	1.76
XII	$[Y(NO_3)_3(m\text{-}OHptu)_3]2H_2O$	10.89 (10.90)	15.42 (15.46)	11.81 (11.79)	—	—

RESULTS AND DISCUSSION

All the complex are either grey or yellow in colour. The molar conductance values of complexes [10^{-3}M solution] subscribe to 1 : 1 electrolytic nature for complex XI (80 mho cm^2 mole^{-1}) and non electrolytic behaviour [6–70 mho cm^2 mole^{-1}] for others.[7] The paramagnetic behaviour of Ln(III) ions is consistent with the presence of n unparied electrons (n = 1 to 7). Slight deviation of experimental values from those of Van-Vleck[8] indicate participation of 4f electrons to some extent in bond formation. The slightly higher values observed in case of Sm(III) complexes may presumably be due to TIP[9] on account of J separation. In Sm(III) complexes, the energy difference between the ground level ($^6H_{5/2}$) and the next higher J level ($^6H_{7/2}$) is only of the order of KT leading to population of the higher energy levels and susceptibilities due to first order zeeman effect.[10]

The important IR frequencies exhibited by the ligands and complexes are assigned according to the procedure laid down by Jensen and Nielsen.[11] The N-thioureas exhibit three medium sharp bands in the region 3450–3100 cm^{-1} due to νNH vibration. These bands suffer positive shift (15–20 cm^{-1}) on complexation leading to non participation of **N** in bonding. Appearance of νOH at lower region [*ca* 3100 cm^{-1}] in hydroxy thiourea complexes compared to free νOH [ca 3500 cm^{-1}] indicates the presence of inter and intramolecular hydrogen bonding. Weakening of hydrogen bonding can be expected in case of Sm(III) and Y(III) complexes due to slight positive shift experienced by νOH. All complexes possess a broad band at 3600–3500 cm^{-1} and a shoulder at 1680–1640 cm^{-1} indicating the presence of water of hydration.[12]

A strong bond appearing in the region 1630–1600 cm^{-1} due to δNH_2 vibration is shifted to slightly higher frequencies (5–10 cm^{-1}). This is suggestive of non-participation of **N** in bond formation. The 1480–1550 cm^{-1} band which is due to ν_{asy} NCN + δNH_2 shows positive shift on coordination indicating the increased double bond character between carbon and nitrogen atoms. The bands observed in the region 800–700 cm^{-1} and 700–630 cm^{-1} are assigned to νCS with slight contribution of νCN and νCS respectively. The negative shift (5–10 cm^{-1}) along with reduction in intensity of these two bands indicate that **S** is involved in coordination. The bands recorded for νM–S(400–300 cm^{-1})[13] also provide evidence for **S** coordination. The νM–Cl bands are observed in the region 250–300 cm^{-1}.

The IR spectrum of free NO_3^- (D_{3h} symmetry) exhibits ν_2, ν_3, ν_4 and ν_1 (weakly active) bands and it falls into c_{2V} symmetry on coordination to the central Ln(III) either as mono or bidentate where all four bands are IR active.[14] The difference between ν_1 (*ca.* 1480 cm^{-1}) and ν_4 (*ca.* 1389 cm^{-1}) in complexes being less than 100 confirms monodenate nature of NO_3^-.

The electronic spectra of Sm(III) complexes in methanol show a shift towards lower energy as compared to those of the aquo ions due to the relative nephelauxetic effect (β')[15]. If β' values become less than unity, it indicates the covalent bonding between metal and ligand. Sinha[16] proposed a scale to express the covalency ($\delta\%$) of metal ligand bond in lanthanide complexes. The bonding parameter $b^{1/2}$ the magnitude of which suggests the comparative involvement of the 4f orbital in metal-ligand bond formation is related to nephelauxetic ratio (β').[17] The data are presented in Table 2.

The nephelauxetic parameter (β') being less than unity while Sinha's covalency parameter ($\delta\%$) and the bonding parameter ($b^{1/2}$) being positive indicate some what covalent character of metal-ligand bond.

TABLE 2
VISIBLE SPECTRAL DATA FOR THE COMPLEXES

Complex	Possible assignments	Band Maximum (cm^{-1}) Sm^{3+} ion	Band Maximum (cm^{-1}) Complex	β′	Other parameters
I	$^4F_{9/2} \leftarrow {}^6H_{5/2}$	25000	24802	0.9921	$\beta'_{av} = 0.9985$
	$^4P_{5/2} \leftarrow {}^6H_{5/2}$	24062	24004	0.9976	$\delta = 0.1502$
	$^4I_{13/2} \leftarrow {}^6H_{5/2}$	21570	21570	1.0000	$b^{1/2} = 0.0274$
	$^4I_{11/2} \leftarrow {}^6H_{5/2}$	20903	20991	1.0042	
VII	–do–	Same as Above			Same as Above
IX	–do–	25000	24802	0.9921	$\beta'_{av} = 0.9990$
		24062	24039	0.9990	$\delta = 0.1001$
		21570	21589	1.0009	$b^{1/2} = 0.0158$
		20903	20991	1.0042	
XI	–do–	25000	24826	0.9930	$\beta'_{av} = 0.9970$
		24062	24038	0.9990	$\delta = 0.3009$
		21570	21552	0.9992	$b^{1/2} = 0.0387$
		20903 ·	20833	0.9967	

The TG analysis confirms the presence of two noncoordinated water molecules which are lost at 80–120°C in complexes. Further loss at *ca.* 310°C amounts to one NO_3^- and one ligand molecule in case of $[Sm(NO_3)_2(m\text{–}OHptu)_4]$ $NO_3 \cdot 2H_2O$. Thus the conclusions drawn from TG confirm the earlier results deduced from IR and conductivity measurements. The energy of activation and order of reaction have been evaluated from TG data using Freeman-Carrol equation[18] which may be written as

$$\left[\frac{\log(dw/dt)}{\log Wr}\right] = -\frac{E}{2.303R}\left[\frac{(1/T)}{\log Wr}\right] + n$$

Where E = energy of activation, R = gas constant, n = order of decomposition, T = temp (K), Wr = difference between the total loss and loss in weight at time t, *i.e.*, W_0–W_t and dw/dt = value at rate of weight loss obtained from the loss in wt *vs* time curve at specified times. The plots of [log (dw/dt)/log Wr] *vs* [(1/r)/log Wr] have been found to be linear with an intercept equal to one in complexes II and VI which indicates the order of reaction to be one. Much importance is not given for this parameter. The values of energy of activation from the slope (–E/2.303 R) of the plots are found to be 9.15 and 10.06 Kcals mol^{-1} respectively.

ACKNOWLEDGEMENT

The authors acknowledge the services rendered by RSIC, IIT Madras and by Dr. A. Venkataraman, Gulbarga University, Gulbarga for spectral and thermal studies respectively. One of the authors (SAK) thanks UGC, New Delhi for awarding Teacher fellowship.

REFERENCES

1. Yu. G. Sakharova, V.N. Perov and V.I. Loginov, *Zh. Neorg. Khim.*, **23,** 632 (1978).
2. M.B. Adi and A.S.R. Murty, *Curr. Sci (India),* **47,** 539 (1978).
3. F. Kurzer, Organic synthesis, Vol. 31, p–21, Ed by R.S. Schreiber, John Wiley and Sons, New York (1958).
4. P.K. Feng and Q. Fernando, *J. Am. Chem. Soc.*, **82,** 2115 (1960).
5. A.S.R. Murty, T.P. Sharma, and B.H.S.V. Raghava Rao, *Zeit. Fur, Analy. Chem.*, **145,** 418 (1955).
6. W.W. Scott, Standard Methods of Chemical Analysis, 6th Edn., Vol. II, Part A, D. Von Nostrand Co., Inc, New York, p 1202 (1963).
7. W.J. Geary, *Coord. Chem. Rev.*, **7,** 110 (1971).
8. J.H. Van Vleck and A. Frank, *Phys. Rev.*, **34,** 1494 (1929).
9. B.N. Figgis and J. Lewis., Techniques of Inorganic Chemistry, Interscience, New York, Vol. 4, 137 (1965).
10. T.J. Marks, *Prog. Inorg. Chem.*, **24,** 57 (1978).
11. K.A. Jensen and P.H. Nielsen, *Acta Chem. Scand.*, **20,** 597 (1966).
12. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd Edn. Wiley, New York (1970).
13. K.W. Bagnall and E. Yanir, *J. Inorg. Nucl. Chem.*, **36,** 777 (1974).
14. N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4,** 804 (1965).
15. C.K. Jorgensen, *Mat. Fgs. Med. Dan. Vid. Selsk,* **30,** No. 22 (1956).
16. S.P. Sinha, *Spectrochim. Acta.*, **22,** 57 (1966).
17. D.E. Henrie and G.R. Choppin, *J. Chem. Phys.*, **49,** 477 (1986).
18. E.S. Freeman and B. Carrol., *J. Phys. Chem.*, **62,** 394 (1958).

(*Received:* 16 June 1993; *Acceptd*: 30 September 1993) AJC-699