Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2536-2540

Synthesis and Characterization of Some Lanthanide(III) Chelates of Phenyl Thiosemicarbazones

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A series of nine complexes of lanthanide(III) ion with salicylaldehyde N(4)-phenylthiosemicarbazone (SPT) and various anions were synthesized and characterized. From spectral investigations along with elemental analysis, conductance and magnetic measurements, the general formula of the complexes were assigned to be [Ln(SPT)$_2$X] (where Ln = La(III), Pr(III) or Nd(III), X = NO_3^-, NCS^- and ClO_4^-, SPT = salicylaldehyde N(4)-phenylthiosemicarbazone. Thermal stabilities of complexes were sttudied from TG and DTG curves.

Key Words: Synthesis, Characterization, Lanthanide(III) chelates, Salcylaldehyde N(4)-phenylthiosemicarbazone.

INTRODUCTION

Chemotherapeuticaly thiosemicarbazones have assumed great importance as they possess antibacterial, antiviral and antitumour activities. Thiosemicarbazones which comprise a well known group of N–S donors have been extensively used for complexation in recent years. The reported activity of transition metal complexes of thiosemicarbazone and its derivatives against smallpox[1], virus diseases[2] and certain type of tumours[3] prompted us to investigate the complexes containing this type of ligands. The biological activity of thiosemicarbazone is due to their ability to form chelates with trace metals[4]. The present investigation is concered with synthesis of nine new lanthanide (III) chelates of salicylaldehyde N(4)-phenyl thiosemicarbazone (SPT) and their characterization on the basis of elemental analysis, estimation of metal and anion contents determination of molar mass, measurement of molar conductance and magnetic moments along with spectral and thermal studies.

EXPERIMENTAL

The reagents used were of analytical grade. The solvents used were purified by distillation.

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Preparation of ligand: The ligand, salcylaldehyde N(4)-phenyl thiosemicarbazone was prepared[5] by refluxing equimolar (0.01 mol) mixture of N-phenylthiosemicarbazide and salicylaldehyde in methanol for *ca.* 3 h. The pale yellow solid separated was filtered washed and dried. It was recrystallized from methanol (m.p. 176ºC, yield 75 %).

Preparation of complexes: The nitrato and perchlorate complexes were prepared by refluxing methanolic solution of ligand (SPT) with the metal salt in molar ratio 2:1 for *ca.* 8 h. The solid complex separated on concentration was filtered was washed with methanol and petroleum ether to remove the excess ligand and dried over P_4O_{10} *in vacuo*. The nitrato complexes were converted to thiocyanato complexes[6] by refluxing the nitrato complex with stoichiometric amounts of NH_4NCS to replace the NO_3^- by NCS^-.

The lanthanide contents of the complexes were determined gravimetrically as metal oxide by oxalate-oxide method[7]. The nitrato content was estimated gravimetrically using nitron reagent[8] and perchlorate content by Kurz method[9]. The thiocyanate content was determined gravimetrically as AgSCN[8]. The molar conductivities of the complexes in methanol were measured at room temperature using digital control dynamics conductivity meter. The solution had a concentration around 10^{-3} M. The IR spectra of the ligand and complexes were recorded in potassium bromide pellates in the range 4000-400 cm^{-1} on a Perkin Elmer FT-IR spectrometer. The elemental analysis was carried out by micro analytical method. Magnetic susceptibility of the complexes at room temperature was measured by Gouy method[10]. The electronic spectra of the ligand and the complexes in methanol were recorded in Jasco V-550 UV-Vis spectrometer in the range 900-200 nm. Rast method was employed to determine the molar mass of the complexes using biphenyl as solvent[11].

RESULTS AND DISCUSSION

All the complexes were non hygroscopic solids insoluble in benzene and petroleum ether but are sparingly soluble in acetonitrile, methanol and nitrobenzene and completely soluble in DMSO. Analytical data of the complexes are presented in Table-I. The electrical conductivity measurements in the three different solvents, *viz.*, nitrobenzene, methanol and acetonitrile confirm non electrolytic behaviour.

The IR spectrum of the ligand shows a medium intensity band at 3000 cm^{-1} due to intramolecular H-bonded ν(OH) group[12]. This band is absent in the spectra of the complexs indicating the dissociation of phenolic proton and coordinated metal ion through deprotonated phenolic oxygen atom[12]. Another band observed at 1297 cm^{-1} in the spectrum of the ligand is attributed to phenolic ν(C–O) stretching[13] and it has been shifted to higher frequency in the spectra of the complexes. This shift supports the formation of (Ln–O) bond[12,13]. The absence of ν(S–H) band at *ca.* 2600 cm^{-1} in the spectrum of free ligand indicates thatg the ligand remains in thioketoform in solid state[14]. The two bands observed at 1271 and 750 cm^{-1} are assigned to ν(C–S) vibrations[15]. The shift of these bands to lower frequencies in the spectra of the complexes indicates the coordination of the ligand through the S atom of thioketo form. The ν(C–N) observed at 1616 cm^{-1} in spectrum of ligand shows a downward shift in complexes, suggesting the participation of this group in coordination[16]. The mode of coordination through deprotonated phenolic oxygen, azomethine nitrogen and thioketosulphur atoms is further confirmed by appearance of new bands in the IR region 480-505 cm^{-1}, 410-420 and 320-360 cm^{-1} due to ν(Ln–N), ν(Ln–O) and ν(Ln–S) vibrations, respectively. Thus, the ligand SPT behaves as a monobasic tridentate chelating agents in all complexes of Ln(III) ions. In the case of nitrato complexes three additional bands due to coordinated nitro group are also observed which are absent in spectra of the ligand and other anionic complexes. They appear at 1445, 1364 and 1022 cm^{-1} which are assigned to ν_4, ν_1 and ν_2 modes of coordinated nitrate ions. The magnitude of separation between ν_4 and ν_1 is found in the order of 81 cm^{-1} supporting the unidentate coordination of nitrate ion.

TABLE-1
ANALYTICAL DATA OF LANTHANIDE(III) CHELATES OF SALCYLALDEHYDE N(4)-PHENYL THIOSEMICARBAZONE

Complex	Found (Calcd.) % Analysis						
	m.w.	Ln	C	H	N	S	Anion
[La(SPT)$_2$NO$_3$]	740	18.80	45.22	3.10	11.13	8.46	8.17
	(741)	(18.74)	(45.35)	(3.24)	(11.33)	(8.64)	(8.36)
[Pr(SPT)$_2$NO$_3$]	745	18.72	45.34	3.30	11.41	8.50	8.21
	(743)	(18.96)	(45.22)	(3.23)	(11.30)	(8.61)	(8.34)
[Nd(SPT)$_2$NO$_3$]	744	19.40	44.90	3.10	11.12	8.43	8.41
	(746)	(19.32)	(45.02)	(3.21)	(11.25)	(8.57)	(8.30)
[La(SPT)$_2$NCS]	735	18.69	45.48	3.36	11.48	8.59	7.98
	(737)	(18.84)	(45.59)	(3.25)	(11.39)	(8.68)	(7.87)
[Pr(SPT)$_2$NCS]	740	18.90	45.58	3.16	11.45	8.74	7.92
	(739)	(19.06)	(45.47)	(3.24)	(11.36)	(8.66)	(7.84)
[Nd(SPT)$_2$NCS]	744	19.21	45.35	3.30	11.40	8.71	7.90
	(742)	(19.43)	(45.26)	(3.23)	(11.31)	(8.62)	(7.81)
[La(SPT)$_2$ClO$_4$]	776	17.72	43.05	2.98	10.84	8.18	12.85
	(778)	(17.84)	(43.18)	(3.08)	(10.79)	(8.22)	(12.77)
[Pr(SPT)$_2$ClO$_4$]	781	18.16	42.92	3.10	10.82	8.15	12.81
	(780)	(18.05)	(43.05)	(3.06)	(10.76)	(8.20)	(12.73)
[Nd(SPT)$_2$ClO$_4$]	782	18.31	42.93	3.12	10.80	8.21	12.56
	(784)	(18.40)	(42.87)	(3.06)	(10.71)	(8.16)	(12.67)

The infrared spectra of thiocyanate complexes exhibit three additional bands at 2050, 810 and 480 cm^{-1} which are assigned, respectively to ν(C–N), ν(C–S) and δ(NCS) modes of the coordinated thiocyanate ion. Since ν(CN) is lower than 2100 cm^{-1} and ν(CS) vibrations greater than 720 cm^{-1}, the thiocyanate ion is coordinated to the metal ion through nitrogen atom in unidentate fashion. The spectrum of perchlorato complex shows three additional bands at 1137, 1090 and 625 cm^{-1} assigned to ν_4, ν_1 and ν_3 modes of unidentately coordinated perchlorate ion. The nature of bonding of the various anions are further supported by the non electrolytic behaviour of all the complexes.

The ^1H NMR spectra of the ligand (SPT) and its complex have been recorded in DMSO-d_6. The OH proton signal at δ 11.5 present in the ligand is absent in the spectrum of the complex indicating the SPT behaves as a monobasic ligand and coordinating the metal ion through deprotonated phenolic oxygen atom. A strong signal at δ 8.4 ppm due to CH=N of ligand undergoes a downward shift on complexation indicating the participation of azomethine nitrogen in bonding. Aromatic protons appear as multiplet in the ligand and characteristic shift occurs on complexation. SPT does not show any peak attributable to (S–H) proton indicating that it exist in the thioketoform[17].

The electronic spectrum of the ligand, SPT exhibit two bands at 204 and 268 nm. The band appearing at 204 is assigned to $\pi\rightarrow\pi^*$ transition and the band appearing at 268 nm is assigned to $n\rightarrow\pi^*$ transition of azomethine group. The spectra of the complexes exhibit red shift in $\pi\rightarrow\pi^*$ transition in the range 208-212 nm and blue shift in $n\rightarrow\pi^*$ transition in the range 260-264 nm which further confirms the mode of coordination of ligand. There is an additional band at 310 nm in the spectra of complexes which is not present in the ligand. This band is attributed to L→M charge transfer. There is no absorption band due to *f-f* transition in the electronic spectra of the complexes. Such bands being weak and obscured by the strong bands due to intra ligand as well as L→M charge transfer transition.

The magnetic moment studies on complexes show very little deviation from Van Vleck values indicating little participation of 4*f* electrons in bonding, as these electrons are well shielded by $5s^2$ $5p^6$ octet. Lanthanum complexes are diamagnetic as expected for their noble gas configuration of the tripositive ions. All the complexes of remaining lanthanide ions are paramagnetic. The magnetic moment values of the present complexes are in agreement with values reported for the free lanthanide ions. There 4*f* electrons are not disturbed by the ligand field and 4*f* electrons are not involved in bonding in present complexes.

Thermal decomposition studies were conducted for nitrato complexes and their thermal stabilities were compared. All the complexes decompose above 473 K which shows the absence of water and other coordinated solvent molecules. The TG plateau upto 473 K. It undergoes a single stage decomposition as indicated by the DTG peak at 499 K. This stage of decomposition occurs with a mass loss of *ca*. 73 % which may be due to the dissociation of two ligand molecules. The decomposition continues with a gradual decrease in weight and a constant weight due to stable lanthanum oxide is obtained at *ca*. 875 K. The residual mass is *ca*. 22 %. The independent pyrolysis also shows that the final decomposition product is lanthanum oxide which is in confirmity with mass loss data obtained from TG. The TG plateau upto 483 K for the complex, [Nd $(SPT)_2NO_3$] indicates its stability region. It undergoes a single stage decomposition as indicated by DTG peak at 503 K. This stage of decomposition occurs with a mass loss of *ca*. 72 % which may be due to the dissociation of two ligand molecules. The decomposition continues with a decrease in weight and constant weight due to the formation of Nd_2O_3 at *ca*. 875 K. The residual mass is 22.5 % which shows the final product as Nd_2O_3 which is in agreement with independent pyrolysis experiment.

On the basis of these observations, it is concluded that SPT is acting as tridentate mono negative ligand coordinating through azomethine nitrogen, deprotonated phenolic oxygen and thioketo-sulphur atoms. Thus the proposed formulae of the nitrato, thiocyanato and perchlorato complexes are $[Ln(SPT)_2NO_3]$, $[Ln(SPT)_2NCS]$ and $[Ln(SPT)_2ClO_4]$. Thus coordination number seven is assigned to lanthanide ion in all these complexes.

REFERENCES

1. B. Beecroft, M.J.M. Campbell and R.G. Rowiak, *J. Inorg. Nucl. Chem.*, **36**, 55 (1974).
2. M.J.M. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975).
3. E. Hoggartl, A.R. Martin, N.E. Stoney and E.H.P. Young, *Br. J. Pharmacol.*, **4**, 248 (1949).
4. N.C. Saha, R.J. Butcher, S. Chaudhari and N. Saha, *Polyhedron*, **22**, 375 (2003).
5. A.I. Vogel, Textbook of Practical Organic Chemistry, Longmans, London, edn. 3 (1956).
6. G. Rajendran and K.G. Usha Devi, *Asian J. Chem.*, **15**, 405 (2003).
7. I.M. Kolthoff and P.J. Elving, Treatise on Analytical Chemistry, Inter Science, New York, Vol. 8, Part II (1963).
8. A.I. Vogel's, Textbook of Quantitative Chemical Analysis, Addison Wesley Longman, edn. 5 (1999).
9. E. Kurtz, G. Kober and M. Berl, *Anal. Chem.*, **30**, 1983 (1958).
10. P.W. Selwood, Magnetochemistry, Inter Science, New York, edn. 2 (1958).
11. W.G. Palmer, Experimental Physical Chemistry, University Press, Cambridge (1954).
12. J.T. Makode and A.S. Answar, *Indian J. Chem.*, **43A**, 2120 (2004).
13. P.K. Dwivedi, A.K. Das and P.M. Mishra, *Asian J. Chem.*, **15**, 1439 (2003).
14. M. Yildiz, B. Dugler, S.Y. Koyancu and B.M. Yapier, *J. Indian Chem. Soc.*, **81**, 7 (2004).
15. S.D. Dhumwad, K.B. Gudasi and T.R. Gudar, *Indian J. Chem.*, **33A**, 320 (1994).
16. P. Bindhu and M.R.P. Kurup, *Indian J. Chem.*, **38A**, 388 (1999).
17. P. Bindhu and M.R.P. Kurup, *Indian J. Chem.*, **36A**, 1094 (1997).

(*Received*: 2 December 2005; *Accepted*: 27 November 2006) AJC-5283