Asian Journal of Chemistry Vol. 16, No. 1 (2004), 156–162

Synthesis and Characterization of Mixed Ligand Complexes of Praseodymium(III), Neodymium(III), Samarium(III), Gadolinium(III) and Dysprosium(III) with Piperidinobenzylurea

M. VISWANATHAN* and G. KRISHNAN†
Department of Chemistry, S.N. College for Women, Kollam-691 001, India

A series of mixed ligand complexes of the lanthanide metal ions, *viz.*, Pr(III), Sm(III), Nd(III), Gd(III) and Dy(III) with a Mannich base derived form urea, piperidine and benzaldehyde and various anions such as chloride, nitrate, acetate, thiocyanate and perchlorate have been synthesized and characterized. The analytical data include elemental analysis, determination of molar mass, conductivity, magnetic, spectral and thermal studies. The complexes exhibit the following general formulae: (i) $[Ln(PBU)_2X_3]$ and (ii) $[Ln(PBU)_3ClO_4](ClO_4)_2$ where $Ln = Nd^{3+}$, Pr^{3+}, Gd^{3+}, Sm^{3+} and Dy^{3+}, $X = NO_3$, SCN, CH_3COO and Cl, PBU = piperidinobenzylurea.

Key Words: Lanthanides, Piperidinobenzylurea, Mixed ligand complexes.

INTRODUCTION

Studies of metal complexes with benzaldehyde based Mannich base, N,N′-bis(morpholinobenzyl) urea have been reported[1]. Another work reported is the synthesis and characterization of the Mannich base, piperidinobenzylurea (PBU), and some complexes of it with transition metals.[2] The present communication reports the preparation and characterization of some lanthanide metal complexes with piperidinobenzylurea, ($H_2N—CO—NH—CH(C_6H_5)—NC_5H_{10}$) (PBU) as the primary ligand and various uninegative anions as secondary ligands. The structure of the ligand, PBU, may be represented as in Fig. 1.

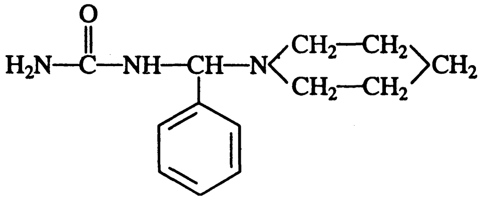

Fig. 1. Piperidinobenzylurea.

---

†Department of Chemistry, University College, Trivandrum-695 034, India.

EXPERIMENTAL

The ligand PBU was prepared by reported method. To a solution of urea in minimum quantity of water, added piperidine followed by benzaldehyde (1 : 1 : 1 mole ratio) maintaining a temperature of 10°C and stirred. The white solid precipitated was washed with water, filtered and crystallized from methanol. The purity of the ligand was checked by recording the IR spectrum and determining the m.p., 159–161°C.

Synthesis of metal complexes: The nitrato and chloro complexes of lanthanides were prepared by digesting an alcoholic solution containing the ligand (PBU) and the metal salt in 2 : 1 mole ratio for 1/2 h. It was concentrated to half its volume; the solid thus formed, was filtered, washed with methanol and dried over calcium chloride in a desiccator. The perchlorato complexes were prepared by digesting an alcoholic solution containing the ligand, PBU, and the metal salt in 3 : 1 mole ratio for about 1/2 h. It was concentrated to half of its volume; the solid thus formed was filtered, washed with methanol and dried over calcium chloride in a desiccator. The preparation of thiocyanato and acetato complexes involves two stages. In the first stage, the metal nitrato complexes with PBU were prepared. In the second stage, these nitrato complexes were treated with stoichiometric amounts of the salts (thiocyanate or acetate) to replace the nitrate ions.

The metal contents of the complexes were determined by gravimetric methods.[3] The carbon, hydrogen and nitrogen contents were determined by microanalytical method. The anions present in the complexes were also analysed wherever possible. The molar conductances of the complexes in methanol, acetonitrile, DMF and nitrobenzene (*ca.* 10^{-3} M solutions) were measured at room temperature (28 ± 2°C). Magnetic susceptibilities were measured at room temperature by the Gouy method. The infrared spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1} employing the KBr disc technique. In the case of chloro complexes, the infrared spectra were recorded in the far infrared region also. Molar masses of the complexes were determined, wherever possible, by the Rast method using biphenyl as the solvent.[4] The TG and DTG curves of the complexes, $[Gd(PBU)_2(CH_3COO)_3]$ and $[Dy(PBU)_2(NO_3)_3]$ were recorded on the thermal analyser from ambient temperature to 800°C. The mass percentage *vs.* temperature curves were redrawn in appropriate scales. Independent pyrolysis experiment in air was carried out for these complexes and loss of mass determined.

A total of twentyfive complexes of the lanthanide metal ions with PBU have been isolated which are non-hygroscopic crystalline solids. They are moderately soluble in methanol, nitrobenzene, DMF, acetonitrile and DMSO. Analytical data, molar masses, and magnetic moments of the complexes are given in Table-1 (a), (b) and (c). The molar conductance data (Table-2) were compared with the data available for standard substances to see whether anions are coordinated or not.[5, 6] It is observed that the nitrato, chloro, acetato and thiocyanato complexes behave like non-electrolytes in all the solvents used indicating that the anions are coordinated to respective metal ions. The comparatively higher values of conductance for the complexes in methanol are probably due to the partial displacement of the coordinated anions by polar methanol molecules.[7] The perchlorato complexes behave like 1 : 2 electrolytes in all the solvents used indicating that one perchlorate ion is coordinated to the metal ion whereas the remaining two are outside the coordination sphere.

TABLE-1 (a)
ANALYTICAL DATA, MOLAR MASS AND μ_{eff} OF THE COMPLEXES OF PIPERIDINOBENZYLUREA WITH LANTHANIDE NITRATES, CHLORIDES AND THIOCYANATES AT ROOM TEMPERATURE

Complex	Molar mass	μ_{eff} (BM)	%Analysis, found (calculated)	
			Metal	Anion
$[Pr(PBU)_2(NO_3)_3]$	780.20 (782.91)	3.55	17.98 (17.77)	23.04 (23.45)
$[Nd(PBU)_2(NO_3)_3]$	784.68 (796.24)	3.57	18.32 (18.11)	23.68 (23.35)
$[Sm(PBU)_2(NO_3)_3]$	814.40 (802.35)	1.62	18.56 (18.73)	25.42 (23.18)
$[Gd(PBU)_2(NO_3)_3]$	820.12 (809.25)	7.83	19.62 (19.43)	22.62 (22.83)
$[Dy(PBU)_2(NO_3)_3]$	822.84 (814.50)	10.46	19.78 (19.95)	22.62 (22.98)
$[Pr(PBU)_2Cl_3]$	701.10 (713.29)	3.54	19.90 (19.75)	14.70 (14.91)
$[Nd(PBU)_2Cl_3]$	728.20 (716.62)	3.56	20.32 (20.12)	14.92 (14.84)
$[Sm(PBU)_2Cl_3]$	711.31 (722.73)	1.38	20.94 (20.80)	13.50 (14.71)
$[Gd(PBU)_2Cl_3]$	740.21 (729.63)	7.86	21.30 (21.55)	14.88 (14.57)
$[Dy(PBU)_2Cl_3]$	720.82 (734.88)	10.50	22.24 (22.11)	14.94 (14.47)
$[Pr(PBU)_2(NCS)_3]$	768.20 (780.91)	3.50	17.62 (18.04)	21.64 (22.28)
$[Nd(PBU)_2(NCS)_3]$	776.22 (784.24)	3.58	18.02 (18.39)	21.56 (22.18)
$[Sm(PBU)_2(NCS)_3]$	780.64 (790.35)	1.34	19.60 (19.02)	22.48 (22.01)
$[Gd(PBU)_2(NCS)_3]$	774.82 (797.25)	7.86	19.22 (19.72)	22.38 (21.82)
$[Dy(PBU)_2(NCS)_3]$	814.50 (802.50)	10.48	20.62 (20.24)	21.20 (21.68)

TABLE-1 (b)
ANALYTICAL DATA, MOLAR MASS AND μ_{eff} OF THE COMPLEXES OF PBU WITH LANTHANIDE ACETATES AT ROOM TEMPERATURE

Complex	Molar mass	μ_{eff} (BM)	% Analysis, found (calculated)			
			M	C	H	N
$[Pr(PBU)_2(CH_3COO)_3]$	760.80	3.52	18.22	29.82	3.41	5.69
	(783.91)		(17.97)	(29.08)	(3.57)	(5.35)
$[Nd(PBU)_2(CH_3COO)_3]$	722.20	3.64	18.64	29.41	3.28	5.48
	(787.24)		(18.32)	(28.96)	(3.55)	(5.33)
$[Sm(PBU)_2(CH_3COO)_3]$	782.20	1.36	18.62	28.29	3.74	5.02
	(793.35)		(18.95)	(28.73)	(3.52)	(5.29)
$[Gd(PBU)_2(CH_3COO)_3]$	818.40	7.82	19.38	28.62	3.68	5.52
	(800.25)		(19.65)	(28.49)	(3.49)	(5.24)
$[Dy(PBU)_2(CH_3COO)_3]$	816.60	10.48	19.88	28.62	3.62	5.38
	(805.50)		(20.17)	(28.30)	(3.47)	(5.21)

TABLE-1 (c)
ANALYTICAL DATA AND μ_{eff} AT ROOM TEMPERATURE OF THE COMPLEXES OF PBU WITH LANTHANIDE PERCHLORATES

Complex	μ_{eff} (BM)	% Analyis, found (calculated)			
		M	C	H	N
$[Pr(PBU)_3ClO_4](ClO_4)_2$	3.50	11.82	13.12	1.78	3.29
		(12.37)	(13.70)	(1.67)	(3.69)
$[Nd(PBU)_3ClO_4](ClO_4)_2$	3.58	11.98	13.98	1.81	3.40
		(12.63)	(13.66)	(1.66)	(3.67)
$[Sm(PBU)_3ClO_4](ClO_4)_2$	1.34	13.42	13.66	1.91	3.82
		(13.09)	(13.59)	(1.65)	(3.65)
$[Gd(PBU)_3ClO_4](ClO_4)_2$	7.86	13.78	13.02	1.52	3.79
		(13.61)	(13.51)	(1.64)	(3.63)
$[Dy(PBU)_3ClO_4](ClO_4)_2$	10.48	14.38	13.98	1.82	3.38
		(14.01)	(13.48)	(1.63)	(3.62)

The room temperature magnetic moments of the lanthanide complexes with PBU are compared with the theoretical spin orbit coupling values[8] (the Hund values) of the respective lanthanide ion and they agree with each other with the exception of samarium(III) complexes. However, it is found that the experimental values of all the complexes including those of samarium(III) agree with the theoretical values calculated from Van Vleck formula.[9] The discrepancies in the case of samarium(III) complexes may be attributed to the fact that the first excited J states of Sm^{3+} are sufficiently close to their ground states so that these states mix with each other even at room temperature causing increase in magnetic moments. This is the reason for the breakdown of the spin orbit coupling models for samarium(III) complexes. The fact that the observed magnetic moments of the present complexes show very little deviation from the Van Vleck values suggests the non-participation of 4f electrons in the bond formation with the ligands.

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES OF PBU WITH LANTHANIDES IN DIFFERENT SOLVENTS

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})			
	Methanol	Acetonitrile	Nitrobenzene	DMF
$[Pr(PBU)_2(NO_3)_3]$	29.28	10.12	5.84	1.98
$[Nd(PBU)_2(NO_3)_3]$	32.16	7.62	3.42	2.62
$[Sm(PBU)_2(NO_3)_3]$	24.15	4.74	2.86	2.48
$[Gd(PBU)_2(NO_3)_3]$	27.34	3.12	2.22	2.56
$[Dy(PBU)_2(NO_3)_3]$	29.42	3.68	4.08	3.16
$[Pr(PBU)_2Cl_3]$	24.62	10.24	5.18	2.80
$[Nd(PBU)_2Cl_3]$	28.28	4.20	3.12	1.68
$[Sm(PBU)_2Cl_3]$	32.42	3.18	2.86	2.26
$[Gd(PBU)_2Cl_3]$	31.62	5.26	4.02	3.12
$[Dy(PBU)_2Cl_3]$	25.22	8.62	3.62	4.12
$[Pr(PBU)_2(NCS)_3]$	26.12	9.28	4.18	2.60
$[Nd(PBU)_2(NCS)_3]$	28.32	3.98	5.02	1.76
$[Sm(PBU)_2(NCS)_3]$	31.18	4.10	2.86	2.14
$[Gd(PBU)_2(NCS)_3]$	34.26	5.16	3.44	3.18
$[Dy(PBU)_2(NCS)_3]$	27.41	8.52	1.98	4.40
$[Pr(PBU)_2(CH_3COO)_3]$	29.16	8.28	5.26	3.02
$[Nd(PBU)_2(CH_3COO)_3]$	31.22	2.96	3.18	2.78
$[Sm(PBU)_2(CH_3COO)_3]$	35.10	4.20	2.14	3.02
$[Gd(PBU)_2(CH_3COO)_3]$	32.16	3.96	5.02	4.12
$[Dy(PBU)_2(CH_3COO)_3]$	26.34	8.50	4.24	1.92
$[Pr(PBU)_3ClO_4](ClO_4)_2$	194.25	242.12	54.12	152.15
$[Nd(PBU)_3ClO_4](ClO_4)_2$	198.14	248.18	56.02	151.85
$[Sm(PBU)_3ClO_4](ClO_4)_2$	188.82	250.12	55.23	155.12
$[Gd(PBU)_3ClO_4](ClO_4)_2$	195.00	245.16	58.12	160.10
$[Dy(PBU)_3ClO_4](ClO_4)_2$	189.10	260.06	55.58	149.80

The infrared spectra of the complexes exhibit characteristic absorptions of all the functional groups of the ligand but at a shifted position in the case of coordinated groups. The infrared spectra of the lanthanide complexes with PBU reveal the bidentate nature of the ligand with carbonyl oxygen and piperidine ring nitrogen acting as donor sites. The infrared spectrum of the ligand shows a band at 1660 cm^{-1} which is due to the carbonyl stretching frequency. The spectra of the complexes show negative shift to 1630–1640 cm^{-1} indicating the coordination through the carbonyl group. The band at 1160 cm^{-1} in the ligand which is due to the C—N—C stretching frequency shifts to 1135–1150 cm^{-1}. This shows the coordination through tertiary nitrogen of the piperidine ring. ν(NH) modes appearing in the spectrum of the ligand remain unaltered in the spectra of the complexes which points to the non-participation of nitrogen of NH_2 group in coordination. There are no additional bands in the region 3500 cm^{-1} showing the absence of any coordinated water. The additional bands in the region 440–420 cm^{-1} and 540–515 cm^{-1} are assigned to ν(Ln—O) and ν(Ln—N) respectively.

The chloro complexes show additional bands in the region 270–285 cm^{-1} which may be assigned to ν(Ln—Cl)[10]. The infrared spectra of nitrato complexes of lanthanide ions with PBU exhibit three additional bands at 1460, 1340 and 1020 cm^{-1} which are not present in the spectrum of the ligand, PBU. These three bands are attributed respectively to ν_4, ν_1 and ν_2 modes of the coordinated nitrate ions[11–13]. Since the difference between ν_4 and ν_1 is *ca.*120 cm^{-1}, it is suggested that the nitrate ions are coordinated unidentately to the lanthanide ions in the present complexes. Molar conductance values also support this conclusion. The infrared spectra of the thiocyanato complexes of lanthanide ions with PBU exhibit three additional bands at 2050–2040, 860 and 460 cm^{-1} which are assigned to ν(CN), ν(CS) and δ(NCS) modes of the coordinated thiocyante ion. It has been well established that ν(CN) occurs at a lower wavenumber around 2050 cm^{-1} in N-bonded complexes compared to the position around 2100 cm^{-1}. Moreover, ν(CS) mode appears in the range 860–780 cm^{-1}, for N-bonded complexes while it appears in the range 720–690 cm^{-1} for S-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to δ(NCS) mode around 460 cm^{-1} and S-bonded complexes[15–17] show several bands with lower intensities around 460 cm^{-1}. In view of these, it can be concluded that the thiocyanate ions are coordinated unidentately to lanthanide ions through the N-atom. Coordination of the thiocyanate ions agrees with the nonelectrolytic conductance values of the complexes.

The infrared spectra of the acetato complexes of lanthanides with PBU show two additional bands at 1670 and 1320 cm^{-1}. These bands are assigned respectively to asymmetric and symmetric stretching vibrations of coordinated carboxylate group. The large separation between these two bands confirms the unidentate coordination of carboxylate ion[18, 19]. Coordination of the acetate ions agrees with the conductance values of the acetato complexes of lanthanide ions with PBU as primary ligand.

In the infrared spectra of the perchlorato complexes of lanthanides with PBU as primary ligand, there are five additional bands which have no corresponding bands in the spectrum of the ligand. These additional bands are at 1100, 1080, 1020, 970 and 620 cm^{-1}. The bands at 1100, 1080 and 620 cm^{-1} may be assigned to the stretching vibrations of coordinated perchlorate ion. This shows the unidentate coordination of perchlorate ion to the lanthanide ions[20]. Two bands observed at 1020 and 970 cm^{-1} are attributed to $\nu(ClO_4)$ (ionic) present in the complexes. Thus, the infrared spectral data of the ligand and perchlorate complexes suggest the presence of ionic as well as unidentately coordinated perchlorate ions in these complexes. The conductance values of the complexes indicate that out of the three perchlorate ions, only one is coordinated to the metal ion whereas the remaining two ions are outside the coordination sphere.

The complexes of PBU with gadolinium nitrate, praseodymium thiocyanate, neodymium perchlorate, and samarium acetate were tested for their antibacterial activity (*E. coli, S. aureus, Ps. aeruginosa* and *K. pneumoniae*) by agar diffusion method. However, the test samples do not show any antibacterial activity at concentrations of 1 mg, 5 mg and 10 mg per disc, under the test conditions.

Thermal studies were conducted on $[Dy(PBU)_2(NO_3)_3]$ and $[Gd(PBU)_2(CH_3COO)_3]$. For the complex $[Dy(PBU)_2(NO_3)_3]$ the TG plateau up to 185°C shows that the complex is stable up to 185°C. The DTG curve has two peaks at 196.2 and 764.64°C. The TG curve shows a second plateau after 787.79°C indicating the completion of decomposition. At 196.2°C the complex shows a weight loss of 37.37%. This weight loss may be due to the breaking up of the organic moiety. A constant weight is obtained at 787.79°C. The residual weight is about 27.8% which is due to Dy_2O_3[21]. For $[Gd(PBU)_2(CH_3COO)_3]$, the plateau up to 190°C shows its stability up to this temperature. The DTG curve shows two peaks at 324.81 and 556.1°C showing the decomposition of the complex in two stages. The TG curve shows the second plateau at 671.17°C. This shows the completion of decomposition. The residual mass is about 22% showing that the decomposition product is Gd_2O_3. Independent pyrolysis also confirms that Gd_2O_3 is the decomposition product[21].

On the basis of the above studies, the following general formulae are suggested for the present complexes.

(i) $[Ln(PBU)_2X_3]$ where Ln = Nd^{3+}, Pr^{3+}, Gd^{3+}, Sm^{3+} and Dy^{3+} and X = NO_3^-, SCN^-, CH_3COO^- and Cl^- and (ii) $[Ln(PBU)_3ClO_4](ClO_4)_2$ where Ln = Nd^{3+}, Pr^{3+}, Gd^{3+}, Sm^{3+} and Dy^{3+}. Thus, a coordination number of 7 is assigned to the lanthanide ion in all the complexes.

REFERENCES

1. G.V. Prabhu, Ph.D. Thesis, Bharathidasan University (1991).
2. G.V. Prabhu and D. Venkappayya, *J. Indian Chem. Soc.*, **72**, 511 (1995).
3. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, John Wiley & Sons, New York (1963).
4. W.G. Palmer, Experimental Physical Chemistry, The University Press, Cambridge (1954).
5. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
6. G.B. Deacon, J.H.S. Green and R.S. Nyholm, *J. Chem. Soc.*, 3411 (1965).
7. D.K. Koppiar and S. Soundararajan, *Inorg. Nucl. Chem. Lett.*, **12**, 735 (1976).
8. E. Hund, *Z. Physik.*, **33**, 855 (1925).
9. J.H. Van Vleck and N. Frank, *Phys. Rev.*, **34**, 1494 (1929).
10. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York (1970).
11. J.R. Ferraro, *J. Mol. Spectra*, **4**, 99 (1960).
12. H. Mohanta and K.C. Dash, *J. Indian Chem. Soc.*, **54**, 166 (1977).
13. B.S. Manhas, A.K. Trikha and M. Singh, *J. Inorg. Nucl. Chem.*, **43**, 305 (1981).
14. P.C.H. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912 (1960).
15. A. Sabatini and Bertini, *Inorg Chem.*, **4**, 959 (1965).
16. J. Lewis, R.S. Nyholm and P.W. Smith, *J. Chem. Soc.*, 4590 (1961).
17. R.K. Agarwal and R.K. Sarin, *Pol. J. Chem.*, **67**, 1209 (1993).
18. A.V.R. Warrier and P.S. Narayanan, *Spectrochim. Acta*, **23A**, 1061 (1969).
19. K. Nakamoto, Y. Morimotto and A.E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).
20. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961).
21. R.K. Agarwal and S.K. Gupta, *Thermochim. Acta*, **99**, 357 (1986).

(*Received*: 22 March 2003; *Accepted*: 10 September 2003) AJC-3158