Asian Journal of Chemistry Vol. 7, No. 1 (1995), 223–224

NOTE

Rare Earth Metal Complexes of N-Phosphonomethyl Glycine

RAMESH PANGUNOORI and KASHI RAM*
Department of Chemistry
Osmania University, Hyderabad-500 007, India

Stability constants of binary complexes of the type M–A, where M = Pr(III), Nd(III), Gd(III) and A = N–phosphonomethyl glycine have been determined in aqueous medium at 303K and 0.10 M (KNO_3) ionic strength by using Irving-Rossotti pH titration technique.

Rare earth metal complexes have received considerable attention because of their application to lasers[1]. The attractiveness of these metal ions lies in their relatively high charge density and greater efficiency of complex forming tendency within a broad range of pH titration values. An exhaustive literature survey shows that no work has been carried out with N-phosphonomethyl glycine (NPMG) with rare earth metal ions so far. Again, the diversified applications of NPMG such as, the formation of stable low mobile complexes with bivalent metal ions which affect its uptake and transport efficiency in plants[2], its high herbicidal activity[3], its metal corrosion inhibition properties by complexation and its major application in radionuclide complexes for bone scintigraphy[4], have become the motivation for us to study its interaction with some inner transition metal ions, *viz.*, praseodymium, neodymium and gadolinium and the same is reported here.

All the reagents used were of AR grade. NPMG was synthesized by known procedure[5] and was purified by repeated recrystallization with water. The proton-ligand and metal-ligand formation constants of these metal complexes, as described elsewhere with transition[6] and alkaline earth[7] metal ions, have been determined by Irving-Rossotti potentiometric titration technique[8] in aqueous medium at 303K and at 0.10 M (KNO_3) ionic strength.

Potentiometric equilibrium curves were employed to calculate the values of metal-ligand formation number $\bar{n}$ ($0.1 < \bar{n} < 1.9$) which indicate the formation of both 1:1 and 1:2 metal chelates in solution. Since the pH region of NPMG complexation reactions falls in between 5–7, the value of its lowest acid dissociation constant ($pK_a = 2.22$) has not been considered in the calculation of metal-ligand stability constants. The proton-ligand ($\log K^H$) and metal-ligand formation constants ($\log K_n$) have been evaluated by using various computational techniques, *viz.*, half-integral method, point-wise calculations and least square measurements and the average values are reported in Table 1. The standard deviation for all the systems studied were found to be less than ± 0.05 log units. These values place the above metal ions in their natural order of stabilities, i.e., Pr(III) < Nd(III) < Gd(III), which is to be expected from a knowledge of stabilities of complexes with structurally related chelating ligands. This order is in accordance with their decreasing ionic size and increasing charge density from Pr(III) to Gd(III). It is also particularly interesting to compare the chelating tendency of NPMG with iminodiacetic acid (whose log K_1 and log K_2 values with Pr(III), Nd(III) and Gd(III) are 6.44, 6.50, 6.68 and 4.78, 4.89, 5.39 respectively[9]) wherein a simple substitution of a carboxylic group by a phosphonic one has increased its chelating capability enormously. This effect, however, does not appear to represent a more general trend for these type of aminopoly acids[10, 11].

TABLE 1
FORMATION CONSTANTS OF BINARY COMPLEXES OF N-PHOSPHONOMETHYL GLYCINE AT 303K AND 0.10 M (KNO_3) IONIC STRENGTH

Metal ion	Stability constant		
	log K_1	log K_2	log β_2
H^+	9.95	5.46	15.41
Pr(III)	11.31	9.15	20.46
Nd(III)	11.80	9.61	21.41
Gd(III)	12.25	10.00	22.25

ACKNOWLEDGEMENT

The authors express their gratitude to Prof. M. Govind Ram Reddy, Principal, UCS, Osmania University for his constant encouragement and Prof. K.S. Sastry, Head, Department of Chemistry, Osmania University, Hyderabad for rendering research facilities.

REFERENCES

1. E.J. Schimitschek and E.G.K. Schwartz, *Nature*, **196**, 832 (1962).
2. L.V. Dolinskaya, A.M. Markeev and D.I. Chkanikov, *Fiziol. Biokhim Kult Rast*, **21**, 70 (1989).
3. V. Subramanyam and E. Patrick, *J. Agri. Food Chem.*, **36**, 1326 (1988).
4. V.I. Levin, V.V. Sedor and I.N. Pronova, *Otkryatiya Izo Bert.*, **29**, 262 (1985).
5. D.K. Parry and C.D.S. Tomlin, *Ger Offen*, **2**, 337, 289 (1974).
6. Ramesh Pangunoori and Kashi Ram, *J. Indian Chem. Soc.*, (in press).
7. G. Mallikarjun Rao, Ramesh Pangunoori and Kashi Ram, *Proc. Ind.* Acad. Sci. (A) (Communicated).
8. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904, 3397 (1954).
9. J. Inczedy, Analytical Applications of Complex Equilibria, Ellis Horwood Limited, England, p. 348 (1976).
10. R.J. Motekaitis and A.E. Martell, *J. Coord. Chem.*, **14**, 139 (1985).
11. H.E. Lundeger Madsen, H.H. Christensen and C. Gottueb-Petersen, *Acta. Chem. Scand.*, **32**, 79 (1978).

(*Received*: 15 March 1994; *Accepted*: 22 June 1994) AJC-843