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Chemistry

Gd(III), Tb(III), Dy(III) and Ho(III)-CHELATES OF N-ACETYLACETONE VALINE AND 3-(3-HYDROXY-2-NAPHTHYLIDENEIMINO)PROPANOIC ACID SCHIFF BASES

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Proton ligand stability constants of N-acetyl acetone valine (H_2AV) and 3-(3-hydroxy-2-naphthylideneimino) propanoic acid (H_2NP) and stability constants of their chelates with Gd(III), Tb(III), Dy(III) and Ho(III) have been determined potentiometrically at 25°, 35° and 45° in aqueous medium ($\mu = 0.1$, 0.05 and 0.01M $NaClO_4$). The stability constants follow the order Gd(III) < Tb(III) < Dy(III) < Ho(III). The solid chelates have also been synthesised and characterized by elemental analysis, magnetic, conductance and spectral studies. An octahedral stereochemistry of these compounds has been established.

INTRODUCTION

A large number of biprotic tridentate Schiff bases have been synthesized and studied in these laboratories (Sankhla *et al.*, 1979; Sehgal *et al.*, 1979; and Mali *et al.*, 1978). No studies have been performed on the chelates of N-acetyl acetone valine (H_2AV) and 3-(3-hydroxy-2-naphthylideneimino) propanoic acid (H_2NP) with Gd(III), Tb(III), Dy(III) and Ho(III). Hence the present study.

EXPERIMENTAL

The apparatus and the reagents employed were the same as reported earlier [(Gupta *et al.* 1979*a*)]. H_2AV and H_2NP were synthesised from acetylacetone and valine and 2-hydroxy-1-naphthaldehyde and β-alanine, respectively by the general procedure already reported [(Gupta *et al.* 1979*b*)], m.p. 160° (H_2AV), 185° (H_2NP); both gave satisfactory C, H and N-analysis.

A precision *p*H-meter type OP : 205 No. 837 (Radelkis) equipped with a glass-calomel electrode assembly was used to determine the *p*H.

Calvin-Bjerrum *p*H-titration technique as used by Irving and Rossotti was adopted to study the stabilities of H_2AV and H_2NP and their metal chelates. Potentiometric titrations of mixtures containing (*a*) perchloric acid alone (*b*) perchloric acid and the ligand (H_2AV and H_2NP) and (*c*) perchloric acid, ligand and metal ion solution, were performed against carbonate free 0.1M NaOH and the titration curves were found to be of the usual shapes.

RESULTS AND DISCUSSION

pK_1 and pK_2 of H_2AV and H_2NP were determined by interpolation at half $\bar{n}$ values method (graphical) and interpolation at various $\bar{n}$ values method (Bjerrum, 1957). The values of pK_1 and pK_2 of H_2AV and H_2NP at 0.1M $NaClO_4$ were 10.50 and

9.07, 10.20 and 8.60 at 25°; 10.41 and 9.02, 9.90 and 8.30 at 35° ; and 10.40 and 8.95, 9.60 and 8.05 at 45°, respectively. The metal-ligand stability constants were read from the formation curves drawn by plotting $\bar{n}$ v/s. pL. The formation curves for metal-ligand systems attain maxima at $\bar{n} > 1.5$ which indicate that 1 : 1 and 1 : 2 chelates are formed and average values of their stability constants (log K_1 and log K_2) at different temperatures are summarised in Table I. Log. K_1 and log K_2 of H_2AV chelates are found slightly higher than those of H_2NP, which may perhaps be due to the steric factors in the latter. The stability of the chelates increases with decreasing ionic size of the metal ion;Gd(III) < Tb(III) < Dy(III) < Ho(III).

The values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) have been evaluated using the Gibb's-Helmholtz equation (Table I). The $\triangle G$ of the chelates have more negative values at higher temperatures. The ΔH values are positive suggesting that some steric strain exists around the metal-ion in the chelates due to the presence of fused rings. The entropy term seems favourable for the complex formation which is evident from the positive values of $\triangle S$.

The data were analysed in terms of Harned's relation between log K^H and temperature, as $[(pK^H - ct^2) = -2\theta t + (pK^H_m - c\theta^2)]$ where $pK^H = -\log K^H$ at t °C; pK^H_m is minimum pK^H value at θ °C and c is a constant having the value 5.0×10^{-5} deg^{-2}. A plot of $(pK^H - ct^2)$ v/s t must be linear and this was found true in the present case. The values of θ° and pK^H_m were found to be 180° and 32.33 (H_2AV) and 217.8 and 12.35 (H_2NP), respectively. The values of $\triangle H$ obtained for H_2AV and H_2NP, by Harned's equation and Gibb's-Helmholtz equation were also found to be similar.

Solid Chelates : The Gd(III), Tb(III), Dy(III) and Ho(III)-chelates of H_2AV and H_2NP were prepared in the solid state by the method reported earlier and the yields were found between 73–80 per cent. These compounds behave as non-electrolytes as indicated by their low molar conductance (Table I). Their molecular weights were determined ebulliometrically (Table I) and 1 : 2 (metal-ligand) stoichiometry was observed in these compounds. These compounds do not possess sharp m.p. but decompose on heating above 250° without melting, giving their oxides between 380°–440°. All the compounds were found paramagnetic (Table I) as revealed by their magnetic moments indicating the presence of 7, 6, 5 and 4 unpaired electrons in Gd(III), Tb(III), Dy(III) and Ho(III)-chelates. It is apparent that in these compounds there is no metal-metal bonding and hence no spin exchange occurs and they exist as monomers.

I. R. Spectra : The results of I.R. studies are shown in Table II. A comparison of i.r. spectra of H_2AV and H_2NP with those of their chelates shows the formation of chelates through nitrogen and oxygen atoms of the ligands. In the i.r. spectra of ligands five bands are observed at 3390 cm^{-1}, 2590 cm^{-1}, 1695 cm^{-1}, 1640 cm^{-1} and 1605 cm^{-1} for H_2AV and 3370 cm^{-1}, 2580 cm^{-1}, 1690 cm^{-1}, 1610 cm^{-1} and 1590 cm^{-1} for H_2NP which correspond to νOH, νCOOH, νC = O, νC=C and νC=N [H_2AV]; νOH, νCOOH, νC=O, νC=N and naphthalene ring (Finar, 1973) [H_2NP], respectively. In the metal chelates the νC = N has lowered from 1605 and 1610 cm^{-1} to 1560–1580 cm^{-1} indicating involvement of azomethine nitrogen in complexation. Appearance of bands in the narrow ranges 400–415

TABLE I

Molecular weight, average stability with standard deviations, thermodynamic parameters, magnetic moment and conductance of rare earth chelates of H_2AV *and* H_2NP

Metal-chelates	Mol. wt. calc. (Found)	Stability constants log K_1 log K_2	—ΔG K. cal/mole	ΔH K cal/mole at 35 °C	ΔS Cal/deg mole at 35 °C	μeff B.M. 308 °K	ΩM ohm⁻¹cm² mole⁻¹
[GdL]	551	10.55 ± 0.04 (10.60 ± 0.06) 10.70 ± 0.03*	24.61 (25.59) 26.63*	5.42	118.4	7.84	5.6
	(545)	7.50 ± 0.02 (7.54 ± 0.05) 7.60 ± 0.04*	[24.69 (25.72) 26.73]+	5.63+	119.3+		
[TbL]	563	10.85 ± 0.01 (10.98 ± 0.04) 11.10 ± 0.06*	25.43 (26.59) 27.72*	13.01	170.1	9.51	3.4
	(552)	7.80 ± 0.06 (7.88 ± 0.02) 7.95 ± 0.04*	[25.52 (26.67) 27.85]+	13.71+	173.4+		
[DyL]	556	11.25 ± 0.03 (11.31 ± 0.03) 11.35 ± 0.5*	26.45 (27.52) 28.52*	4.33	117.3	10.42	6.8
	(541)	8.15 ± 0.01 (8.22 ± 0.04) 8.25 ± 0.06*	[26.52 (27.63) 28.67]+	4.63+	119.6+		
[HoL]	559	11.50 ± 0.01 (11.53 ± 0.05) 11.85 ± 0.02*	27.14 (28.14) 30.32*	5.42	126.9	10.46	8.7
	(545)	8.40 ± 0.03 (8.43 ± 0.06) 9.02 ± 0.01*	[27.18 (28.28) 30.40]+	5.52+	127.1+		
[GdL′]	640	8.75 ± 0.03 (9.10 ± 0.01) 9.30 ± 0.05*	23.11 (24.59) 26.07*	22.11	153.2	7.86	6.7
	(628)	8.20 ± 0.06 (8.35 ± 0.03) 8.62 ± 0.02*	[23.23 (24.64) 26.17]+	21.79+	154.3+		
[TbL′]	652	8.85 ± 0.02 (9.20 ± 0.04) 9.47 ± 0.01*	23.45 (24.95) 26.76*	25.79	165.2	9.49	5.3
	(638)	8.35 ± 0.05 (8.50 ± 0.01) 8.92 ± 0.03*	[23.55 (25.01) 26.81]+	25.14+	164.9+		
[DyL′]	645	9.02 ± 0.01 (9.40 ± 0.06) 9.55 ± 0.04*	23.82 (25.30) 27.13*	25.58	165.8	10.39	5.7
	(629)	8.45 ± 0.03 (8.55 ± 0.02) 9.10 ± 0.05*	[23.87 (25.41) 27.27]+	26.17+	166.9+		
[HoL′]	648	9.15 ± 0.02 (9.50 ± 0.03) 9.75 ± 0.04*	24.14 (25.72) 27.78*	38.20	203.3	10.44	9.3
	(635)	8.55 ± 0.05 (8.75 ± 0.01) 9.35 ± 0.02*	[24.23 (25.78) 27.87]+	38.12+	202.1+		

$L = (C_{20}H_{30}N_2O_8)$ and $L' = (C_{23}H_{28}N_2O_6)$.
The values in parantheses are at 35° and those with asterisk marks at 45° C, rest at 25 °C.
+Theoretical values.

TABLE II

I. R. spectra of H_2AV *and* H_2NP *and their rare-earth chelates* (in cm^{-1})

Complex	ν(OH)	ν(COOH)	ν(C=O)	ν(C=O)	ν(C=N)		ν(m—N)	ν)M—O)
H_2AV	3390	2590	1695	1640	1605		—	—
Rare-earth H_2AV chelates	3350–3370	—	1675–1685	1590–1595	1570–1580		400–415	505–510
H_2NP	3370	2580	1690	—	1610	1590*	—	—
Rare-earth H_2NP chelates	3330–3350	—	1665–1675	—	1560–1580	1590*	410–415	500–525

*Naphthalene ring (after Finar, 1973)

and 410–415 cm^{-1} suggest metal-nitrogen bondings in the chelates. Formation of (M-O) bonds due to the deprotonation of carboxylic group of the H_2AV and H_2NP is evidenced by the appearance of bands in the ranges 505–510 cm^{-1} and and 500–525 cm^{-1} respectively. In the case of H_2NP chelates the band at 1590 cm^{-1} may be attributed to the presence of the naphthalene ring (Finar, 1973).

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