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Synthesis characterisation and stability constants of lanthanide (III) ion complexes of schiff base and their chemical speciation

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Abstract

The proton-ligand and metal ligand stability constant of 2,4 Diamino thiazole with R-substituted salicylaldehyde (R-5-SH₃ and 5-Cl) or 2-hydroxy-1-Nathanldyde ie, (5 mS)₂ DCT, (5 CS)₂ DCT and (HN)₂DCT and lanthanide (III) ion complexes have been determined in ethanol-water (v/v) medium at different ionic strength (μ)=0.2,0.15,0.1 and 0.05 m NaClO₄ and different temperatures 35 °C and 45 °C. The effect of dielectric constant on stability has also been studied at different percentages of solvent and variation in different solvent system.

The stability constants of the complexes are found to decrease with increasing ionic strength which is in agreement with Debye-Huckel equation. The stability of complexes containing an O-H or O-M link increases with increasing organic content of the solvent due to decrease in dielectric constant of the bulk solvent.

The thermodynamic parameters (ΔG , ΔH and ΔS) were calculated and over all free energy, enthalpy and entropy changes at room temperature. The negative free energy change (G) in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The positive values for S indicates the complexation reaction are entropically favored under the experimental condition.

Keywords: Synthesis characterisation, stability constants, lanthanide (III) ion, schiff base

Introduction

In our earlier communication ^[1-3] we have reported the stability constant of transition metals (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) and Schiff bases derived fro 4-(P-bromophenyl)-2-amino thiazole and 2,4 Diamino-5-chlorothiazole and 2,4-Diamino thiazole with R-substitued slicylaldehyde. The literature survey reveals that no PH-metric work has been done on the lanthenide complexes of above Schiff bases so present study was undertaken to determine the stability constants of lanthanide with above Schiff bases at various ionic strengths, different temperatures and different percentage of solvent, in different solvent system.

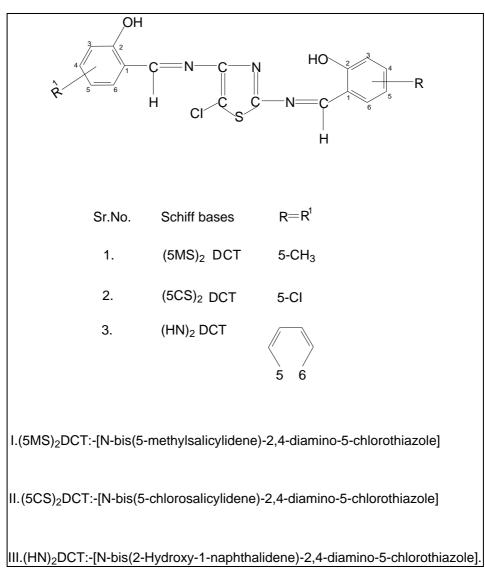
Experimental

All chemicals are AR grade. The Schiff bases were prepared by condensation of 2,4 Diamino-5-chlorothiazole and 5-methyl salicilaldehyde, 5-chlorosalicylaldehyde and 2-hydroxy-1napthaldehyde, ie, (MS)₂DCT, (CS)₂DCT and (HN)₂DCT respectively. The structure I, II and III.

The titrations were carried out in nitrogen atmosphere using Elico-4T-120 PH- meter coupled with combined glass electrode. The PH meter was calibrated with standard buffer and readings were corrected as per literature4. The method of BJerm and calvin as modified by Irving and ROSotti has been used to determine the PK and logK values. The measurements were made at 25 °C, 35 °C and 45 °C also the measurements were made at ionic strength μ =0.1 m (Nacl)₄ in 25:75 ethanol-water medium. The PH-metric titrations were performed against standard alkali (NaOH) as under

- 1. Acid titration: A mixture [2 ml 0.2 m HNO₃ + 1 mL 0.1 m NaclO₄ + 27 distilled water + 10ml ethanol]
- 2. Schiff base titration: A mixture (2 ml $0.2 \text{ HNO}_3 + 1 \text{ ml } 0.1 \text{ m } \text{Naclo}_4 + 5 \text{ ml ligand}$ solution + 27 distilled water + 5 ml ethanol]
- 3. **Metal ligand titration:** A mixture (2 ml 0.2 HNO₃ + 1 ml 0.1 m Naclo₄ + 5 ml ligand solution + 2 ml metal ion solution]

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In other sets, a requisite amount of NaclO₄ was added to maintain the ionic strength μ =0.5 m, 0.15 m and 0.2 m. The mixture at 1 m ionic strength was individually titrated against Schiff base I, II and III at different percentage and at various solvents ie, 30%, 35% and 40% EtOH 30% DMF and 30% MeOH.

Result and Discussion

Proton ligand stability constant (PK) vales of the ligands (5 $mS)_2$ DCT, (CS)₂ DCT and (HN)₂DCT were calculated using half integral method.

The ligand possesses only one PK value due to dissociable proton of the phenolic group. The protonation of imino nitrogen (-HC=N-) does nottake place in the pH range under study. The Pk values of ligands follow the trend (5 mS)₂>(5CS)₂DCT>(HN)₂DCT and it is explained on the grounds of basic nature of azomethine nitrogen and phenolic oxygen ^[5-7].

The ligand $(5CS)_2DCT$ exhibit higher protin-ligand stability constant value that e ligand $(HN)_2DCT$ and this may be due to presence of Cl-in the aromatic ring. Cl behaves as electron releasing group die to meosmeric effect (+M) rather than Ieffect (inductive effect). Hence electron density on phenyl ring increases and azomethine nitrogen and p[henolic oxygen becomes more basic.

The Ligand $(5 \text{ mS})_2\text{DCT}$ posses methyl group at meta position with respect to azomethine group, due to +I effect of methyl group, electron density over phenyl ring increases and

azomethine nitrogen and phenolic oxygen becomes more basic. Hence ligand possess higher stability constant values than other ligands.

Thus +I effect of Methyl and stronger (+M) effect of halogen group present in the phenyl ring oif the Schiff bases supports the trend proposed for proton-ligand stability values of the ligand.

Metal-Ligand stability constants

The titration curves of acid, ligand and the metal ions studied. The metal ion curve shows departure from ligand curve at pH much lower than the pH of hydrolysis of metal ion and therefore the liberation of proton is due to chelation. The metal-ligand stability constants were determined by using Half-integral method, values a s summarized in table 1.

The data in table-1 reveal that the stability constant increases with increase in atomic number Yb(III) with a break at gadolinium. Similar observations were made for lanthanide compalxes with number of Schiff base ^[5-9]. The following trend observed in present work, ie, La<Ce<Pr<Nd<Sm>Gd>Tb>Ho<DY>Yb.

The stability constants of lathenide (III) ion complexes were determined at various temperatures 35 °C and 45 °C in ethanol water medium. Thethermodynamic parameters (ΔG , ΔH and ΔS) are also calculated that are sumerised in table-2. The values metal ligand stability constanat, decrese suggesting that low temperature is favorable for

complexation. The negative free energy change (ΔG) in each case indicates that the complexation is spontaneous.

The enthalpy changes are exothermic. The positive values for ΔS indiates that entrop effects is found to be predominant over enthalpy effect.

Generally, the stability of the complexes containing with an O-H or O-M link increases with increasing organic content of the solventdue to decrease in dielectric constant of the bulk solvent ^[8, 10-12]. The dielectric constant decrease the ion-ion interaction involving the proton (or metal-ion) and the anionic oxygen donor of the ligand increases to a greater extent that the ion-diopole interaction between the proton (or metal ion) and the solvent molecules.

In a used composition, stability constant of metal compleses follow the trend 30%Et-OH>30%MeOH>30%DMF.

The high values of stability constant in ethanol is propgressive of hydrogen bonding in water ^[12], ie, hydrogen bonded structure is less prevalent in ethanol than methanol and least in DMF.

The metal-ligand titration curve describe from the acid dissociation curve in the pH range 4.7 to 7 indicates that the complexation takes place in the pH range. The maximum value of n- is found 1.2 in all complexes which indicates that the lanthanide forms 1:1 complexes.

Sr. No.		Stability constant logK, Ionic strength (µ) (Nacl)4								
		0.05 m	0.1 m	0.15 m	0.2 m					
1	H+ I	9.18,1185	8.86,11.60	8.7,11.44	8.51,11.20					
	pk1pk2II	9.44,11.40	9.125,11.10	9.012,10.95	8.81,10.74					
	III	9.41,11.45	9.025,11.05	8.84,10.90	8.63,10.68					
2	La(III) I	7.12	6.35	6.25	5.85					
	Π	7.50	6.60	6.50	6.10					
	III	8.04	7.55	6.05	6.55					
3	Ca(III) I	7.22	6.55	6.44	5.05					
	Π	7.63	7.14	6.99	5.58					
	III	8.09	7.62	7.46	7.06					
4	pr(III) I	7.30	6.54	6.43	6.03					
	II	7.18	7.05	6.91	6.52					
	III	8.15	7.65	7.53	7.02					
5	Sm(III) I	7.50	6.71	6.60	6.42					
	II	7.91	7.10	7.10	6.62					
	III	8.28	7.55	7.34	7.03					
6	Gd(III) I	7.12	6.30	6.20	5.81					
	II	7.40	6.60	6.51	5.11					
	III	7.92	7.13	7.01	6.62					
7	Tb(III) I	7.35	6.66	6.56	6.15					
	II	7.47	6.72	6.60	6.21					
	III	7.803	7.60	7.48	7.08					
8	Ho(III) I	7.42	6.71	6.59	6.20					
	II	7.55	6.86	6.75	6.35					
	III	8.09	7.42	7.31	6.92					
9	Dy(III) I	7.48	6.73	5.61	6.23					
	Π	7.61	6.81	5.96	5.62					
	III	8.11	7.35	7.22	6.77					
10	Yb(III) I	7.54	6.84	6.72	6.31					
	Π	7.68	7.05	6.94	6.63					
	III	8.16	8.52	8.41	8.03					

Table 1: Stability constants of lanthanide (III) ion in ethanol-water medium at different ionic strength

Table 2: Stability constants of lanthanide (III) ion complexes of schiff bases in ethanol-water medium at ionic strength μ=0.1 m NaclO4 atdifferent temperatures 25 °C, 35 °C and 45 °C and thermodynamic parameters

Sr. No		LogK			-ΔG KJMOL ⁻¹		-ΔH KJMOL ⁻¹		ΔS JKMOL ⁻¹			
		25 °C	35 °C	45 °C	Ι	II	III	Ι	II	Ι	II	III
1	La(III) I	6.35	5.80	5.15	37.5	29.94	53.33	57.45	32.46	0.0669	0.0081	0.0090
	II	6.60	6.15	5.85	38.24	39.24	30.76	25.45	78.31	0.0429	0.1268	0.149
	III	7.55	7.05	6.70	41.69	36.23	31.27	40.52	65.52	0.0039	0.0983	0.107
2	Ce(III) I	6.55	6.06	5.65	35.94	35.78	31.46	43.87	15.31	0.0266	0.0653	0.0507
	II	7.14	6.66	6.03	45.10	35.54	33.50	70.74	29.63	0.0860	0.0200	0.0130
	III	7.62	7.12	6.72	41.92	45.55	37.26	29.84	34.75	0.04053	0.053	0.078
3	Pr(III) I	6.54	6.01	5.63	35.99	35.65	31.55	29.39	8.95	0.1892	0.086	0.0715
	II	7.05	6.49	6.14	36.18	36.28	41.60	36.83	24.29	0.0011	0.389	0.054
	III	7.65	7.12	6.73	41.27	45.55	37.23	30.69	79.68	0.03550	0.1108	0.130
4	Nd(III) I	6.62	6.09	5.72	35.64	29.01	31.20	48.62	20.41	0.0436	0.027	0.0341
	II	7.07	6.56	6.16	35.34	35.95	41.23	72.99	24.29	0.0246	0.036	0.0532
	III	7.41	6.92	6.65	42.42	34.71	37.53	42.29	67.34	0.0004	0.1059	0.0937
5	Sm(III) I	6.71	6.20	5.86	35.31	83.52	30.73	23.40	72.95	0.0411	0.1117	0.132
	II	6.10	6.55	6.09	34.45	36.00	30.61	30.98	54.21	0.0116	0.0591	0.055
	III	6.55	7.04	6.72	41.69	38.52	37.26	36.06	11.40	0.0195	0.088	0.0813

6	Gd(III) I	6.30	6.81	6.41	37.45	35.03	38.75	18.05	13.20	0.0651	0.0708	0.0803
	II	6.60	6.08	5.74	35.73	29.30	32.20	36.58	15.09	0.0028	0.046	0.0538
	III	7.13	6.61	6.24	35.28	35.74	40.16	44.84	18.09	0.0014	0.057	0.0882
7	Tb(III) I	6.66	6.14	5.76	35.49	40.27	31.05	28.18	77.47	0.0245	0.120	0.1459
	II	6.72	6.13	5.80	35.27	40.46	30.92	31.11	79.90	0.0139	0.128	0.1540
	III	7.60	7.11	6.82	41.46	46.76	36.92	30.83	83.62	0.0356	0.119	0.1468
8	Ho(III) I	6.71	6.21	5.84	41.01	39.23	30.79	22.14	72.66	0.0633	0.108	0.131
	II	6.86	6.32	5.92	34.88	38.16	30.05	17.96	55.14	0.0557	0.097	01109
	III	7.40	6.93	5.61	42.42	34.44	31.63	56.30	36.46	0.0465	0.0033	0.0183
9	Dy(III) I	6.73	6.11	5.73	35.29	40.89	31.16	34.40	18.37	0.0027	0.132	0.1578
	II	6.10	6.58	5.25	34.50	30.77	33.98	43.08	16.32	0.0287	0.046	0.0547
	III	7.35	6.66	6.22	42.88	30.44	40.39	53.38	21.30	0.0352	0.0296	0.0287
10	Yb(III) I	6.84	6.31	5.29	34.93	38.24	30.55	10.08	65.76	0.0827	0.089	0.1107
	II	7.05	6.52	5.15	36.23	36.92	35.33	42.56	20.54	0.0212	0.052	0.455
	III	7.52	8.01	7.66	41.89	53.25	43.56	38.34	57.34	0.0103	0.071	0.0433

Table 3: Stability constants of lanthanide (III) ion complexes of schiff bases. In different percentage of solvent and in various solvent system ateionic strength $\mu = 0.1$ MNaclO₄ at temperature 25 °C±1C

Sr. No.	Cation	Different	percentage of solve	Different solvent system			
		Et-OH 30%	Et-OH 35%	Et-OH 40%	Me-OH 30%	DMF 30%	
1	La(III) I	6.32	6.51	6.81	5.22	5.10	
	II	6.61	6.87	7.10	5.50	5.38	
	III	7.41	7.40	7.70	6.06	6.00	
2	Ce(III) I	6.42	6.70	7.05	5.30	5.20	
	II	6.83	7.05	7.30	5.71	5.60	
	III	7.29	7.56	7.87	6.20	6.11	
3	Pr(III) I	6.34	6.62	7.93	5.25	5.13	
	II	6.81	6.98	7.25	5.72	5.61	
	III	7.35	7.57	7.80	6.26	6.17	
4	Nd(III) I	6.65	6.92	7.24	5.55	5.50	
	II	6.90	7.15	7.42	5.52	5.75	
	III	7.34	7.62	7.91	6.23	6.13	
5	Sm(III) I	6.65	6.90	7.20	5.53	5.41	
	II	6.98	7.24	7.55	5.80	5.74	
	III	7.50	7.71	7.96	6.39	6.30	
6	Gd(III) I	6.36	6.62	6.90	5.27	5.18	
	II	6.66	6.62	7.24	5.60	5.52	
	III	6.98	7.24	7.55	5.91	5.87	
7	Tb(III) I	6.45	6.63	6.94	5.63	6.30	
	II	6.61	6.86	7.10	5.56	5.41	
	III	7.23	7.55	7.77	5.16	6.05	
8	Ho(III) I	6.63	6.91	7.17	5.60	5.50	
	II	6.67	6.98	7.32	5.63	5.52	
	III	7.29	7.62	7.92	6.20	6.09	
9	Dy(III) I	6.61	6.92	7.31	5.52	5.41	
	II	6.82	7.10	7.42	5.75	5.68	
	III	7.33	7.62	7.92	6.29	6.18	
10	Yb(III) I	6.74	6.99	7.52	5.68	5.59	
	II	6.77	7.05	7.36	5.71	5.60	
	III	7.38	7.65	7.97	6.37	6.29	

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