

the results presented in this note. The diamines employed were: ethylenediamine (en), 1,2-propylenediamine (1,2-pn) and 1,3-propylenediamine (1,3-pn).

A stock solution of metal nitrate (BDH, AR) was prepared in doubly distilled water and standardized as described earlier⁶. The hydrochlorides of the diamines (Riedel) were first prepared and then recrystallized several times. Their solutions were prepared in doubly distilled water by direct weighing. Tripotassium salt of DTPA was used for preparing its solution in doubly distilled water. The ligand solutions were standardized potentiometrically against a standard KOH solution. The ionic strength of all the reaction mixtures was maintained constant ($\mu = 0.1$) using 0.1M potassium nitrate and low concentrations ($5 \times 10^{-3}M$) of the ligand and metal ion.

The hydrolysis constant (pK_H) of the normal 1:1 Th(IV)-DTPA chelate and the dissociation constants of diamines were taken from the literature⁷. The formation constants of the mixed ligand complexes were calculated by the methods similar to those employed by Thompson and Loraas⁸.

The potentiometric titration curves of dihydrochlorides of en and 1,2-pn indicate a small difference in their pK values and only one well-defined inflexion at $m = 1$ ($m =$ moles of alkali added per mole of the ligand or metal ion) in both the cases.

When the reaction mixture containing Th(IV) and the primary ligand (DTPA) in the molar ratio of 1:1 was titrated, an inflexion at $m = 2$ was observed due to the neutralization of two protons from the ligand. This indicated the formation of the normal hydrated 1:1 Th(IV)-DTPA chelate in the buffer region. Further addition of one mole of alkali resulted in a second buffer region, which may be ascribed to the hydrolysis of the 1:1 binary chelate⁹.

The potentiometric titration curves of 1:1:1 Th(IV)-DTPA-en and 1:1:1 Th(IV)-DTPA-1,2-pn systems exhibit inflexions at $m = 2$ and $m = 4$. In both the cases up to $m = 2$, the curves overlap with that of 1:1 Th(IV)-DTPA curve indicating the formation of 1:1 binary complex in the initial stages of titration. Occurrence of a second buffer region between $m = 2$ and $m = 4$ corresponds to the neutralization of two hydrogen ions from the diamines resulting in the stepwise formation of 1:1:1 mixed ligand complexes.

The formation of the mixed ligand derivatives was further supported by drawing a composite curve [drawn by the horizontal addition of the 1:1 Th(IV)-DTPA curve to the respective free secondary ligand curve], which was found to be well above the experimental curve between $m = 2$ and $m = 4$ in these cases.

However, in the Th(IV)-DTPA-1,3-pn system, definite support in favour of the ternary complex formation was not available from the pH -metric curves. A similar observation was made in the case of Th(IV)-EDTA or CDTA-1,3-pn system. In these systems, no appreciable lowering of pH in comparison to the theoretical composite curve was noted.

A comparison of the formation constants listed in Table I indicates that the stability of mixed ligand complexes in terms of primary ligand follows the order: EDTA > CDTA > DTPA and in terms of secondary ligands 1,2-pn > en.

TABLE I — FORMATION CONSTANTS OF 1:1:1 MIXED LIGAND CHELATES AT TEMP. = $30^\circ \pm 1^\circ$ AND $\mu = 0.1$ (KNO₃)

System	$\log K_{MAB}^{MA}$
Th(IV)-DTPA-en	4.41 ± 0.08
Th(IV)-DTPA-1,2-pn	4.62 ± 0.04
Th(IV)-CDTA-en	5.30 ± 0.08 (ref. 1)
Th(IV)-CDTA-1,2-pn	5.48 ± 0.09 (ref. 1)
Th(IV)-EDTA-en	6.55 ± 0.03 (ref. 1)
Th(IV)-EDTA-1,2-pn	6.70 ± 0.02 (ref. 1)

The lower stabilities of the ternary derivatives with DTPA as compared to the analogous CDTA or EDTA complexes may be explained on the basis of the relative stabilities of their binary chelates⁹. Due to the higher basicity of 1,2-pn, its complexes have been found to be more stable than the corresponding en derivatives.

A plot of $\log K_{MAB}^{MA}$ against $\log K_{MA}$ (where A = EDTA, CDTA, or DTPA, and B = en or 1,2-pn) was linear indicating that the relative stabilities of the ternary complexes follow the same order as the binary complexes.

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Stability Constants of Some Transition Metal Complexes with Schiff Bases Derived from Salicylaldehyde & *m*-Aminophenol or *m*-Anisidine

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Received 13 February 1976; accepted 24 March 1976

Stability constants of a number of transition metal complexes with Schiff bases derived from salicylaldehyde, and *m*-aminophenol (SMAP) or *m*-anisidine (SMA) have been determined in 50% ethanol at $\mu = 0.05M$ (KNO₃), using the Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The order of stabilities for the complexes of first row transition metals is: $Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$. The order of stabilities in the case of some other transition metal complexes is: $Cr^{3+} > UO_2^{2+} > Be^{2+} > Nd^{2+} > Pr^{3+} > La^{3+}$.

NOTES

WE report here stability constants of Cu^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Cr^{3+} , UO_2^{2+} , Be^{2+} , Nd^{3+} , Pr^{3+} and La^{3+} with Schiff bases derived from salicylaldehydes and *m*-aminophenol (SMAP) or *m*-anisidine (SMA) using the Calvin-Bjerrum *p*H titration technique as modified by Irving and Rossotti. Since the ligands were insoluble in water, measurements were carried out in aqueous ethanol (50%, v/v) at $\mu = 0.05M$ (KNO_3).

A Philips *p*H-meter model PR 9405 with a glass calomel electrode assembly was used for *p*H measurements. The Schiff bases were prepared by refluxing salicylaldehyde with the corresponding amine. The products obtained were recrystallized from ethanol and dried in an oven at 50-60°. Solutions of ligands were prepared in pure ethanol. The metal ion solutions were prepared from the corresponding nitrates (BDH, AR) or sulphates (BDH, AR) and were standardized by conventional methods¹. Potassium nitrate (AR) and nitric acid were used to maintain constant ionic strength. All other chemicals used were also of AR grade. All the measurements were carried out at 25° ± 0.1°.

The following solutions (total volume 50 ml) were titrated against carbonate-free standard NaOH:

- (i) 5 ml KNO_3 (0.5M) + 10 ml HNO_3 (0.01M)
- (ii) 5 ml KNO_3 (0.5M) + 10 ml HNO_3 (0.01M) + 5 ml ligand solution (0.01M)
- (iii) 5 ml KNO_3 (0.5M) + 10 ml HNO_3 (0.01M) + 5 ml ligand solution (0.01M) + 2 ml metal solution (0.005M)

From the titration curves of solutions (i) and (ii), $\bar{n}H$ at different *p*H values were calculated using the method of Bjerrum and Calvin as modified by Irving and Rossotti². From the experimentally determined $\bar{n}H$ -*p*H data, protonation constants were evaluated using Bjerrum's half \bar{n} method.

The values of the protonation constants are: For SMAP: $\log K_1$, 9.90; $\log K_2$, 8.05; $\log K_3$, 4.65. For SMA: $\log K_1$, 8.18; $\log K_2$, 4.25.

The average number of ligand molecules attached per metal ion (\bar{n}) and the free ligand exponent ϕ_L were calculated from the titration curves of solutions (ii) and (iii). The stepwise stability constants were evaluated from the formation curves using the method of intrapolation at $\bar{n} = 0.5$. The values are given in Table 1.

In all the cases the complexes hydrolyse and the metal hydroxides precipitate in the *p*H range 6-10. All the calculations were carried out below the range of the formation of metal hydroxides.

From the $\log K_1$ values of complexes δH (thermodynamic stabilization energy) values were calculated according to the method described by George and McClure³. The values are given in Table 1. The values for stability constants at 25°, and the calculated overall change in free energy ($\Delta F = -RT \ln K$) for some other transition metal ion complexes are recorded in Table 2.

The data in Table 1 show that the order of stabilities of first row transition metal complexes is as follows: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. Except for the ferrous complex, this sequence is in agreement with the order given by Mellor and Maley^{4,5}. Abnormally high stabilities for the Fe(II) complexes have been observed in many cases, particularly with aromatic ligands, e.g. riboflavin⁶, etc. The effect has been attributed to the resonance stabilization energy of Fe(II) complexes on coordination with a ligand having aromatic ring system⁷.

The values of δH observed for Co(II), Ni(II) and Cu(II) complexes are also of the same order as for some other ligands coordinating through one nitrogen and one oxygen atom. This indicates that the

TABLE 1 — STABILITY CONSTANTS OF DIFFERENT TRANSITION METAL IONS WITH SMAP AND SMA

Cations	$\log K_1$	$\log K_2$	$\log \beta$	δH	$\log K_1$	$\log K_2$	$\log \beta$	δH
	COMPLEXES WITH SMAP				COMPLEXES WITH SMA			
Mn^{2+}	4.7	4.4	9.10	—	3.45	2.75	6.20	—
Fe^{2+}	7.15	5.7	12.85	19	5.55	4.65	10.20	19
Co^{2+}	6.15	4.8	10.95	25	3.90	3.25	7.15	24
Ni^{2+}	6.4	4.9	11.30	34	4.35	3.60	7.95	33
Cu^{2+}	10.3	6.8	17.10	31	5.75	4.65	10.40	26
Zn^{2+}	5.3	5.1	10.40	—	3.55	3.05	6.60	—

TABLE 2 — STABILITY CONSTANTS AND THERMODYNAMIC DATA FOR COMPLEXES OF SMPA AND SMA

Cations	$\log K_1$	$\log K_2$	$\log K_3$	β_n	$-\Delta F$ (kcal/ mole)	$\log K_1$	$\log K_2$	β_n	$-\Delta F$ (kcal/ mole)
	COMPLEXES WITH SMAP					COMPLEXES WITH SMA			
Be^{2+}	9.05	5.10	—	14.15	19.3	6.80	5.55	12.35	16.9
UO_2^{2+}	11.30	5.80	—	17.10	23.3	7.15	6.40	13.55	18.5
Cr^{3+}	12.10	5.9	—	18.00	24.6	7.70	6.20	13.90	19.0
La^{3+}	6.15	4.1	—	10.25	14.00	3.75	3.40	7.15	9.8
Nd^{3+}	5.4	4.0	3.8	13.20	18.0	5.35	4.15	9.50	13.0
Pr^{3+}	6.15	3.20	3.6	12.95	17.7	4.80	4.00	8.80	12.00

metal ions in the present case are also bonded through one nitrogen and one oxygen atom of the ligand molecule. This is supported by the slight shift to higher atomic numbers in the curve ΔH_L (heat of complexation) against atomic number as compared to the curve of ΔH_H (heat of hydration of metal ion) against atomic number. A straight line joining Mn and Zn represents the situation in the absence of crystal field stabilization.

The order of stabilities of other transition metal ion complexes is: $\text{Cr}^{3+} > \text{UO}_2^{2+} > \text{Be}^{2+} > \text{Nd}^{3+} > \text{Pr}^{3+} > \text{La}^{3+}$.

In general, SMA complexes are less stable than SMAP complexes because pK_n of SMA is lower than pK_n of SMAP.

The authors thank Prof. C. N. Kachru, Head, Chemistry Department, Kashmir University, for providing facilities.

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Stability Constants of Complexes of VO(II), Cu(II), Co(II) & Ni(II) with 2-Hydroxy-1-naphthaldehyde-4-m-chlorophenyl-3-thiosemicarbazone

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Received 3 March 1976; accepted 12 May 1976

The stability constants of the complexes of VO(II), Cu(II), Co(II) and Ni(II) with 2-hydroxy-1-naphthaldehyde-4-m-chlorophenyl-3-thiosemicarbazone have been determined in 70% aq. dioxane employing modified form of Irving and Rossotti titration technique at $25^\circ \pm 0.1^\circ$. The order of stability in terms of $\log K_1$ is $\text{VO}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$.

THIOSEMICARBAZONES as ligands have not been much studied pH -metrically. In this note, the formation constants of the complexes of VO(II), Cu(II), Co(II) and Ni(II) with 2-hydroxy-1-naphthaldehyde-4-m-chlorophenyl-3-thiosemicarbazone (*m*-CINPT) employing Calvin and Wilson pH -titration technique as modified by Irving and Rossotti in 70% aq. dioxane are reported.

m-CINPT was synthesized and crystallized to get analytically pure compound. Its solution was prepared in dioxane (BDH, AR) which was purified by the standard method². Metal nitrates used were of AR grade and their stock solutions were standardized by gravimetric and volumetric methods. A

TABLE 1 — STABILITY CONSTANTS OF THE COMPLEXES IN 70% AQ. DIOXANE

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$
Cu^{2+}	9.54 ± 0.05	9.46 ± 0.05	19.00 ± 0.05
Co^{2+}	9.27 ± 0.05	9.07 ± 0.05	18.34 ± 0.05
VO^{2+}	9.83 ± 0.05	9.08 ± 0.05	18.91 ± 0.05
Ni^{2+}	9.29 ± 0.05	8.34 ± 0.05	17.66 ± 0.05

Philips pH -meter calibrated with buffer solution having pH 4.33 and 9.1 at $25.2^\circ \pm 0.1^\circ$ was used for pH measurements.

All titrations were carried out at $25.2^\circ \pm 0.1^\circ$. Each of the titrations was repeated to get reproducible results. The metal-ligand ratio was maintained 1:5.

Following solutions (total vol. 50 ml) were titrated against 0.2M NaOH:

(i) 2 ml of 0.1M HNO_3 + 5 ml of 1.0M KNO_3 + 35 ml dioxane + 8 ml of water.

(ii) 2 ml of 0.1M HNO_3 + 5 ml of 1.0M KNO_3 + 5 ml of 0.01M ligand + 30 ml of dioxane + 8 ml of water.

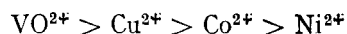
(iii) 2 ml of 0.1M HNO_3 + 5 ml of KNO_3 + 5 ml of 0.91M ligand + 1 ml of 0.01M metal nitrate solution (in case of cobalt 0.5 ml solution was taken) + 30 ml of dioxane + 7 ml of water.

The practical proton-ligand stability constant ($\log {}^pK_1^H$) for the ligand was calculated with the help of \bar{n}_A values at different B values (pH -meter readings). \bar{n}_A is then calculated by the method of Irving and Rossotti³ as adopted by Jabalpurwala *et al.*⁴. The value of $\log {}^pK_1^H$ ($= 9.82 \pm 0.05$) was then obtained from linear plots of $\log \bar{n}_A/1 - \bar{n}_A$ against B and using relation (1)

$$\log {}^pK_1^H = B + \log \frac{\bar{n}_A}{1 - \bar{n}_A} \quad \dots(1)$$

For metal-ligand stability constants \bar{n} and pL were calculated by the method of Jabalpurwala *et al.*⁴. The values of \bar{n} are plotted against pL . The values of $\log K_1$ were calculated by half integral method while those of $\log K_2$ were calculated using Olerup's⁵ and least squares methods⁶ since there was not much difference between $\log K_1$ and $\log K_2$.

The average stability constants are given in Table 1. The order of stability in terms of $\log K_1$ is



The authors are thankful to Dr K. A. Thaker, Head, Department of Chemistry, Saurashtra University, Bhavnagar, for providing laboratory facilities and to the CSIR, New Delhi, for awarding scholarships (to Y.N.B., R.S.P. and K.K.P.).

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