

- SAXENA, R. S. & BHATIA, S. K., *Indian J. Chem.*, **12** (1974), 528.
- SAXENA, R. S. & BHATIA, S. K., *Bull. chem. Soc. Japan*, **49** (1974), 2580.
- SAXENA, R. S. & BHATIA, S. K., *J. Indian chem. Soc.*, **51** (1974), 660.
- SAXENA, R. S. & BHATIA, S. K., *J. inorg. nucl. Chem.*, **37** (1975), 309.
- MEITES, L., *Polarographic techniques* (Interscience Publishers, New York), 1965, 241.
- KOUTECKY, J., *Colln Czech. chem. Commun.*, **18** (1953), 597.
- MEITES, L. & ISRAEL, Y., *J. Am. chem. Soc.*, **83** (1961), 4903.
- SAXENA, R. S. & GUPTA, K. C., *J. polarogr. Soc.*, **14** (1968), 24.

Complexes of Cu(II), Ni(II) & Co(II) with Schiff Bases Derived from Sulphadiazines & Salicylaldehyde

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Conductometric titrations show that Cu(II), Ni(II) and Co(II) form 1:2 complexes with the Schiff base derived from sulphadiazine and salicylaldehyde. Job's method of continuous variation has been applied to determine the stability constants and free energy of formation of the complexes. In addition, Cu(II), Ni(II) and Co(II) complexes with the Schiff base, derived from sulphamerazine and salicylaldehyde, have been studied using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The log K values have been computed by the method of least squares. Free energy changes and probability errors have been also evaluated.

A PERUSAL of literature reveals that condensation products of sulphadiazines with salicylaldehyde and substituted salicylaldehydes are not only good complexing agents¹⁻⁴ but good bacteriostatic agents also⁵⁻⁷. We describe here the results of our studies on Cu(II), Ni(II) and Co(II) complexes with Schiff bases derived from sulphadiazine and salicylaldehyde (SUDSA) and sulphamerazine and salicylaldehyde (SUMRA).

All the chemicals employed were of AR grade. Metal perchlorates were prepared and analysed as reported earlier².

Schiff bases were prepared by condensing sulphadiazine or sulphamerazine and salicylaldehyde in stoichiometric ratio in ethanol. The products obtained were crystallized from acetone.

Conductometric measurements were carried out in 50% acetone using a W.T.W. (German) conductivity bridge and a dip-type conductivity cell (cell constant=0.616 at 20°). 10 ml of 0.005M SUDSA in 50% acetone were diluted to 100 ml and titrated against 0.005M salt solution. The results indicate 1:2 (metal-ligand) stoichiometry for the complexes.

Job's method of continuous variation⁸ was also applied to determine the metal-ligand ratio using $2 \times 10^{-3}M$ solutions. The stability constants were calculated by extrapolation of job curves as suggested by Subbarama Rao and Raghav Rao⁹

TABLE 1—METAL-LIGAND STABILITY CONSTANTS OF SUMRSA COMPLEXES

Ion	Log K_1	Log K_2	Log β	Log K_1K_2	ΔF (kcal/mole)
Cu(II)	4.88	2.72	7.60	2.16	-10.38±0.0023
Ni(II)	4.37	2.13	6.50	2.24	-8.88±0.0043
Co(II)	3.90	1.58	5.48	2.32	-7.49±0.0120

using the expression (1).

$$K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \dots(1)$$

where α is the degree of dissociation and C is the concentration of metal ion. The stability constant values (log K) of Cu(II), Ni(II) and Co(II) complexes with SUDSA are 8.07, 6.94 and 6.71 respectively while the values for degree of dissociation are 0.0789, 0.1800 and 0.2121 respectively. Values for the change in free energy (ΔF) are -10.84, -9.32 and -9.01 kcal/mole for the Cu(II), Ni(II) and Co(II) complexes respectively.

The Calvin-Bjerrum^{10,11} pH titration technique as modified by Irving and Rossotti¹² was applied to determine the protonation constant of the ligand SUMRSA and formation constants of its complexes.

The experimental procedure involved potentiometric titration of the following mixtures (containing equimolar concentrations of the common constituents) against CO₂-free sodium hydroxide at $\mu=0.2M$ (NaClO₄). (i) Perchloric acid, (ii) perchloric acid +SUMRSA, and (iii) perchloric acid +SUMRSA + metal salt solution.

From the titration curves, it is observed that the metal-ligand curve is well separated from the ligand titration curve indicating that the liberation of protons is due to chelation.

The metal-ligand stability constants were obtained from the analysis of metal-ligand formation curves drawn between \bar{n} and pL values. The proton-ligand stability constant came out to be 5.2.

Least-square method¹³ was used to obtain the metal-ligand stability constants. The values obtained at $\mu=0.2M$ are summarized in Table 1.

The above results reveal that Cu(II), Ni(II) and Co(II) form 1:2 complexes and the sequence of stability is found to be Cu>Ni>Co in accordance with the Irving-Williams¹⁴ series.

The large difference between successive formation constants may be attributed to the greater steric hindrance in the case of SUMRSA.

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References

- MUKHERJEA, A. K. & RAY, P., *J. Indian chem. Soc.*, **32** (1955), 604.
- JAIN, PRABUDDHA & CHATURVEDI, KAMAL K., *J. inorg. & nucle. Chem.*, **38** (1976), 799.
- JAIN, PRABUDDHA & CHATURVEDI, KAMAL K., *J. Indian chem. Soc.* **52** (1975), 805.
- JAIN, PRABUDDHA & CHATURVEDI, KAMAL K., *J. Indian chem. Soc.*, **52** (1975), 1220, 1225.
- MACROVICI, M. & MACROVICI, C. *Chem. Abstr.*, **52** (1958) 14561b.
- TSUKAMATO, T. & KENOSUBE, Y., *Chem. Abstr.*, **52** (1958) 18293b.

7. TSUKAMATO, T., *Chem. Abstr.*, **55** (1961), 5879f.
8. JOB, P., *Ann. Chim.*, **6** (1936), 97.
9. SUBBARAMA RAO, K. V. & RAGHAVRAO, B. H. S. V., *J. scient. ind. Res.*, **14B** (1955), 278.
10. CALVIN, M. & WILSON, K. W., *J. Am. chem. Soc.*, **67** (1945), 2003.
11. BJERRUM, J., *Metal aminine formation in aqueous solution* (Haase, Copenhagen), 1941.
12. IRVING, H. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
13. IRVING, H. & ROSSOTTI, H. S., *J. chem. Soc.*, (1953), 3397.
14. IRVING, H. & WILLIAMS, R. J. P., *Nature*, **162** (1948), 746.

Stepwise Formation Constants of La(III), Ce(III), Pr(III) & Nd(III) with 4-Hydroxy-3-formyl-(2'/4')-methylazobenzenes

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Stepwise formation constants of La(III), Ce(III), Pr(III) and Nd(III) complexes with 4-hydroxy-3-formyl-(2'/4')-methylazobenzenes (HF2MB and HF4MB) have been determined in 60% aq. ethanol (w/w) at 28±0.1° under N₂ atmosphere, using the Calvin-Bjerrum pH titration technique. The order of formation constants of the complexes is Nd(III) > Pr(III) > Ce(III) > La(III).

SYNTHESIS and chelating tendencies of some substituted azo benzenes have been reported by Mohan Das *et al.*¹⁻³. The formation constants of La(III), Ce(III), Pr(III) and Nd(III) complexes with 4-hydroxy-3-formyl-(2'/4')-methylazobenzenes (HF2MB and HF4MB) have now been determined in 60% aq. ethanol (w/w) employing Bjerrum-Calvin potentiometric titration technique.

All the reagents were of AR grade (BDH). Preparation of ligands and details of experimental procedure have been reported earlier². Metal nitrate (La, Ce, Pr or Nd) solutions were prepared in conductivity water. Corrections in pH values were made according to the method of Bates⁴. The metal hydroxides precipitated at pH 7.30 and 7.50 for Nd(III), 7.55 and 7.60 for Pr(III), 7.65 and 7.70 for Ce(III) and 7.80 and 7.85 for La(III) in the case of HF2MB and HF4MB complexes respectively. Despite the tendency of the complexes of these metal ions to hydrolyse, such effects were ignored in the

present study, since the complexes are stable in the pH range studied.

All the ligands being monoprotic, neutralize one equivalent of the base to give one buffer region in the titration curves in accordance with the equilibrium (1).



The acid dissociation constants of HF2MB and HF4MB were found to be 8.05 and 8.02 respectively by the methods of Irving and Rossotti⁵ and Bjerrum. The formation curves for the metal-ligand systems were drawn between \bar{n} and pA , the values of which were calculated according to the method of Bjerrum and Calvin⁶. The complex equilibria may be represented by Eqs. (2-4).



The log *k* values for these systems were obtained from the formation curves and are given in Table 1 along with probable errors. Refined values of log β were also calculated by the correction-term method and are given in Table 1. HF2MB and HF4MB behave as bidentate ligands forming 1:3 complexes. The order of stability of the metal complexes is: Nd(III) > Pr(III) > Ce(III) > La(III) (Table 1). La(III), Ce(III), Pr(III) and Nd(III) have ionic radii of 1.061, 1.034, 1.013 and 0.995 Å respectively. Since the stability of the complexes of the metal ions having similar electronic configuration increases with decreasing ionic size, the above order of stabilities is in accordance with the expected trend. This is also justified by considering Z²/r values for these metal ions.

The order of ligands according to their chelating tendency is HF2MB > HF4MB.

References

1. MOHAN DAS, P. N., SUNAR, O. P. & TRIVEDI, C. P., *Indian J. Chem.*, **11** (1973), 196.
2. JOSEPH, P. T., THOMAS, O. F., IBRAHIM RAWTHER & MOHAN DAS, P. N., *Indian J. Chem.* (in press).
3. MOHAN DAS, P. N., SUNAR, O. P. & TRIVEDI, C. P., *J. inorg. nucl. Chem.*, **35** (1973), 849.
4. BATES, R. G., PAABO, M. & ROBINSON, R. A., *J. phys. Chem.*, **67** (1963), 1833.
5. IRVING, H. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
6. CALVIN, M. & WILSON, L. W., *J. Am. chem. Soc.*, **67** (1945), 2003.

TABLE 1 — STEPWISE FORMATION CONSTANTS OF VARIOUS METAL COMPLEXES OBTAINED BY BJERRUM-CALVIN METHOD

Metal ion	HF2MB				HF4MB			
	log <i>k</i> ₁	log <i>k</i> ₂	log <i>k</i> ₃	log β ₃	log <i>k</i> ₁	log <i>k</i> ₂	log <i>k</i> ₃	log β ₃
Nd(III)	5.64	4.31	3.70	13.65 (13.57)	5.22	3.97	3.60	12.79 (12.69)
Pr(III)	5.22	3.92	3.55	12.69 (12.80)	5.10	3.92	3.50	12.52 (12.62)
Ce(III)	5.27	3.86	3.47	12.60 (12.20)	4.97	4.88	3.47	12.32 (12.50)
La(III)	5.06	3.70	3.37	12.13 (12.15)	4.65	3.60	3.35	11.60 (11.31)

Values in parentheses have been obtained by correction-term method.