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** (1954), 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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Received 17 *June* 1975; *accepted* 4 *October* 1975

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 N_2 atmosphere, using the Calvin-Bjerrum *p*H 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 drocedure have been reported earlier[2]. Metal nitrate (La, Ce, Pr or Nd) solutions were prepared in conductivity water. Corrections in *p*H values were made according to the method of Bates[4]. The metal hydroxides precipitated at *p*H 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 *p*H 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).

$$HA \rightleftharpoons H^+ + A^- \quad ...(1)$$

The acid dissociation constants of HF2MB and HF4MB were found to be 8·05 and 8·02 respectively by the methods of Irving and Rossotti[5] 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 Calvin[6]. The complex equilibria may be represented by Eqs. (2-4).

$$HA + M^{3+} = MA^{2+} + H^+ \quad ...(2)$$

$$MA^{2+} + HA = MA_2^+ + H^+ \quad ...(3)$$

$$MA_2^+ + HA = MA_3 + H^+ \quad ...(4)$$

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 Z^2/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 k_1	log k_2	log k_3	log β_3	log k_1	log k_2	log k_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.