Notes

Formation Constants of Transition Metal Complexes of Salicylidene-2-Iminopyridine**

G. P. SENGUPTA* and C. R. BERA

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, India

SCHIFF bases derived from the reaction of aromatic aldehydes with aliphatic or aromatic amines represent an important series of widely studied ligands[1-4]. The present communication describes the results of potentiometric studies on copper (II), nickel (II) and cobalt (II) chelates of the Schiff-base ligand, salicylidene-2-iminopyridine in aqueous-ethanol medium. .

Experimental

All chemicals and reagents used in the study were of A. R. Grade or purified before use.

(a) *Preparation of the ligand* : The Schiff-base ligand was prepared by taking stoichiometric amounts of salicylaldehyde and 2-aminopyridine in absolute alcohol. The mixture was heated under reflux on a water-bath when shining yellow coloured crystals appeared. It was repeatedly recrystallised in alcohol. The purity of the ligand was checked by elemental analysis and melting point determination.

(b) *Solution* : Lime distilled absolute alcohol and carbonate free sodium hydroxide solution were prepared[5]. Nitric acid $(0.1M)$ and potassium nitrate solution were prepared in double distilled water. The ligand $(0.04M)$ solution was made in absolute alcohol and solutions of the metal nitrates $(0.01M)$ were done in $0.1M$ HNO_3. Estimation of the metal ions was made by the EDTA method[6].

(c) *Apparatus* : A digital pH-meter of Electronics Corporation of India, Model No. PH '651 (accuracy $\pm$ 0.01 units) with combined glass electrode assembly was used for the present study. All the computation works were carried out in a programmable calculator (EC 62p).

(d) *Titration* : Bjerrum-Calvin[7,8] pH-titration technique as adopted by Irving and Rossotti[9] was followed to determine the metal-ligand stability constants.

Following sets of titrations were performed at a constant temperature of $30 \pm 0.1°$:

(i) 10 ml $0.1M$ HNO_3 +5 ml $1M$ KNO_3 +10 ml water+25 ml absolute alcohol.

(ii) 10 ml $0.1M$ HNO_3 +5 ml $1M$ KNO_3+5 ml $0.04M$ ligand solution+10 ml water+20 ml alcohol.

(iii) 5 ml $0.1M$ HNO_3 +5 ml $1M$ KNO_3 +5 ml $0.04M$ ligand solution+5 ml $0.01M$ metal solution+10 ml water+20 ml alcohol.

The total volume in each case was 50 ml and the ionic strength was maintained constant at $0.1M$ KNO_3. The ratio of metal salt to reagent was maintained at nearly 1 : 4 in all titrations in order to satisfy the maximum coordination possibility of the metal ions.

Results and Discussion

In the ligand, the chelated phenolic – OH group takes part in the complex formation and the proton is replaced from it by the metal ions during complexation. Since only one proton is liberated during complexation the number of dissociable protons per ligand, (y) was taken as one.
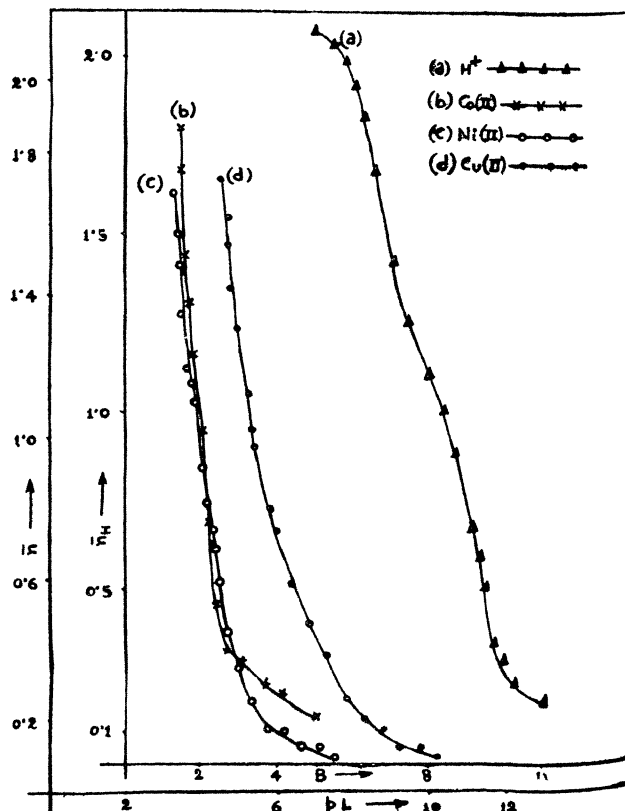

Fig. 1.   Formation constant curves of metal-ligand complexes

From the titration curves using solutions (i) and (ii) $\bar{n}_H$ was calculated and plotted against B-values (pH-meter readings) Fig. 1 (a). The values for the 'practical' proton-ligand stability constants $\log^P K_1^H$ and $\log^P K_2^H$ were evaluted by using (i) Bjerrum's half integral method and (ii) pointwise calculation method[10]. The values agree closely.

From the titration curves of the solutions (ii) and (iii) $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complexation equilibria [Fig. 1 (b), (c), (d)]. The values of metal-ligand stability constants $\log k_1$ and $\log k_2$ along with the standard deviation values were determined by using the following methods : (i) Half-integral method, (ii) Schroder's method[11], (iii) Numerical method[12], (iv) Pointwise calculation[10], (v) Least square method[13] and (vi) Correction-term method[18]. In this connection it may be mentioned that Pollard et al[14] have made a similar study with this ligand in different mediums and under different experimental conditions and the relative magnitude of their values are nearly similar to those obtained by us. The values obtained have been given in Table1.

dimine Schiff base ligands coordinate through the azomethine nitrogen and the phenolic-OH. The azomethine nitrogen of salicylidene-2-iminopyridine shows little proton affinity while the corresponding value in case of N-phenyl salicylaldimine is relatively significant ($p\text{K}_{NH}{}^+ = 3.75$) thus indicating that the azomethine nitrogen in N-phenyl salicylaldimine is more basic compared to that in salicylidene-2-iminopyridine. The $p\text{K}_{OH}$ value of N-phenyl salicylaldimine is also higher (9.7) than that of the present ligand. The pyridine nitrogen of salicylidene-2-iminopyridine which shows a high proton affinity ($p\text{K}_{NH}{}^+ = 5.85$)[16] does not take part in metal bonding. This has also been shown by the infra-red spectral study of the solid complexes of a similar ligand, salicylidene-2-imino-5 methyl pyridine[17], which suggest that the pyridine nitrogen is not involved in coordination and that coordination takes place through -C=N- and phenolic-OH only.

The order of log k_1 values of the bivalent metal chelates was

$$Cu^{+2} > Ni^{+2} > Co^{+2}$$

This follows the Irving-Williams order[18]. Parallelisms

TABLE 1—STABILITY CONSTANTS OF SALICYLIDENE-2-IMINOPYRIDINE COMPLEXES IN 50% (V/V) ETHANOL-WATER MEDIUM
TEMP. = 30°C ± 0.1°C ; $\mu = 0.1M$ KNO$_3$ |

Method used	(H$^+$)			Cu(II)				Ni(II)				Co(II)			
	$\log^P k_1^H$	$\log^P k_2^H$	$\log \beta_2$	$\log k_1$	$\log k_2$	$\log \beta_2$	δ	$\log k_1$	$\log k_2$	$\log \beta_2$	δ	$\log k_1$	$\log k_2$	$\log \beta_2$	δ
(a)	9.13	6.57	15.70	6.60	4.59	11.19	0.11	4.61	3.40	8.01	0.07	4.45	3.50	7.95	0.12
(b)	9.13	6.58	15.71	6.70	4.60	11.30	0.11	4.83	3.36	8.19	0.09	4.60	3.45	8.05	0.13
(c)				6.66	4.47	11.13	0.12	4.67	3.26	7.93	0.07	4.62	3.41	8.04	0.15
(d)				6.59	4.60	11.19	0.11	4.49	3.52	8.01	0.09	4.27	3.70	8.07	0.13
(e)				6.60	4.60	11.20	0.11	4.53	3.49	8.02	0.08	4.30	3.71	8.01	0.12
(f)				6.42	4.58	11.00	0.10	4.63	3.57	8.20	0.07	4.46	3.50	7.97	0.12
Mean Value	—	—		11.17			—	—	8.06		—	—		8.01	

(a)=Bjerrum Half $\bar{n}$ method ; (b)=Pointwise Calculation ; (c)=Least Square method ;

(d)=Schroder Method ; (e)=Numerical Method ; (f)=Correction term method.

The formation constant values of the copper complex may now be compared with the corresponding values reported earlier[15] for the salicylaldehyde and N-phenyl salicylaldimine ligands, though carried out in a different experimental condition. Compared to N-phenyl salicylaldimine, salicylaldehyde forms less stable complex with copper which has been attributed to the absence of chelate-ring stabilization in the copper-salicylaldehyde complex[15]. The log k values of the present Schiff base metal complexes are lower than those of N-phenyl salicylaldimine. The observed deviation may be due to the difference in the basicity of the chelating atoms present in the different coordinating sites of the Schiff base ligands. The salicylal-

have been observed between log k_1 and second ionization potential values, on the one hand, and the atomic number of the metals, on the other.

Perusal of log β_2 values shows that copper chelate is appreciably more stable than nickel and cobalt chelates. This may be due to the difference in preferred configuration between copper, nickel and cobalt complexes. The former might be forming a square plannar complex while the latter two might be forming tetrahedron complexes in solution with the Schiff base ligand under study.

Study of the solution spectra of the solid Schiff base complexes in chloroform, with their limitations in solubility, has revealed a broad transition ($\sim$14.92 KK) for Cu (II) complex which points to a square planar geometry[2], may be slightly distorted due to steric reasons. In case of Ni(II) chelate, a weak broad band could be identified at $\sim$14.70 KK. One broad band, under the envelope of another intense ligand absorption band, has also been observed in the short wave length region ($\sim$23.5 KK). The spectral profile shows more or less a tetrahedral geometry for the Ni(II) complex. Cobalt (II) does not exhibit any absorption band in the visible range suggesting thereby a tetrahedral stereochemistry. The magnetic moment values of Cu (1.73 BM), Ni (3.4 BM) and Co (5.1 BM) also indicate the above stereochemistries for the Schiff base chelats, at least in solid state.

Acknowledgement

References

1. R. H. HOLM, G. W. EVERETT and A. CHAKRAVORTY, "Progr. Inorg. Chem.", (Ed.) F. A. Cotton, Interscience Publication, New York, 1966, Vol. 7, p. 83.

2. L. SACCONI, Coord. Chem. Rev., 1966, 1, 126.

3. S. YAMADA, Coord. Chem. Rev., 1966, 1, 415.

4. R. L. DUTTA and G. P. SENGUPTA, J. Indian Chem. Soc., 1971, 48, 83.

5. A. I. VOGEL, "Quantitative Inorganic Analysis", Longman Publication, London, 1961, p. 239.

6. G. SCHWARZENBACH, "Complexometric Titrations" Methuen & Co. Ltd., London, 1956, p. 60.

7. J. BJERRUM, "Metal Amine Formation in Aqueous Solution", Haase, Copenhagen, 1941.

8. M. CALVIN and K. W. WILSON, J. Amer. Chem. Soc., 1945, 67, 2003.

9. H. IRVING and H. ROSSOTTI, J. Chem. Soc., 1954, 2904.

10. K. E. JABALPURWALA, K. A. VENKATACHALAM and M. B. KABADI, J. Inorg. Nuclear Chem., 1964, 26, 1011.

11. K. H. SCHRODER, Acta. Chem. Scand., 1966, 20, 1401.

12. R. P. BLOCK and G. H. McINTYRE, J. Amer. Chem. Soc., 1953, 75, 5667.

13. H. IRVING and H. S. ROSSOTTI, J. Chem. Soc., 1953, 3397.

14. N. J. GEARY, G. NICKLESS and F. H. POLLARD, Analyt. Chim. Acta, 1962, 27, 71.

15. K. E. JABALPURWALA, K. A. VENKATACHALAM and M. B. KABADI, J. Inorg. Nuclear Chem., 1964, 26, 1027.

16. C. R. BERA, S. CHATTOPADHYAY and G. P. SENGUPTA, J. Indian Chem. Soc., 1979, 56, 416.

17. D. RAMASWAMY and H. RANGANATHAN, Curr. Sci., 1978, 47, 330.

18. H. IRVING and R. J. P. WILLIAMS, Nature, 1948, 162, 746; J. Chem. Soc., 1953, 3192.

Coordination Behaviour of a Tetra-substituted Pyrazole: Cobalt(II), Nickel(II) and Copper(II) Complexes with 3,4,5-Trimethyl-1-Nitroguanyl Pyrazole

NITYANANDA SAHA* and N. C. GAYEN

Department of Chemistry, University College of Science, Calcutta-700 009

RECENTLY, a significant amount of research has centered around the transition-metal complexes of pyrazole-derived ligands[1] primarily because of the biological implications of the free ligands. As part of our programme[2] devoted to the study of the coordination behaviour of substituted pyrazoles, the present communication reports the synthesis of a hitherto unreported tetra-substituted pyrazole, namely, 3,4,5-trimethyl-1-nitroguanyl pyrazole (LH, Fig. 1) and its coordination behaviour by complexation with cobalt(II), nickel(II) and copper(II) salts ; the solid metal complexes have been characterised from elemental analyses, magnetic susceptibility measurements, electronic and vibrational spectral data.
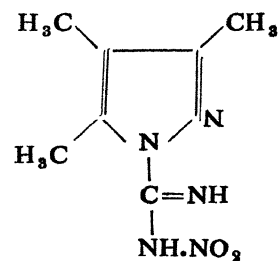

Fig. 1

Experimental

All the chemicals used were of AnalaR grade and the solvents used were purified by usual methods.

3,4,5-Trimethyl-1-nitroguanyl pyrazole (LH) was prepared by condensation of 3-methylacetylacetone[3] and nitroaminoguanidine[4] following a method similar to that adopted by R. A. Henry[5]. The product on recrystallisation from hot ethanol gave shining white crystals, m.p. 155°. The compound is soluble in hot low molecular weight alcohols, but insoluble in water. (Found : C, 42.40 ; H, 5.45; N, 35.80%. $C_7H_{11}N_5O_2$ requires C, 42.60 ; H, 5.58 ; N, 35.73%).

(a) [$ML_2.nH_2O$] [n=0, M=Ni ; n=2 ; M=Co(II), Cu(II)] : The solution obtained by mixing ethanolic solution of metalchloride hexahydrate (0.002 mole) and the ligand (0.004 mole) was adjusted to have pH 6 with dil. ammonia solution ; the microcrystalline compound separated within few minutes (except the orange-red, NiL₂ which separated usually on heating over water-bath for 4-5 hours), in each case, this was filtered off,