

TABLE 1 — MELTING POINTS AND ANALYSES OF MIXED LIGAND COMPLEXES OF CADMIUM(II)

Compound	Colour	m.p. (°C)	Cd (%)		S (%)	
			Found	Reqd	Found	Reqd
Cd(dtc) ₂	White	240	27.01	27.52	30.2	31.3
Cd(Mdtc) ₂	do	>280	25.9	25.7	29.1	29.3
Cd(Pdtc) ₂	do	>280	25.3	25.9	29.1	29.6
Cd(dtc) ₂ Q	Pale yellow	135	20.0	20.9	23.1	23.8
Cd(dtc) ₂ IQ ₂	Light yellow	85	16.9	16.8	20.0	19.3
Cd(dtc) ₂ 3,5-Lut.	Brown	150	20.4	21.8	24.2	24.8
Cd(dtc) ₂ 2,4-Lut.	Light yellow	248	21.3	21.8	24.1	24.8
Cd(Mdtc) ₂ IQ	Light rose	>280	19.3	19.8	22.2	22.6
Cd(Pdtc) ₂ IQ ₃	Shining grey	130	14.2	13.7	15.1	15.6

dtc = diethyldithiocarbamate; Mdtc = morpholyl dithiocarbamate; Pdtc = piperidyl dithiocarbamate; Q = quinoline; IQ = isoquinoline; 3,5-Lut. = 3,5-lutidine; and 2,4-Lut. = 2,4-lutidine.

cm⁻¹ in Cd(dtc)₂, Cd(Pdtc)₂ and Cd(Mdtc)₂ respectively.

When these cadmium dithiocarbamates react with nitrogen donor ligands, it is expected that C—N bond order will decrease as compared to parent dithiocarbamates which is actually substantiated in this investigation. Thus the $\nu(\text{C}-\text{N})$ in Cd(dtc)₂, Cd(dtc)₂Q, Cd(dtc)₂IQ₂, Cd(dtc)₂(3,5-lut) and Cd(dtc)₂(2,4-lut) occurs at 1508, 1480, 1480 1480 and 1482 cm⁻¹ respectively.

The more interesting feature in this investigation is the attainment of different coordination numbers with different ligands, depending on the basicity or polarizability of the ligand donor atom. Two molecules of less basic isoquinoline are added forming a six coordinated Cd(dtc)₂IQ₂ whilst only one mole of comparatively more basic quinoline is added giving rise to a penta-coordinated Cd(dtc)₂Q. In the case of 2,4- and 3,5-lutidines also, one mole of the ligand is added giving rise to penta-coordination. Another interesting observation is the fact that when less basic isoquinoline is used with morpholyl-, diethyl- and piperidyl-dithiocarbamates, five, six and seven-coordinated compounds are formed having the formulae Cd(Mdtc)₂IQ, Cd(dtc)₂IQ₂ and Cd(Pdtc)₂IQ₃ respectively. This shows that Pauling's electroneutrality conditions for stability are attained for cadmium only with different moles of bonded ligand (IQ). This once again confirms the view that the coordination number round a particular metal ion depends on the donor-acceptor characteristics of the participating ligand and metal. The compound Cd(Pdtc)₂IQ₃ now reported appears to be the first example of hepta-coordination for cadmium involving the use of 5s 5p³ 5d³ hybrid orbitals. The X-ray crystallographic and thermogravimetric studies on this compound are being pursued to confirm hepta-coordination.

One of the authors (B.P.M.) is thankful to UGC, New Delhi for the award of a teacher fellowship and to Godavaris Mahavidyalaya, Banpur (Orissa) for granting study leave.

References

1. PRABHAKARAN, C. P. & PATEL, C. C., *Indian J. Chem.*, **7** (1969), 1257.
2. VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, Green, London), 1959, 428.
3. CHATT, J., DUNCANSON, L. A. & VENANZI, L. M., *Nature, Lond.*, **177** (1956), 1042.

pH-metric Investigation of Stepwise Formation Constants of Vanadyl(IV) Complexes of Benzoyl & Nicotinoyl Hydrazines*

P. V. KRISHNA RAO, R. SAMBASIVA RAO & A. SATYANARAYANA

Department of Chemistry, Andhra University
Waltair 530003

Received 10 October 1977; revised 9 February 1978
accepted 5 May 1978

Proton-ligand stability constants of benzoyl and nicotinoyl hydrazines and stability constants of their complexes with vanadyl(IV) have been determined pH metrically in aquo-DMF media of varying concentrations. The log K_1^H values for the ligands pass through a minimum at 40% (v/v) DMF. The complexes are suggested to be cationic species involving five-membered chelate rings.

ALTHOUGH the ligand characteristics of the aroyl hydrazines which find extensive use in chemotherapy, agriculture and industry have been investigated in both the solid and the aqueous phases¹⁻⁴, a survey of literature shows that study of hydrazide complexes in non-aqueous media is scarce. In continuation of our earlier studies on aroyl hydrazines in aquo-organic media⁵, we report here pH-metric determination of proton-ligand and vanadyl(IV)-ligand stability constants in aquo-dimethyl formamide media.

Approximately 0.1M aqueous solutions of nicotinoyl and benzoyl hydrazines were prepared from Fluka's pure samples and were standardized by the procedure due to Vulterin *et al.*⁶. The preparation and standardization of vanadyl(IV) perchlorate is described elsewhere⁵. All the other chemicals used were of AR grade. Systronics expanded pH meter (0.02 pH) type 331 was used.

The equilibration of glass electrode and calculation of hydrogen ion concentration from pH meter readings were carried out according to the procedure described by McBryde *et al.*⁷. The proton-ligand stability constants of nicotinoyl and benzoyl hydrazines were determined by titrating 0.02M perchloric

*Part of the present work was presented at the 63rd annual session of Indian Science Congress held at Andhra University, Waltair, 1976.

acid with 0.20M sodium hydroxide in presence and absence of the ligands in varying proportions (vol/vol) of dimethyl formamide solutions. The metal-ligand formation constants were evaluated by titrating 50% (vol/vol) aquo-dimethyl formamide solutions containing 0.02M perchloric acid, 0.08M sodium perchlorate and $4.393 \times 10^{-3}M$ vanadyl(IV) perchlorate in presence and absence of 8.78×10^{-3} and $1.76 \times 10^{-2}M$ nicotinoyl or benzoyl hydrazines with 0.2M sodium hydroxide.

The log K_1^H values for the ligands pass through a minimum at 40% (vol/vol) DMF in conformity with the observations of Rorabacher⁸, Irving⁹ and McBryde⁷ who reported that in case of ligands with dissociable protons (such as COOH in glycine) the log K_1^H values increase more or less linearly with the increasing concentration of the co-solvent whereas with ligands having substituted ammonium hydrogen ions the relation is non-linear and in most cases passes through a minimum at some solvent composition. These observations may be attributed to the predominant role of the non-electrostatic parameters like basicity effects, interaction of ions with dipoles of the solvent that increase the basicity of the medium. The average number of ligands bound per metal ion (\bar{n}) and pL where L is the free ligand concentration were calculated by Irving and Rossotti technique⁹. Except in the case where ligand to metal ion ratio is 1:1, the formation curves are similar and the \bar{n} values approach a limiting value of 2 suggesting that only two ligand species are bound per metal ion in the complex. The stepwise formation constants obtained from various computational techniques are summarized in Table 2.

TABLE 1 — PROTON-LIGAND ASSOCIATION CONSTANTS OF BENZOYL AND NICOTINOYL HYDRAZINES IN AQUO-DIMETHYL FORMAMIDE MEDIUM AT $28.0^\circ \pm 0.2^\circ$

Co-solvent (%) (vol/vol)	Dielectric constant*	Mole fraction of solvent*	log K_1^H	
			Benzoyl hydrazine	Nicotinoyl hydrazine
20	74.0	0.055	3.98	4.08
40	69.0	0.135	2.08	2.12
50	65.0	0.189	2.65	3.78
60	60.8	0.259	2.70	3.90
70	56.2	0.352	2.80	4.00

*Data adopted from ref. 7.

TABLE 2 — STABILITY CONSTANTS OF VANADYL(IV)-AROYL HYDRAZINE COMPLEXES

Method	Benzoyl hydrazine		Nicotinoyl hydrazine	
	log β_1	log β_2	log β_1	log β_2
Bjerrum half- \bar{n} method	2.68	4.58	2.38	4.57
Schroder's method	2.72	4.64	2.44	4.64
McIntyre's procedure	2.42	4.53	3.31	6.48
Least-squares	2.38	4.56	3.39	6.52

Aroyl hydrazines function as neutral or mono-basic bidentate ligands forming cationic or neutral chelates with bivalent metal ions. The cationic complex may be deprotonated by bases resulting in the neutral species¹⁰. However, recently Chatt *et al.*¹¹ reported that benzoyl hydrazine acts as a tribasic monodentate ligand in Re(V) complexes. Although no conclusive evidence regarding the structural details of the complexes can be obtained from the electrometric studies alone, we tentatively propose chelation with vanadyl(IV) taking place through the oxygen of the carbonyl group and nitrogen of the terminal amino group resulting in five-membered cationic species. The cationic nature of the complexes has been confirmed by ion-exchange experiments.

References

1. NAGANO, K., TSUKAHARA, H. & TAMURA, Z., *Chem. pharm. Bull. Tokyo*, **11** (1963), 651, 793,999; **12** (1964), 1198, 1207.
2. AGARWAL, R. C. & PRASAD, B., *Indian J. Chem.*, **10** (1972), 1183.
3. AGARWAL, R. C. & PRASAD, B., *Indian J. Chem.*, **13** (1975), 728.
4. AGARWAL, R. C., PRASAD, B. & YADAV, B. N., *J. inorg. nucl. Chem.*, **37** (1975), 899.
5. KRISHNA RAO, P. V., SAMBASIVA RAO, R. & RAMBABU, CH., *Chemia Analit. Warsaw* (in press); *J. inorg. nucl. Chem.*, **39** (1977), 708.
6. VULTERIN, J., *Colln Czech. chem. Commun.*, **28** (1963), 1391.
7. MUI, K. K., MCBRYDE, W. A. E. & NIEBOER, E., *Can. J. Chem.*, **52** (1974), 1821.
8. RORABACHER, D. B., MAKELLAR, H. J., SHU, E. R. & BONNAVITA, *Analyt. Chem.*, **43** (1971), 561.
9. IRVING, H. M. & ROSSOTTI, R. S., *J. chem. Soc.*, (1954), 2904; (1953), 3397; *Acta chem. scand.*, **10** (1956), 72.
10. AHMED, A. & CHAUDARI, N. R., *J. inorg. nucl. Chem.*, **33** (1971), 189.
11. CHATT, J., DILWORTH, J., TIEIG, G. I. & GUPTA, V. D., *J. chem. Soc. (A)* (1971), 2531.

Thermodynamic & Physico-chemical Investigations of Cr(II), Mn(II), Fe(II), Co(II), Ni(II) & Cu(II) Chelates of 3-(N-2-Furfuralideneimino)propionic Acid

D. C. SEHGAL, C. P. GUPTA & R. K. MEHTA

Department of Chemistry, University of Jodhpur, Jodhpur

Received 20 December 1977; revised 31 March 1978; accepted 15 May 1978

Stability constants of the chelates of Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with 3-(N-2-furfuralideneimino)propionic acid (HFP) have been determined by Calvin-Bjerrum pH-titration technique in aqueous media at 25°, 30° and 35°. Thermodynamic stability constants have been obtained by extrapolation of values at various ionic strengths ($\mu = 0.1$; 0.05 and 0.01M NaClO₄). The order of stability constants has been found to be, Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II) > Cr(II), which is in agreement with the Irving-Williams rule. Magnetic moment, conductance, electronic absorption and IR spectral studies of the solid chelates indicate a near octahedral stereochemistry.