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Synthesis, Formation Constants and Thermodynamic Functions for Some Bivalent Transition Metal Complexes with Di(3-chlorophenyl) Carbazone

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Complex formation between transition metal ions *viz.*, Cu(II), Ni(II), Zn(II), Cd(II), Co(II) and Mn(II) with di(3-chlorophenyl) carbazone (DMClPC) has been investigated by potentiometric measurements of hydrogen ions liberated on complexation at 25, 35 and 45 ± 0.1°C in 50% (v/v) aqueous-dioxane at an ionic strength of 0.1 M $NaClO_4$. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of $\bar{n}$ and pL. The stability constants have been calculated using a PC-XT computer by the weighted least squares method. The stability costants have also been calculated by Bjerrum half $\bar{n}$ method. The order of stability constants is found to be: Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) > Mn(II). Thermodynamic functions, ΔG, ΔH and ΔS have also been calculated.

INTRODUCTION

A survey of literature reveals that diphenylcarbazone (DPC) forms highly coloured metal complexes which provides the basis for its use as a sensitive reagent for the detection and spectrophotometric determination of several cations in micro-amounts[1,2]. Accurate values of stability constants are needed to understand biological activity of metals, and metal transport in both plants and animals[3]. In continuation of our studies on the synthesis and complexing abilities of the nuclear substituted diphenylcarbazones[4,5] and keeping in view their applications, we report here the synthesis, characterization and complexing behaviour of di-(3-chlorophenyl) carbazone with bivalent transition metals. The stepwise and overall stability constants of these chelates have been determined by the Irving-Rossotti titration technique[6].

EXPERIMENTAL

The ^1H NMR spectra in $CDCl_3$ were recorded on a Varian XL-300 MHz spectrometer using TMS as an internal reference (chemical shift in δ, ppm). Electron-impact mass spectra were obtained using an AEI MS30 instrument equipped with an MSS system. The IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin-Elmer 1430 spectrophotometer. A digital pH-meter (Systronics 335) with glass and saturated calomel electrodes assembly was used for the pH measurements. The pH-meter was standardized with potassium hydrogen phthalate and phosphate buffers before preforming titrations.

3-Chlorophenylhydrazine (1): It was synthesized according to the method reported previously[7]. It was then dissolved in hot water and neutralised with sodium hydroxide solution (10%) while maintaining the temperature below 25°C. The pale oily liquid was separated and extracted with diethyl ether. The ether extract was washed thoroughly with water and on evaporation of ether, the liquid 3-chlorophenylhydrazine was obtained. It was then dried *in vacuo* over P_2O_5 for 12 h, b.p. 205°C.

Di-(3-chlorophenyl) carbazide (2): In a 50 mL round-bottomed flask 3-chlorophenylhydrazine (1; 0.08 mole) was mixed with urea (0.04 mole; previously dried for 3 h at 100°C) and the mixture was heated in an oil bath fitted with a reflux condenser for 3 h, maintaining the temperature at 140–155°C and cooled. The resulting solid was dissolved by refluxing in alcohol (40 mL), filtered and the filtrate concentrated to 20–25 mL. The solid was separated, washed with water and petroleum ether thoroughly. It was crystallized in alcohol and the crystals were dried *in vacuo*. m.p. 120°C, yield 68%, m.f. $C_{13}H_{12}N_4OCl$ Anal: Calcd, C, 50.18; H, 3.89; N, 18.01; Found: C, 50.05; H, 4.02; N, 17.83%.

Di-(3-Chlorophenyl) carbazone (3): Di-(3-chlorophenyl) carbazide (**2**; 0.013 mole) was dissolved in glacial acetic acid (240 mL), diluted with 1 N sulphuric acid (80 mL) and 2–3 drops of ferric alum (10%) were added to it. Then a solution of potassium persulphate (0.018 mole) in water (80 mL) was added dropwise with vigorous stirring, allowed to stand for 1/2 h, diluted with ice-cold water and then extracted with ether. The ethereal extract was washed thoroughly with distilled water till it was free from acetic acid. On evaporation of ether the product was obtained. It was chromatographed over SiO_2 (80.0 g, 60–120 mesh). Elusion with acetone-chloroform mixture (20 : 80) and evaporation of the solvent mixture gave (**3**) in the form of pale yellow crystals. m.p. 110°C, yield 42%; MS: M/z 310 (m^+); IR (KBr) cm^{-1}: 3360, 3250, 3000, 1700, 1565, 1490, 753; ^1H NMR: 1.6 (s, 1 H, NH), 6.5 (s, 1 H, OH), 6.6–7.5 (m, 8 H, Ar—H). m.f. $C_{13}H_{10}N_4OCl_2$ Anal: Calcd: C, 50.50; H, 3.26; N, 18.12; Found: C, 49.60; H, 3.30; N, 17.40%.

The solution of the ligand was prepared in dioxane. All the metal ion solutions were prepared from their corresponding sulphates or nitrates (AR, BDH) in double distilled water and were standardised by EDTA method[8]. Sodium perchlorate (Riedel) was used to maintain constant ionic strength. Carbonate-free sodium hydroxide solution was prepared by conventional method[9]. Dioxane (AR) was purified by the method used by Math *et al.*[10] A solution of sodium hydroxide was used as the titrant. It was standardised with potassium hydrogen phthalate. The titrations were carried out in an inert atmosphere by passing nitrogen gas, presaturated with 50% (v/v) aqueous dioxane before passing through the reaction mixture. The titrations were carried out in a specially designed double-walled beaker.

The method of Calvin-Bjerrum as modified by Irving and Rossotti[6] was followed to determine the proton-ligand and metal-ligand stability constants.

The following sets of titrations were preformed at three different temperatures, 25 ± 0.1°, 35 ± 0.1° and 45 ± 0.1°C in 50% dioxane-water medium.

(i) 5 mL $HClO_4$ (0.1 M) + 5 mL $NaClO_4$ (1.0 M) + 25 mL dioxane + 15 mL H_2O.

(ii) 5 mL $HClO_4$ (0.1 M) + 5 mL $NaClO_4$ (1.0 M) + 5 mL ligand (2.0×10^{-2} M) + 20 mL dioxane + 15 mL H_2O.

(iii) 5 mL $HClO_4$ (0.1 M) + 5 mL $NaClO_4$ (1.0 M) + 5 mL ligand (2.0×10^{-2} M) + 5 mL metal ion solution (5×10^{-9} M) + 20 mL dioxane + 10 mL H_2O.

Total volume in each case was 50 mL and ionic strength was maintained constant at 0.1 M $NaClO_4$. The ratio of the metal salt to reagent was maintained at nearly 1 : 4 in all the titrations in order to satisfy the maximum coordination possibility of the metal ions.

TABLE-1
STABILITY CONSTANTS OF BIVALENT METAL COMPLEXES OF DI-(3-CHLOROPHENYL) CARBAZONE (DMClPC) AT DIFFERENT TEMPERATURES (μ = 0.1 M $NaClO_4$) IN 50% (v/v) DIOXANE-WATER MEDIUM

System	Stability Constants	Weighted least squares method		
		25°C	35°C	45°C
DMClPC	pKa	8.70	8.12	7.82
Cu(II)-DMClPC	log K_1	9.69	7.75	7.30
	log K_2	9.34	7.45	7.11
	log β_2	19.03	15.20	14.41
Ni(II)-DMClPC	log K_1	7.20	6.02	5.35
	log K_2	5.33	5.31	4.90
	log β_2	12.53	11.33	10.25
Zn(II)-DMClPC	log K_1	6.10	5.32	4.25
	log K_2	5.35	4.79	3.97
	log β_2	11.45	10.11	8.22
Co(II)-DMClPC	log K_1	5.50	4.80	4.20
	log K_2	4.90	4.40	3.85
	log β_2	10.40	9.20	8.05
Cd(II)-DMClPC	log K_1	6.10	5.55	5.09
	log K_2	5.18	4.78	4.33
	log β_2	11.28	10.33	9.42
Mn(II)-DMClPC	log K_1	3.33	3.00	2.81
	log K_2	3.21	2.79	2.59
	log β_2	6.54	5.79	5.40

In all the calculations, pH correction and volume correction factors have been applied for dioxane-water mixture. From the titration curves of solutions (i) and (ii) the values of $\bar{n}_A$ (average number of protons associated/ligand molecule) were calculated at various pH values using the Irving-Rossotti relation. The pKa values were determined by plotting $\bar{n}_A$ *vs* pH, as well as from the intercepts of the linear plots of log $[\bar{n}_A/(1-\bar{n}_A)]$ vs pH. From the titration curves using the solutions (i), (ii) and (iii), $\bar{n}$ (metal-ligand formation number) values of the metal complexes were determined at various pH values. From pKa and $\bar{n}$ values at different pH values, the corresponding values of ρ*L* were calculated. The $\bar{n}$ and ρ*L* data were subjected to the weighted least squares method developed by Sullivan *et al.*[11] on a PC-XT computer to get β_n values. The weighted least squares treatment determined the set of β_n values which make the function U,

$$U = \sum_{n=o}^{N} (y - x - nz)\, \beta_n \chi^n$$

nearest to zero, by minimising S,

$$S = \sum_{i=1}^{I} W_i U^2 (x_i, y_i, z_i)$$

with respect to variation in β_n. S_{min} has the same statistical distribution as χ^2 with K degrees of freedom and the weights defined in accordance with Rydberg and Sullivan[12]. S_{min} can be equated to χ^2. The stability constants thus calculated are given in Table-1. The ΔH was calculated by the graphical method of Yatsimirskii *et al.*[13] while ΔG and ΔS were calculated by conventional methods (Table-2).

TABLE-2
THERMODYNAMIC PARAMETERS OF BIVALENT METAL COMPLEXES WITH DI-(3-CHLOROPHENYL) CARBAZONE AT 25 ± 0.1°C ($\mu = 0.1$ M $NaClO_4$)

Metal ion	–ΔG (kcal mole^{-1})	–ΔH (kcal mole^{-1})	–ΔS (e.u.)
Cu(II)	12.95	49.06	121.16
Ni(II)	9.07	27.96	63.39
Zn(II)	8.32	32.34	80.61

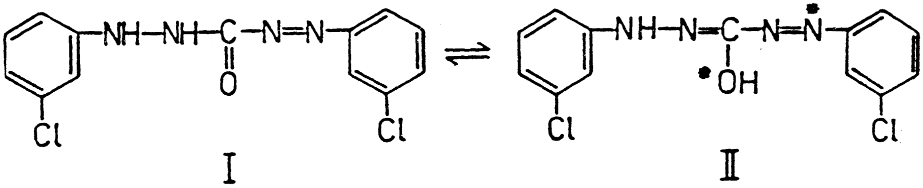
RESULTS AND DISCUSSION

The formation curve of DMClPC is found to be a single wave extending from 0 to 1 and the slope of the plot of $\bar{n}_A/(1-\bar{n}_A)$ *versus* pH is 0.98; both of these indicate that the ligand exists in monoprotonic form, due to the presence of only one OH group in its enolic tautomeric form. The higher value of acid dissociation constant of the ligand (pKa = 8.70) compared to its parent (pKa = 9.26) at 25°C reveals that the introduction of Cl atom in the *meta* position of the phenyl ring increases the acid strength of the ligand. The pKa value can also be evaluated from the Hammett relation

$$\log K = \log K_0 + \sigma\rho$$

Siddalingaish *et al.*[14] have determined the value of ρ for the diphenylcarbazone systems in 50% (v/v) aqueous-dioxane as 2.32. Substituting the value of $\sigma_{m\text{-}Cl}$ (0.372)[15] in the above expression, the value of pKa for (DMClPC) comes out as 8.40, which is in good agreement with the experimental value of 8.70. The maximum value of $\bar{n}$ for each metal complex remains somewhere below 2 *i.e.*, $0 < \bar{n} < 2$ indicating thereby the formation of ML_2 type of the complex in conformity with the previous works reported for other diphenylcarbazone derivatives[4, 5].

On the basis of the analytical data and spectral study, Structurse I and II may be assigned to DMClPC (Chart 1). Detailed studies[14, 16] on DPC complexes have shown that the complex formation takes place at —$\bar{O}$ and —N< of the ligand with metal ions. The sites of coordination are shown by asterisks on the nitrogen and oxygen atoms in II.



The result summarises the formation constants of metal DMClPC systems at 25, 35 and 45°C. Our studies reveal that Ca(II), Mg(II), Ba(II) and Sr(II) form very weak complexes and hence are not included in Table-1. The order of overall formation constants investigated is as follows:

$$\mathrm{Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) > Mn(II)}$$

This order is in agreement with the order as determined by Mellor and Maley[17] and Irving and Williams[18]. The additional high stability of the Cu(II) complex may be attributed to the unique electronic configuration ($3d^9$) of Cu(II) ion which is capable of additional stabilisation due to John Teller distortion.

In general $\log K_1 > \log K_2$ for a given metal ion; however, the difference between the two constants is not much, indicating that there is almost an equal tendency for the formation of neutral complex species. In fact, the maximum $\bar{n}$ values observed in our present experiments are *ca.* 2.0 which supports our assumption of 1 : 2 stoichiometry. In view of the fact that very low concentrations of metal ions have been used in the titrations, the possibility of formation of polynuclear complexes is negligibly small.

The values of the thermodynamic parameters relating to the complex formation reactions are given in Table-2. The negative values of ΔG indicate that the complexation reactions are spontaneous and metal chelates are thermodynamically stable. Negative values of ΔH indicate that the metal ligand bonds are fairly strong and complexation reactions are exothermic in nature. The negative ΔS values in all the complexes show loss of entropy during the formation of complexes, which are more polar than the reactants and hence strongly solvated.

Relation between log K_1 and atomic numbers, ionisation potentials and electronegativities of metal ions

The $\log K_1$ values of the metal-ligand systems were plotted against the atomic numbers of the metal ions. The plot showed a monotonic rise with a maximum at Cu followed by a fall and lower value of Mn[18]. In the plot of $\log K_1$ versus second ionisation potential of the metals, it is observed that stability increases from Mn to Cu and falls marginally with the fact that Zn is not a member of the first transition series. The plot of log K_1 *versus* electronegativities of the metals indicats that the stability increases with increase in elctronegativity of the metals.

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REFERENCES

1. N.M. Blaton, O.M. Peeters, C.J. DeRantr and G.J. Willems, *Acta Cryst.*, **B35**, 2629 (1979).
2. N. Czech, B. Friese and F. Umland, *Anal. Chem. Acta*, **121**, 275 (1980).
3. A.E. Martel and R.J. Motekaitis, Determination and Use of Stability Constants, 2nd Edn., VCH, New York, p. 195 (1992).
4. E.S. Jayadevappa, K.S. Math and A.H.M. Siddalingaiah, *J. Indian Chem. Soc.*, **60**, 333 (1983).
5. ________. *J. Electrochem Soc.*, **32**, 163 (1983).
6. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
7. M.W. Bullock and J. J. Hand, *J. Am. Chem. Soc.*, **78**, 5854 (1956).
8. H.A. Flaschka, EDTA Titrations, Pergamon, New York (1959).
9. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Edn., Longmans Green, London (1961).
10. K.S. Math, Q. Fernando and H. Freiser, *Anal. Chem.*, **36**, 1762 (1964).
11. J.C. Sullivan, J. Rydberg and W.F. Miller, *Acta Chem. Scand.*, **3**, 2023 (1959).
12. J. Rydberg and J.C. Sullivan, *Acta Chem. Scand.*, **13**, 2057 (1959).
13. K.B. Yatsimirskii and V.P. Vaslev, Instability Constants of Complex Compounds, Van Nostrand, New York, p. 63 (1960).
14. A.H.M. Siddalingaiah, Stabilities of the metal complexes of diphenylcarbazone and its nuclear substituted derivatives Ph. D. Thesis, Karnatak University, Dharwad (1980).
15. D.H. Daniel and H.C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
16. M.Y. Kariduraganavar, Physico-chemical studies on metal complexes, Ph.D. Thesis, Karnatak University, Dharwad (1993).
17. D.P. Mellor and L. Maley, *Nature*, **159**, 370 (1948).
18. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953).

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