

Synthesis, Stability Constants and Thermodynamic Parameters of Binary Complexes of Di(2-chlorophenyl) Carbazone

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The ligand di(2-chlorophenyl) carbazone (DOCIPC) has been synthesised for the first time and characterised by melting point, thin layer chromatography, elemental analysis, mass, ^1H NMR and IR spectra. Stability constants of the complexes of Mn(II), Co(II), Cd(II), Zn(II), Cu(II), Ni(II) and Fe(II) with DOCIPC have been determined potentiometrically in 50% (v/v) aqueous-dioxane at an ionic strength of 0.1 M NaClO_4 and at different temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of \bar{n} and ρL . The stability constants have been calculated using a PC-XT computer by the weighted least squares method. The stability constants have also been calculated by Bjerrum half \bar{n} method. The order of stability constants is found to be: Mn(II) < Co(II) < Cd(II) < Ni(II) < Zn(II) < Fe(II) < Cu(II). Thermodynamic parameters, ΔG , ΔH and ΔS have been calculated.

INTRODUCTION

The nuclear substituted diphenylcarbazones react with cations more sensitively than the original diphenylcarbazone (DPC). These derivatives give intense colouration with cations suggesting the possibility of developing them as useful analytical reagents for the determination of several cations in micro-amounts. Quite a good number of substituted diphenylcarbazones have been synthesised mainly in our laboratory¹. In continuation of our studies on the synthesis and complexing abilities of the nuclear substituted diphenylcarbazones and keeping in view their applications, we report here the synthesis and studies on di(2-chlorophenyl) carbazone.

EXPERIMENTAL

The ^1H NMR spectra in CDCl_3 were recorded on a Varian XL-300 MHz spectrometer using TMS as 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 performing titrations.

2-Chlorophenylhydrazine (1): It was synthesized according to the method reported previously². It was then dissolved in hot water and treated with sodium hydroxide solution (10%) while maintaining the temperature below 15°C . The pale yellow hydrazine was extracted with diethyl ether. The ether extract was washed with water, dried (Na_2SO_4) and concentrated until the crystallisation of the 2-chlorophenylhydrazine occurred and dried *in vacuo* over P_2O_5 for 12 h, m.p. 48°C .

Di(2-Chlorophenyl) carbazide (2): In a 50 mL round-bottomed flask 2-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 temperature at $140\text{--}155^\circ\text{C}$ 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. 160°C , yield 44%. Anal. Calcd.: $\text{C}_{13}\text{H}_{12}\text{N}_4\text{OCl}_2$: C, 50.18; H, 3.89; N, 18.01; Found: C, 50.16; H, 3.85; N, 18.03%.

Di(2-chlorophenyl) carbazone (3): Di(2-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%) was added to it. Then a solution of potassium persulphate (0.018 mole) in water (80 mL) was added dropwise with a vigorous stirring, allowed to stand for $\frac{1}{2}$ 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). On elusion with acetone-chloroform mixture (20:80) and evaporation the solvent mixture gave 3 in the form of pale yellow crystals. M.p. 134°C , yield 45%; MS: M/z 310 (m^+); IR (KBr) cm^{-1} : 3382, 3238, 3076, 1705, 1584, 1494, 759; ^1H NMR: 1.64 (s, 1H, NH), 6.5 (s, 1H, OH), 6.7–7.8 (m, 8H, Ar-H). Anal. Calcd.: $\text{C}_{13}\text{H}_{10}\text{N}_4\text{OCl}_2$: C, 50.50; H, 3.26; N, 18.12; Found: C, 49.80; H, 3.12; N, 17.32%.

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 method³. Sodium perchlorate (Riedel) was used to maintain constant ionic strength. Double distilled water and carbonate-free sodium hydroxide solution were prepared by conventional methods⁴. Dioxane (AR) was purified by the method used by Math *et al.*⁵ 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 Rossotti⁶ was followed to determine the proton-ligand and metal-ligand stability constants.

The following sets of titrations were performed at three different temperatures: $25 \pm 0.1^\circ$, $35 \pm 0.1^\circ$, and $45 \pm 0.1^\circ$ 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.

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 solution (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 ρL were calculated. The \bar{n} and ρL data were subjected to the weighted least squares method developed by Sullivan *et al.*⁷ 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,

$$U = \sum_{n=0}^N (y - x - nz) \beta_n \chi^n$$

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 Sullivan⁸. 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.*⁹ while ΔG and ΔS were calculated by conventional methods (Table-2).

TABLE-1
 STABILITY CONSTANTS OF BIVALENT METAL COMPLEXES OF DI(2-CHLORO-PHENYL) CARBAZONE (DOCIPC) AT DIFFERENT TEMPERATURES
 ($\mu = 0.1$ M NaClO₄) IN 50% (v/v) DIOXANE-WATER MEDIUM

System	Stability constants	Weighted least squares method		
		25°C	35°C	45°C
DOCIPC	pKa	8.44	8.32	8.24
Cu(II)-DOCIPC	log K ₁	7.35	6.86	6.82
	log K ₂	6.85	6.47	6.45
	log β_2	14.20	13.33	13.27
Ni(II)-DOCIPC	log K ₁	4.78	4.64	4.60
	log K ₂	4.15	4.08	3.84
	log β_2	8.93	8.72	8.44
Zn(II)-DOCIPC	log K ₁	5.05	4.90	4.88
	log K ₂	4.25	4.20	4.12
	log β_2	9.30	9.10	9.00
Co(II)-DOCIPC	log K ₁	4.54	—	—
	log K ₂	3.96	—	—
	log β_2	8.50	—	—
Cd(II)-DOCIPC	log K ₁	4.63	—	—
	log K ₂	4.00	—	—
	log β_2	8.63	—	—
Mn(II)-DOCIPC	log K ₁	3.36	—	—
	log K ₂	2.98	—	—
	log β_2	6.34	—	—
Fe(II)-DOCIPC	log K ₁	7.65	—	—
	log K ₂	4.90	—	—
	log β_2	12.55	—	—

TABLE-2
 THERMODYNAMIC PARAMETERS OF BIVALENT METAL COMPLEXES WITH
 DI(2-CHLOROPHENYL) CARBAZONE AT 25 ± 0.1°C ($\mu = 0.1$ M NaClO₄)

Metal ion	$-\Delta G$ (Kcal mole ⁻¹)	$-\Delta H$ (Kcal mole ⁻¹)	ΔS (e.u.)
Cu(II)	10.02	11.80	-5.96
Ni(II)	6.52	3.92	8.73
Zn(II)	6.89	3.72	10.64

RESULTS AND DISCUSSION

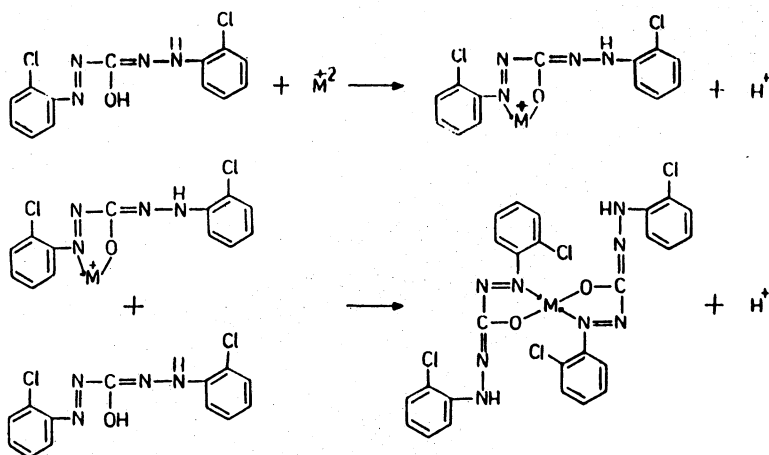
The formation curve of DOCIPC is found to be a single wave extending from 0 to 1 and the slope of the plot of $\bar{n}_A/(1 - \bar{n}_A)$ versus pH is 0.98; both of these indicate the presence of only one ionisable proton. The pKa value of DOCIPC

determined as described above is 8.44 at 25° which is considerably less than that of DPC (9.26). This is due to the substitution of electron withdrawing inductive effect (-I) of the chloro group at the *ortho* position. From the linear plot of $\log K/K_0$ values versus σ (Hammett constant) for *para* and *meta* substituents, Siddalingaiah¹⁰ has evaluated the constants ρ and σ for DOCIPC in the Hammett equation

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

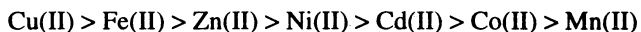
as 2.32 and -0.32 respectively. Inserting these values in the above equation, a semiquantitative value of pKa equal to 8.52 can be obtained for DOCIPC which is in very good agreement with the experimental value 8.44.

Detailed studies on DPC complexes have shown¹¹ that the complex formation takes place at $-\text{O}^-$ and $-\text{N}<$ of the ligand and metal ions. The formation of 1:1 and 1:2 complexes may be represented as in the Scheme 1 shown below.



Scheme 1. Formation of 1:1 and 1:2 complexes

The result summarises the formation constants of metal DOCIPC systems at 25°C and in some cases also at 35° and 45°C. The order of formation constants investigated is as follows:



This order is in agreement with the order as determined by Mellor and Maley¹² and Irving and Williams¹³. The additional high stability of the Cu(II) complex is attributed to the unique electronic configuration ($3d^9$) of Cu(II) ion which is capable of additional stabilisation due to Jahn Teller distortion. Similar conclusions were also drawn by Saleh *et al.*¹⁴ in explaining the high stability of Cu(II) complexes of salicylic acid derivatives.

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.

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 estimate of the thermodynamic parameters relating to the complex formation reactions are given in Table-2. All the complexation reactions are associated with negative ΔH values indicating the exothermic nature of all these reactions. In so far as ΔH is a measure of the strength of the covalent bonding, one can conclude that Cu(II) complexes are more strongly bound than Ni(II) and Zn(II) complexes.

In the case of Ni(II) and Zn(II), ΔS values are positive and therefore are favourable to the complex formation. The complex formation in these cases may be said to be due to charge neutralization as the neutralization of the charge will lower the solvation sheath of the complex molecule. In the case of Cu(II), the complex formation is associated with a large ΔH indicating a high degree of covalent character. Such interactions where large values of ΔH are opposed by large unfavourable ΔS may be referred to as "soft-soft" interactions. The other cases which are typical of charge neutralisation may be considered as "hard-hard" interactions.

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