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THERMOCHEMISTRY FOR THE FORMATION OF METHYL AND CHLORO MALEANILIC ACID COMPLEXES OF BIVALENT TRANSITION METAL IONS

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ABSTRACT

The stepwise stability constants, free energy, enthalpy and entropy changes for the formation of Co(II), Ni(II) and Cu(II) complexes with 4-methyl maleanilic and 4-chloro-maleanilic acids have been determined. Analysis of thermochemical parameters indicates coordination of the ligands through the nitrogen of secondary amide and the oxygen of carboxylate groups. The complexes have been isolated in solid state and characterised on the basis of analytical results; conductance, magnetic, electrical and infrared data. The Cu(II) complexes have been assigned square planar while Co(II) and Ni(II) were found to have octahedral structures.

INTRODUCTION

Anilic acids have been widely used for the gravimetric [1] and amperometric [2,3] determination of zirconium and thorium. The chemistry of anilic acids, which contain secondary amide groups and carboxylate groups as coordination sites, is of great importance because of their pharmacological, analytical and industrial use [4–6]. Studies on the interactions of bivalent transition metal ions with phthalanilic acids [7] and lanthanide(III) ions with maleanilic acids [8] have also been carried out, applying various physicochemical methods. The present paper deals with thermochemical studies on complex formation of 4-chloro- and 4-methyl-maleanilic acids with copper(II), nickel(II) and cobalt(II) ions in solution. These complexes could also be isolated in pure solid form and characterised on the basis of various physicochemical techniques.

EXPERIMENTAL

Reagents and solutions

Solutions of the metal chlorides (0.004 M), perchloric acid (0.01 M), sodium perchlorate (0.50 M) and potassium hydroxide (0.05 M) were pre-

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pared in 20% (v/v) aqueous methanol. Solutions of the ligands, prepared by the method of Rao and Ratnam [9], were made in the same solvent. CO_2-free potassium hydroxide solution was used in titration. CO_2-free nitrogen presaturated with 20% aqueous methanol was continuously bubbled through the solution to provide an inert atmosphere.

Physical measurements

These were the same as previously described [10]. The accuracy of the pH-meter was ±0.02 pH units. Buffers (pH 4.01 and pH 9.20) were used for standardisation of the instrument. The pH-metric titrations were carried out at constant temperature (variation ±0.1°C) using a thermostat.

Magnetic moments were determined using a VS magnetometer (PAR model 155). Electrical conductance was measured with a systronic conductivity bridge (type 302). The cell constant was 0.69. IR spectra were run on a Beckman IR-20 instrument.

Titration procedure

The following sets of solutions were prepared for titration: (I) 5.0 ml of 0.01 M $HClO_4$; (II) 5.0 ml of 0.01 M $HClO_4$ + 5.0 ml of 0.004 M ligand solution; (III) 5.0 ml of 0.01 M $HClO_4$ + 5.0 ml of 0.004 M ligand solution + 1.0 ml of 0.004 M metal ion solution. The total volume in each case was made up to 25.0 ml with the solvent and the required ionic concentration was maintained with $NaClO_4$.

Titrations were carried out at three temperatures (22, 30 and 40 ± 0.1°C) and at an ionic strength of 0.1 M $NaClO_4$, and the stability constant calculated by half integral and least squares methods. The stability constants are given in Table 1. The accuracies of the pK values of acids and log K values of the complex are ±0.02 and ±0.04 log units, respectively. Table 2 summarises the values of ΔF, ΔH and ΔS, corresponding to the first and second step reactions, which were calculated from the temperature coefficient of the equilibrium constant in a medium of 0.1 M $NaClO_4$. The accuracy of these values varies from ±3.35 to ±5.02 kJ mol^{-1} for ΔH and from ±4.18 to ±6.28 K J^{-1} mol^{-1} for ΔS.

Preparation of complexes

The metal hydroxides, freshly prepared by addition of potassium hydroxide to the solution of metal chlorides, were mixed with malaenilic acids in the ratio of 1 : 2. Ethanol was added to make a suspension. The pH of the mixture was raised to approximately 6.0 for Cu(II) and 8.0 for Ni(II) and Co(II) complexes by addition of sodium hydroxide. The mixture was then refluxed on water bath for 6 h. Precipitates formed, which were filtered,

TABLE 1

Dissociation constants of maleanilic acids in 0.1 M $NaClO_4$ and thermodynamic stability constants of their metal complexes at 22, 30 and 40°C by half integral methods

Acids	Stability constants	Temp. (°C)	Co(II)	Ni(II)	Cu(II)	Dissociation constants	
						pK_1	pK_2
4-methyl M [a]	log K_1^T	22	7.01	7.10	9.65	4.35	11.70
		30	6.90	7.00	9.45	4.20	11.60
		40	6.75	6.90	9.20	4.15	11.50
	log K_2^T	22	5.95	6.25	8.80		
		30	5.85	6.15	8.65		
		40	5.80	6.05	8.50		
	log β_2^T	22	12.96	13.35	18.45		
		30	12.75	13.15	18.10		
		40	12.55	12.95	17.70		
4-chloro M [a]	log K_1^T	22	7.80	7.80	9.20	4.00	11.45
		30	7.70	7.65	9.05	3.95	11.30
		40	7.55	7.50	8.85	3.90	11.10
	log K_2^T	22	5.75	6.05	8.20		
		30	5.70	6.00	8.10		
		40	5.60	5.90	7.95		
	log β_2^T	22	13.55	13.85	17.40		
		30	13.40	13.65	17.15		
		40	13.15	13.40	16.80		

[a] M = maleanilic acid.

The stability constants determined by the least squares method were in good agreement with the above data.

TABLE 2

Stepwise ΔF (kJ mol^{-1}), ΔH (kJ mol^{-1}) and ΔS (kJ^{-1} mol^{-1}) values at 30°C

Acids	Thermodynamic parameters	Co(II)	Ni(II)	Cu(II)
4-chloro M	$-\Delta F_1$	44.22	43.93	52.05
	$-\Delta F_2$	33.18	34.39	47.15
	$-\Delta H_1$	27.36	28.70	34.64
	$-\Delta H_2$	15.52	16.86	22.72
	ΔS_1	55.65	50.25	57.45
	ΔS_2	58.28	57.86	80.63
4-methyl M	$-\Delta F_1$	39.58	39.96	54.35
	$-\Delta F_2$	34.52	36.19	50.75
	$-\Delta H_1$	22.97	22.97	42.89
	$-\Delta H_2$	14.73	19.16	29.12
	ΔS_1	54.81	56.07	37.82
	ΔS_2	65.31	56.19	71.38

TABLE 3

Analytical data and magnetic moments of complexes at room temperature

Sl. No.	Complex	Colour	Percentage calculated (found)				μ_{eff} (B.M.)
			M	C	H	N	
1	$[Cu(4\text{-methyl } M)_2]\cdot 2H_2O$	Green	12.52 (12.45)	52.06 (52.20)	4.73 (4.65)	5.52 (5.55)	1.94
2	$[Cu(4\text{-chloro } M)_2]\cdot 2H_2O$	Green	11.58 (11.62)	43.78 (43.55)	3.30 (3.24)	5.10 (5.05)	1.93
3	$[Ni(4\text{-methyl } M)_2(H_2O)_2]$	Light green	11.68 (11.80)	52.56 (52.10)	4.78 (4.80)	5.58 (5.61)	3.10
4	$[Ni(4\text{-chloro } M)_2(H_2O)_2]$	Light green	10.83 (10.90)	44.16 (44.50)	3.34 (3.35)	5.16 (5.20)	3.10
5	$[Co(4\text{-methyl } M)_2(H_2O)_2]$	Pinkish violet	11.72 (11.80)	52.54 (52.30)	4.78 (4.82)	5.58 (5.55)	4.94
6	$[Co(4\text{-chloro } M)_2(H_2O)_2]$	Light pink	10.83 (10.98)	44.16 (44.50)	3.34 (3.30)	5.16 (5.20)	4.85

washed with aqueous ethanol and then dried in vacuo over anhydrous sulphuric acids.

The complexes were soluble in absolute alcohol. The results of chemical analysis and the values of molar conductance are given in Table 3.

RESULTS AND DISCUSSION

Thermochemical studies

Values of the dissociation constants pK_1 and pK_2 given in Table 1 correspond to deprotonation of –COOH and –NH groups of the ligand, respectively (Fig. 1). The order of pK_2 values is 4-methyl M > 4-chloro M. Thus, liberation of a proton from –NH is affected by substituent inductive effects. The chloro group reduces electron density at the reaction centre and readily causes proton liberation, while the electron-donating CH_3 group has the reverse effect.

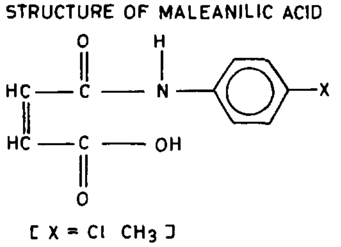

Fig. 1.

In view of the high metal-to-ligand ratios (1 : 5) used in these studies, the presence of polynuclear species is neglected. The formation curves determined from ligand–metal ratios of 5 : 1 and 10 : 1 were found to be identical and the λ_{max} in the visible region further confirmed the presence of identical species at these ratios. The highest value of $\bar{n}$ (average number of ligands attached per metal ion) was found to be 2, indicating a 1 : 2 stoichiometry in the complexes. The stability order is Co(II) < Ni(II) < Cu(II).

It is known that these metal ions exist in solution as octahedrally hydrated species, and ΔH values reflect the changes in the number and strength of bonds made and broken during the process of coordination. ΔH increases in the order Co(II) < Ni(II) < Cu(II).

The positive entropy changes are due to the negative charge on the ligand and to chelate formation [11]. The additional stabilisation of copper(II) complexes may be due to tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect [12]. At the distortion limit, a change of coordination from six in the aqua ion to four in the complex will also result in a more positive entropy of formation. The formation curves ($\bar{n}$ vs. pA) are given in Fig. 2 for 4-methyl M complexes.

The elemental analysis and conductance of the complex in absolute ethanol are given in Table 3. These results correspond to the 1 : 2 metal to ligand stoichiometry for the isolated complexes. Molar conductance values confirm their non-electrolytic nature.

The magnetic moment of copper(II) complexes was about 1.92 B.M. (Table 3), which indicated the complete quenching of orbital contribution by the crystal field. The electronic spectra of all complexes in ethanol gave three bands at 17 500, 20 000 and 37 000 cm^{-1} corresponding to the transitions $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2E$, and a charge-transfer band, respectively. These bands are generally found in the complexes of square planar stereochemistry [13].

In the case of cobalt(II) complexes the values of magnetic moment are 4.85 and 4.94 B.M., a characteristic of high-spin octahedral complexes. Octahedral cobalt(II) compounds are expected to give three spin-allowed *d–d* transitions.

For the present system two bands were obtained which could be assigned to the transitions $^4T_1(F) \rightarrow {}^4A_2(F)$ (ν_2) and $^4T_1(F) \rightarrow {}^4T_1(P)$ (ν_3). These were at 18 000 and 20 000 cm^{-1} in case of 4-methyl M and at 18 100 and 20 100 cm^{-1} for the 4-chloro M complex. The calculated values of ν_2 and ν_3 were checked against the observed values, which agree well and confirm the octahedral nature. The transition $^4T_1(F) \rightarrow {}^4T_2(F)$ (ν_1) could not be observed due to the limited range of the instrument. Values were calculated assuming the ratio $\nu_2/\nu_1 = 2.10$, as suggested by Lever [14], which occurred at 8570 and 8670 cm^{-1}. Thus, the values of B, β_{35} and 10 Dq were found to be 839 and 840; 0.86 and 0.86; 9727 and 9837 cm^{-1}, respectively, for the two complexes.

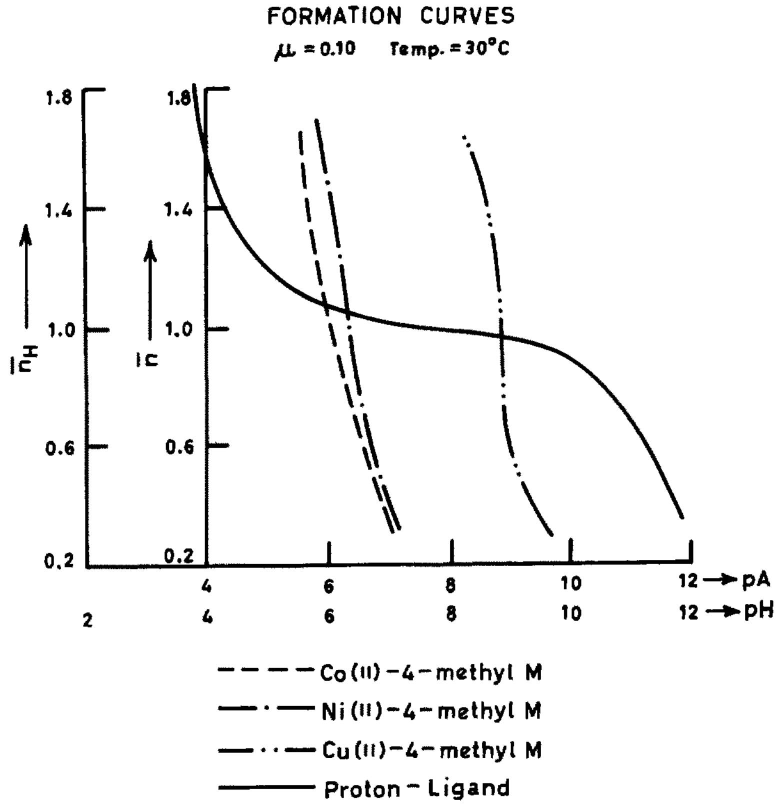

Fig. 2.

The magnetic moment for the nickel(II) complexes was found to be 3.10 for both complexes, indicating the presence of two unpaired electrons. Three bands, ν_1, ν_2 and ν_3, in an octahedral field corresponding to the transitions $^3A_2(F) \rightarrow {}^3T_2(F)$, $^3A_2(F) \rightarrow {}^3T_1(F)$ and $^3A_2(F) \rightarrow {}^3T_1(P)$ were obtained at 10200, 16700, 27200 cm^{-1} and 10600, 17200 and 26400 cm^{-1} for the 4-methyl M and 4-chloro M complexes. The calculated band positions of ν_2 and ν_3 agree well with the experimental results, justifying their cubic symmetry. The values of ν_2/ν_1 are in the range 1.62–1.68 as expected for octahedral complexes. The values of B and β_{35} were found to be 887 and 787, 0.82 and 0.73 for 4-methyl M and 4-chloro M, respectively.

All these results show that 4-chloro maleanilic acid is a better ligand than 4-methyl maleanilic acid. A good correlation exists owing to their inductive nature.

IR spectra

The band observed at 3350 cm^{-1} in ligand spectra, which is due to the N–H stretching vibration, undergoes no observable shift in the complexes.

The carbonyl stretching frequencies of the secondary amide in complexed form fall within the range 1660–1680 cm^{-1}, which is far from the 1700 cm^{-1} band in the free secondary amide. The C=O group does not take part in coordination and this lowering of frequency is a common feature of secondary amide coordination through nitrogen [7]. The stretching frequency around 1470 cm^{-1} due to C–N in the spectra of maleanilic acids shifted to about 1480–1485 cm^{-1} in the spectra of their metal complexes. The bands obtained in the regions 1600–1620 and 1365–1400 cm^{-1} indicate the coordination and unidentate nature of the carboxylate group [15]. The stretching bands due to M–O and M–N were obtained at approximately 350 and 410 cm^{-1}, respectively, in the spectra of all complexes [16]. A broad band at 3400–3480 cm^{-1} and a sharp one at 810 cm^{-1} were assigned to the presence of water molecules inside and outside of the coordination sphere. The HOH bending mode of the water molecule, which appears at 1600–1620 cm^{-1}, may have been mixed up with the carboxylate group signal. However, the bands at 3400–3480 and 810 cm^{-1} for both Ni(II) and Co(II) complexes remained unaffected up to around 110°C, whereas in case of Cu(II) complexes these bands disappear at around 90°C. This confirms the presence of coordinated water in the former case and lattice water in the latter case.

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