

ENTHALPY OF COMPLEX FORMATION IN AQUEOUS SOLUTIONS: COPPER BENZYL MALONATE

S. PARTHASARATHY* AND S. AMBUJAVALLI**

Institute of Physico-Chemical Research, Madras (India)

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ABSTRACT

The enthalpy of formation of 1/1 copper benzyl malonate complex in aqueous solution determined by precision calorimetry is reported. The value is compared with that for the malonate complex and the influence of the bulky substituent in the ligand molecule on the stability of the complex, the thermodynamic parameters, and the Jahn–Teller distortion are discussed.

INTRODUCTION

The formation of dicarboxylate complexes like malonates, succinates etc., in aqueous solutions with metal ions of the first transition series, is accompanied by endothermic enthalpy changes (in the case of copper this endothermicity is often more pronounced). In spite of this fact, complex formation is favoured by a large positive entropy change resulting from the release of the loosely bound H₂O molecules in the outer sphere of the metal–hexaquo ions on complex formation with the ligand. In the case of copper with its d^9 electronic configuration, additional stabilisation is possible by a tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect.

The stability of the Cu malonate ion complex, and the enthalpy of its formation determined by direct calorimetric measurements have been reported previously¹. The introduction of a bulky substituent like the benzyl group in the ligand molecule can be expected to affect the thermodynamic functions of a complex in a number of ways. In the first place stability may be impaired due to weakening of the ion–ion interaction by the larger ionic size of the substituted ligand. Secondly, the inductive effect of the substituent may cause a closer interaction of the metal ion and the charged co-ordinating sites of the ligand, thereby increasing the covalency of the metal–ligand bond in the x–y plane and the exothermicity of the enthalpy change. Thirdly, an entropy loss may also be expected from restrictions of the freedom of movement of the bulky ligand in the metal complex². We intend to verify these interesting trends by

* Present address: Centre for Advance Study in Physics, University of Madras, Madras, India.

** Present address: Chemical Testing and Analytical Laboratory, Guindy, Madras, India.

a direct calorimetric measurement of the enthalpy change and a precise determination of the thermodynamic stability constant of formation of the copper benzyl malonate complex with copper.

EXPERIMENTAL

Apparatus

The calorimeter and accessories used have been described previously³ except for a few modifications. The high-gain d.c. amplifier incorporating chopper modulation of the input signal, with several stages of a.c. amplification, synchronous detection and further d.c. amplification for recorder operation, had the drawback of a rather high noise level and instability (except at low sensitivity settings); the delicate high-sensitivity galvanometer was found to be equally inconvenient in use due to the difficulty in handling and setting up, and the annoying zero wandering. Therefore we decided to use a rugged galvanometer as a null indicator in a twin photocell amplifier

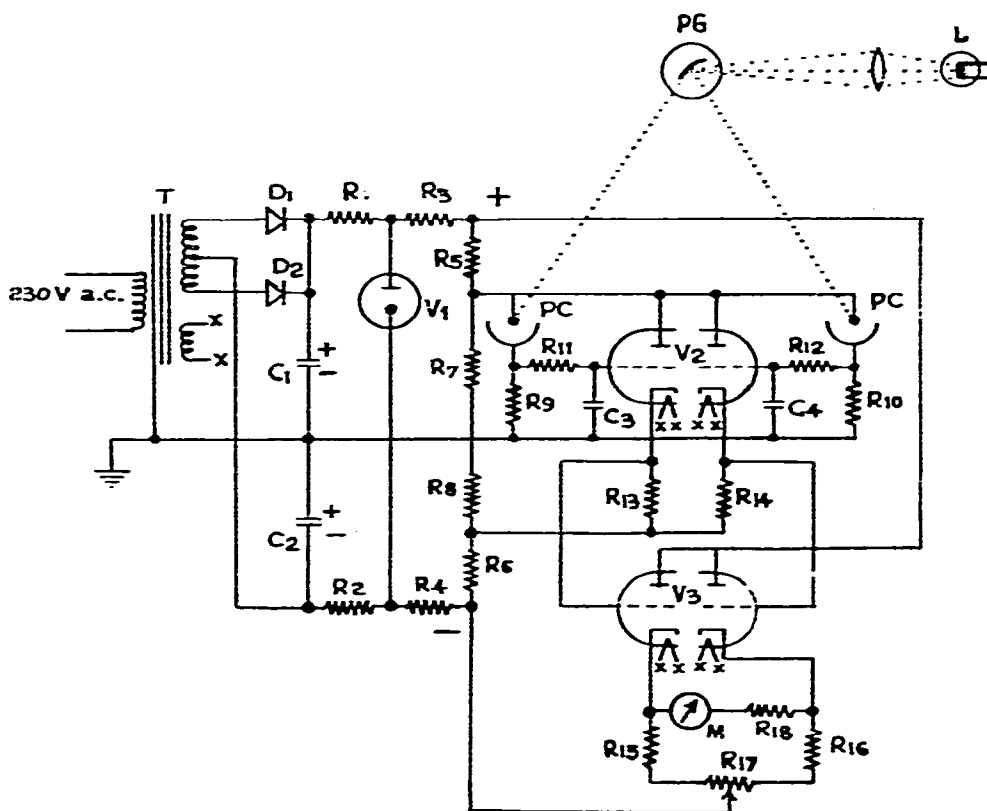


Fig. 1. Photo-cell galvo amplifier. $C_1, C_2 = 16 \mu\text{F}$ capacitors 350 V, $C_3, C_4 = 0.01 \mu\text{F}$, Mica, $R_1, R_2, R_7, R_8 = 5 \text{ k}\Omega$ 1 Watt, $R_3, R_4 = 10 \text{ k}$ 1 Watt, $R_5, R_6 = 25 \text{ k}$ 1 Watt, $R_9, R_{10} = 100 \text{ m}\Omega$ 0.5 Watt, $R_{11}, R_{12} = 1 \text{ m}\Omega$ 0.5 Watt, $R_{13}, R_{14} = 4.7 \text{ m}\Omega$ 0.5 Watt, $R_{15}, R_{16} = 47 \text{ k}\Omega$ 0.5 Watt, $R_{17} =$ Potentiometer, $25 \text{ k}\Omega$, $R_{18} = 50 \text{ k}\Omega$ 0.5 Watt, $V_1 = \text{VR } 150$, $V_2, V_3 = \text{ECC } 82$, $D_1, D_2 = \text{Silicon diodes } 1 \text{ amp}$, $T = \text{power transformer}$, $\text{PG} = \text{primary galvo } (10 \Omega)$, $M = \text{micro ammeter } 5.0\text{--}5 \mu\text{A}$, $\text{PC} = \text{RCA } 920 \text{ photocell}$, $L = \text{light source for PG}$.

of a low-resistance primary galvanometer and the arrangement was found to be sensitive enough with remarkable freedom from noise. The amplifier circuit given in Fig. 1 is a double-bridge with two pairs of cathode followers in bridge circuits, resulting in high-input impedance and low-grid current.

The balanced circuit stabilises the amplifier against changes in power line voltage. Zero drift after the first 10 minutes warm-up is about 2% of full scale and after a 1 hour warm-up the drift over 4 hours is unnoticeable. The input resistor is chosen so that with normal illumination reaching the photo tube about 1.5-2 V are produced across the input.

The thermocouple output is measured in terms of arbitrary divisions on a simple microvolt potentiometer (Fig. 2).

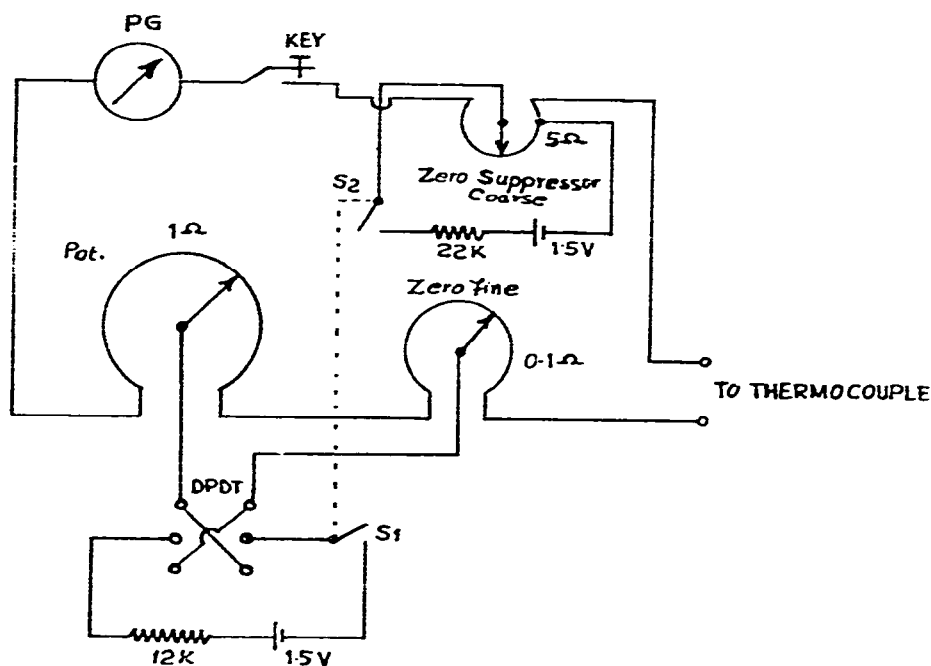


Fig. 2. Micro-volt potentiometer. The moving contacts and the slide wire of the potentiometer are of the same material; and the moving contacts are arranged to be in the battery circuit to minimise spurious thermal emf's.

Reagents

Analar chemicals and deionised water were used throughout. 0.005 M copper solution: 0.4262 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in water, treated with 5 ml 0.1 M HCl and made up to 500 ml. 0.4 M sodium benzyl malonate: 2.3814 g Na_2BM was dissolved in 25 ml water. 0.015 M KCl solution: 0.5591 g KCl was dissolved in water, treated with 5 ml 0.1 M HCl and made up to 500 ml. The strength of the copper solutions were determined volumetrically; chloride was estimated gravimetrically as AgCl .

Procedure

200 ml of distilled water was placed in the reference Dewar vessel and 200 ml metal chloride solution in the reaction calorimeter; 5 ml of the ligand solution was placed in the mixing vessel and the twin calorimeter was allowed to attain the temperature of the thermostatic bath maintained at 25°C.

The calorimeter constant was determined by electrical calibration described previously. The microvolt potentiometer reading was noted every minute for 10 minutes and the corrected value is found by extrapolation of the graph to zero time at the start of heating. The number of calories of heat corresponding to each division of the potentiometer is the calorimeter constant.

Heat of reaction

The potentiometer was brought to the original position and the galvanometer adjusted to zero by the zero suppressor. The ligand and metal solutions were mixed and the stop watch started. The corrected potentiometer reading was found as before and the heat change was calculated from the calorimeter constant.

A blank was done using a KCl solution of equal ionic strength instead of the metal chloride solution and repeating the experiment. The net heat change was determined.

The concentration of the MA species in the solution was calculated from the relation

$$[\text{MA}] = T_A - \frac{2T_A - \mu}{2 + \frac{k_1}{\{\text{H}^+\}f}} \left[1 + \frac{k_1}{\{\text{H}^+\}f} + \frac{k_1 k_2}{\{\text{H}^+\}^2 f^2} \right]$$

where $\mu = [\text{H}^+] + [\text{Na}^+] + 2T_M - [\text{Cl}^-]$; T_A is the total ligand concentration. T_M is the total metal concentration; k_1 and k_2 are the dissociation constants of benzyl malonic acid. $\{\text{H}^+\}$ is hydrogen ion activity from the pH of the solution; f is the mean activity coefficient of the univalent ion calculated from Davies equation by successive approximation⁴.

Stability constant

The stability constant of the 1/1 copper benzyl malonate complex was determined using pH measurements. The experimental technique and the mode of calculation have been described previously⁵.

RESULTS AND DISCUSSION

The formation constants of the complex in the 1/1 metal-ligand molecular ratio, calculated for each point of titration in the pH range 4–5 are presented in Table 1. The log K value and the thermodynamic functions calculated from calorimetric data for the Cu benzyl malonate complex are given in Table 2, along with those for Cu malonate for purposes of comparison. The lower stability of the benzyl

TABLE 1
STABILITY OF Cu^{2+} BENZYL MALONATE COMPLEX
[Base] = 0.4697 M, [Ligand] = 0.0100 M, $[\text{CuCl}_2]$ = 0.0100 M.

Titre (ml)	pH	$I \times 10^4$	$[\text{HA}^-] \times 10^3$	$[\text{A}^{2-}] \times 10^5$	$[\text{MA}] \times 10^3$	$K \times 10^3$ ($l^{-1} \text{mole}^{-1}$)
0.770	4.080	84.47	1.566	3.459	7.935	294
0.775	4.123	80.11	1.487	3.602	8.023	297
0.780	4.177	75.89	1.409	3.840	8.109	292
0.785	4.241	71.71	1.331	4.173	8.194	283
0.790	4.307	67.38	1.248	4.521	8.282	276
0.792	4.333	65.59	1.214	4.652	8.318	275
0.794	4.369	63.96	1.181	4.904	8.351	267
0.796	4.395	62.11	1.145	5.030	8.389	267
0.798	4.422	60.26	1.108	5.163	8.426	267
0.800	4.457	58.52	1.073	5.399	8.461	262
0.805	4.534	53.86	0.978	5.827	8.555	262
0.810	4.620	49.18	0.882	6.341	8.650	261
0.815	4.726	44.65	0.784	7.124	8.742	253
0.820	4.848	40.19	0.683	8.140	8.834	245
0.825	4.992	35.87	0.586	9.528	8.924	233

Av: 269

TABLE 2
THERMODYNAMIC DATA FOR 1/1 COMPLEX OF Cu^{2+} BENZYL MALONATE

	$\text{Log}_{10} K$	$-\Delta G$ (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS ($\text{cal deg}^{-1} \text{mole}^{-1}$)
Cu^{2+} benzyl malonate	5.430	7.41	0.47	26.4
Cu^{2+} malonate ⁵	5.637	7.69	2.85	35.4

malonate complex is attributable to steric hindrance due to the benzyl group reducing the bond strength between the ligand and the central metal ion. Also, the presence of the bulky substituent group in the ligand molecule, would reduce the freedom of movement of the ligand in the complex, and thus entail a loss of entropy; the observed lower entropy change compared to that in malonate formation is explained on this basis. A Jahn-Teller distortion of the octahedral symmetry resulting in shortened metal-ligand bonds in the x-y plane has possibly contributed to the less positive enthalpy of formation of the benzyl malonate complex. However, this distortion has not been sufficiently large as to cause a break of the metal-ligand bonds along the z-axis necessitating an absorption of heat and a positive increase in entropy.

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