Thermodynamic and Spectroscopic Properties of Mixed Complexes in Aqueous Solution. Copper(II) Complexes of 2,2′-Bipyridyl and Dicarboxylic Acids

By **Giuseppe Arena, Rosario Calì, Enrico Rizzarelli,*** and **Silvio Sammartano,** Istituto di Chimica Generale Università di Catania, Viale A. Doria 8, 95125 Catania, Italy
Rolando Barbucci,* Istituto Chimico, Università di Napoli, Via Mezzacannone 4, 80134 Napoli, Italy
Michel J. M. Campbell, School of Chemistry, Thames Polytechnic, Woolwich, London SE18 6PF

The heats of formation of mixed copper(II) complexes [Cu(bipy)L] (bipy = 2,2′-bipyridyl; L = malonate, succinate maleate, or phthalate) have been determined calorimetrically at 25 °C in 0.1 mol dm^{-3} Na[ClO$_4$], and have been used to calculate the relative enthalpies. Consideration of thermodynamic and e.s.r. and electronic spectroscopic data shows that all the mixed complexes have the same structure because of the requirements of the bipy ligand, the only exception being [Cu(bipy)(succ)] for which a square-pyramidal structure has been proposed. This difference in behaviour between the succinate anion and the other acid anions has also been found to occur for the simple complexes [CuL] as shown by a plot of their partial molar entropies against those of the corresponding ligands.

In a previous paper[1] we reported the thermodynamic and spectroscopic properties of some mixed complexes of Cu^{II} with 2,2′-bipyridyl (bipy) and some cycloalkane-1,1-dicarboxylic acids. The negative value of $\Delta H^\ominus$ was attributed mainly to the contribution from Cu–N-(bipy) bond formation and the high positive value of

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[1] G. Arena, R. Calìi, E. Rizzarelli, S. Sammartano, R. Barbucci, and M. J. M. Campbell, *J.C.S. Dalton*, 1977, 581.

$\Delta S^\ominus$ to the release of water molecules following charge neutralisation by the dicarboxylate anion. Only the $\Delta S^\ominus$ values differentiated the anions from each other. The spectroscopic parameters showed the presence of a stronger in-plane ligand field than in the parent complexes.

In the light of these results we have studied the thermodynamic and e.s.r. and electronic spectroscopic properties of another series of mixed complexes having the same formula, [Cu(bipy)L] [L = either the anion of a saturated dicarboxylic acid, *e.g.* malonic (mal) or succinic (succ), or of an unsaturated acid, *e.g.* maleic (male) or phthalic (pht)]. It was therefore possible to estimate the effects both of the increased size of the chelate ring and of the presence of unsaturated groups on the thermodynamic properties associated with the formation of mixed complexes, as well as the effects on their structural parameters. The thermodynamic data obtained are compared with those of the corresponding parent complexes measured under the same experimental conditions, and we have also obtained the $\Delta H^\ominus$ and $\Delta S^\ominus$ values for the formation of the protonated complexes $[Cu(bipy)(succ)H]^+$ and $[Cu(bipy)(pht)H]^+$ by using previously reported potentiometric data.[2]

TABLE 1

Experimental details of the calorimetric measurements

L	Calorimetric vessel [a] c_{Cu}	c_L	c_{bipy}	c_H	Titrant [a]	q [b]/J	No. of titrations
mal	1.52		1.00	1.42	c_{mal} 60.1, c_H 20.2	-0.65	1
	1.46—1.97	2.00—4.20		0.9—30	c_{bipy} 4.99, c_H 1.01	3.8—6.7	8
	1.25	6.61		4.17	c_{bipy} 10.0, c_H 7.5	4.61—4.69	2
succ	2.49		1.51	0.81	c_{succ} 100.0, c_H 20.0	-0.9 to -1.1	4
	1.25	6.00		2.97	c_{bipy} 10.0, c_H 7.5	4.7—5.2	4
male		3.99—4.11	0.99—1.11	0.83—7.23	c_{Cu} 48.0	1.9—2.8	6
	1.25	6.14		3.28	c_{bipy} 10.0, c_H 7.5	4.74—4.86	2
pht		3.58—4.02	1.02	2.0—3.6	c_{Cu} 48.0	2.4—2.8	7
	1.25	6.53		3.96	c_{bipy} 10.0, c_H 7.5	5.24—5.26	2

[a] Concentrations in 10^{-3} mol dm^{-3}. [b] Corrected for the heat of dilution.

EXPERIMENTAL

Chemicals.—The dicarboxylic acids (Erba RP) were recrystallised from diethyl ether–benzene. Their purity was checked by: (*i*) titration with CO_2-free standard Na[OH] and in all cases a purity >99.7% was found; and (*ii*) determination of the pK (the agreement was within 0.02 and 0.01 logarithmic units for pK_1 and pK_2 respectively).[2,3] 2,2′-Bipyridyl (Erba RP) was recrystallised from ethanol–water. Its pK_1 value was in agreement with the value previously determined.[4] The preparation of the solid mixed complexes has been described elsewhere.[5]

All the standard solutions were prepared with twice-distilled water and their ionic strengths were kept at 0.1 mol dm^{-3} by the addition of $Na[ClO_4]$. The preparation and standardisation of these solutions have been previously described.[1]

E.M.F. Measurements.—The potentiometric measurements were carried out by means of a model 332 Amel potentiometer using an Ingold 201 NS glass electrode and a double-junction calomel electrode (Orion model 90-02-200). Other details were as previously described.[4-6]

The ligand concentrations used to check the pK were 2×10^{-3}—8×10^{-3} mol dm^{-3}. For the determination of the formation constants in the Cu^{II}–bipy–succ system the concentrations used were $c_{Cu} = c_{bipy} = 1.5 \times 10^{-3}$ mol dm^{-3} and the ratios of $[Cu]_T : [succ]_T$ were 1 : 1, 1 : 2, and 1 : 3. These titrations were performed with Na[OH] solutions.

Calorimetric Measurements.—The calorimetric measurements were made at 25 ± 0.001 °C employing a model 8700 LKB precision calorimeter and a model 8726-1 titration vessel (100 cm^3). The change in the thermistor resistance during the titration was recorded by means of a Leeds and Northrup recorder (Speedomax W). The reproducibility of the system and other details have already been reported.[7] In order to determine the enthalpies of formation of the ternary complexes, at least six calorimetric titrations were carried out for each system. The measurements were made using each of the components in turn as titrant in order to avoid systematic errors. Experimental details of the calorimetric measurements are listed in Table 1.

Spectroscopic Measurements.—First-derivative e.s.r. *X*-band spectra were recorded at room temperature and at −140 °C using a Varian E-9 spectrometer and were calibrated using diphenylpicrylhydrazyl (dpph) as a *g* marker. Simulated spectra were obtained using our variant of Venable's program [8] and in each case it was possible to fit the experimental spectra closely. The e.s.r. parameters given in Table 2 are the best fits to the final simulation.

In the case of the parent complexes [Cu(pht)] and [Cu(succ)] it was not possible to obtain any e.s.r. signal other than that of the aquated Cu^{2+} ion. It is probable that, because of the low values of the formation constants of these complexes, the quantity present in solution was insufficient to characterise the species. Attempts to obtain spectra starting with the solid salts CuL were similarly unsuccessful owing to the very low solubility of the solids in water.

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[2] R. P. Bonomo, S. Musumeci, E. Rizzarelli, and S. Sammartano, *Talanta*, 1976, **23**, 253.

[3] G. Arena, R. Cali, E. Rizzarelli, and S. Sammartano, *Transition Metal Chem.*, 1978, **3**, in the press.

[4] R. Maggiore, S. Musumeci, E. Rizzarelli, and S. Sammartano, *Inorg. Chim. Acta*, 1976, **18**, 155.

[5] S. Musumeci, E. Rizzarelli, S. Sammartano, and A. Seminara, *Z. anorg. Chem.*, 1977, **433**, 297.

[6] R. P. Bonomo, S. Musumeci, E. Rizzarelli, and S. Sammartano, *Inorg. Chim. Acta*, 1975, **14**, 251.

[7] G. Arena, R. Calii, E. Rizzarelli, and S. Sammartano, *Thermochim. Acta*, 1976, **16**, 315; **17**, 155.

[8] R. Barbucci and M. J. M. Campbell, *Inorg. Chim. Acta*, 1976, **16**, 113.

Electronic-absorption spectra in solution were recorded on a Beckmann DK-2A spectrophotometer.

Calculations.—The formation constants of [Cu(bipy)(succ)] complex were refined by means of the least-squares computer program MINIQUAD.[9] Computations relative to the purity of the acids, to the refinement of the protonation constants, to the $E^\ominus$ determination, and to the calculations of the concentrations of the standard solutions were performed by means of the least-squares computer program ACBA,[10] which refines all the parameters of an acid-base titration. The enthalpics of formation of the ternary systems were determined by means of the least-squares program DOEC.[11] Thermodynamic data for the protonation and complexation of the acids [3] and for the formation of the simple complexes of bipy with Cu^{II} have already been reported.[7]

RESULTS AND DISCUSSION

Simple Complexes.—The e.s.r. parameters of the parent complexes of Cu^{II} with malonic and maleic acids are shown in Table 2. The e.s.r. and electronic spectroscopic data for [Cu(mal)] are not different from those of the previously studied complexes with cyclic dicarboxylates [1] for which the data were consistent with copper(II) complexes containing a $CuO_2'O_2$ chromophore (O′ is a carboxylate oxygen) having a $d_{x^2-y^2}$ ground state. This indicates a marked similarity both between the structures and between the strengths of the metal–ligand bonds in these complexes, all of which contain six-membered chelate rings.

However, the case of [Cu(male)] is different. It not only has a lower value of the molar absorption coefficient but it also has a higher value of $g_{\parallel}$ and a lower value of $A_{\parallel}$ than the other complexes. The difference in the ligand structure, *i.e.* a seven-membered chelate ring with unsaturation, leads, we believe, to a tetragonally distorted octahedral geometry with a stronger axial field than that present in the other complexes.

At first sight the thermodynamic data for the equilibrium $Cu^{2+} + L^{2-} \rightleftharpoons [CuL]$ (Table 2) exhibit the same endothermic character and the same large entropic contribution previously found for the analogous reactions with cyclic dicarboxylates.[1] However, we notice that: (*i*) the endothermic effect increases with the size of the chelate ring whereas the entropy effect decreases along the same series, *i.e.* from oxalate (ox) to succ; (*ii*) if the size of the chelate ring is kept constant at seven members, for a more rigid ligand structure such as in [Cu(male)] there is a lower negative $\Delta H^\ominus$ and a larger positive $\Delta S^\ominus$ than for a simple saturated aliphatic ring as in [Cu(succ)]; and (*iii*) the presence of an aromatic ring as in [Cu(pht)] leads to lower and higher values of $\Delta H^\ominus$ and $\Delta S^\ominus$ respectively.

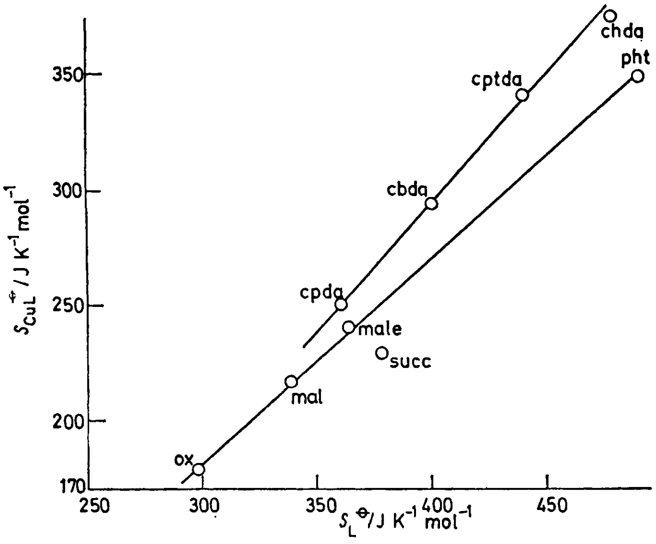
TABLE 2

Thermodynamic functions [a] for the formation of the binary complexes at 25 °C and I = 0.1 mol dm^{-3} (Na[ClO$_4$]), and relative spectral (e.s.r. and electronic) parameters

Reaction	$-\Delta G^\ominus$ / kJ mol^{-1}	$\Delta H^\ominus$ / kJ mol^{-1}	$\Delta S^\ominus$ / J K^{-1} mol^{-1}
$Cu^{2+} + ox^{2-} \rightleftharpoons [Cu(ox)]$ [e]	35.5	−0.2	118.4
$Cu^{2+} + mal^{2-} \rightleftharpoons [Cu(mal)]$	28.8(1)	5.9(4)	116.7(1.7)
$Cu^{2+} + succ^{2-} \rightleftharpoons [Cu(succ)]$	14.9(1)	11.3(6)	87.9(2.1)
$Cu^{2+} + male^{2-} \rightleftharpoons [Cu(male)]$	19.4(1)	14.4(2)	113.8(8)
$Cu^{2+} + pht^{2-} \rightleftharpoons [Cu(pht)]$	18.5(1)	10.3(2)	96.7(8)

	E.s.r. spectra								Electronic spectra
Complex	g_{iso}	A_{iso}	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$g_{\perp}'$ [b]	$A_{\perp}$	$A_{\perp}'$ [b,c]	(10^3 cm^{-1}) [d]
[Cu(mal)]	2.162	57	2.334	153	2.073	2.076	5	9	13.1(31)
[Cu(male)]	2.178	45	2.354	144	2.070	2.090	8	5	13.3(8)

[a] The figures in parentheses are standard deviations. [b] $g_{\perp}' = \frac{1}{2}(3\ g_{iso} - g_{\parallel})$, $A_{\perp}' = \frac{1}{2}(3\ A_{iso} - A_{\parallel})$. [c] All the hyperfine coupling constants have units of 10^4 cm^{-1}. [d] The values in parentheses are the molar absorption coefficients in dm^3 mol^{-1} cm^{-1}. A. McAuley, G. H. Nancollas, and K. Torrance, *Inorg. Chem.*, 1967, **6**, 196.



Molar partial entropies of cycloalkane-1,1-dicarboxylic acids (cpda = cyclopropane-, cbda = cyclobutane-, cptda = cyclopentane-, and chda = cyclohexane-1,1-dicarboxylic acid) and linear dicarboxylic acids plotted against the molar partial entropies of their [CuL] complexes

In order to evaluate the contribution of the ligand to the enthalpy and entropy of formation of these complexes, we have plotted the partial molar entropies of the ligands, obtained using Cobble's formula,[12] against the

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[9] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[10] G. Arena, C. Rigano, E. Rizzarelli, and S. Sammartano, *Chimica e Industria*, 1976, **58**, 581.

[11] C. Rigano, E. Rizzarelli, and S. Sammartano, *Thermochim. Acta*, submitted for publication.

[12] J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.

partial molar entropies of the complexes, obtained according to Powell and Curtis.[13] To simplify the calculation we have assumed that the number of water molecules displaced by the dicarboxylate anion is the same as the number of co-ordination sites occupied, *i.e.* two. In the Figure we see that the points for [Cu(ox)], [Cu(mal)], [Cu(male)], and [Cu(pht)] lie on a straight line, which shows that the differences between the $\Delta S^{\ominus}$ values must be due to differences in the loss of conformational energy by the ligands, the desolvation process being the same in each case. Accordingly we can assume an essentially identical geometry for each of the complexes, with the exception of [Cu(succ)] which does not lie on the straight line. The $\Delta S^{\ominus}$ value for the reaction $Cu^{2+} + succ^{2-} \rightleftharpoons [Cu(succ)]$ is comparatively small and this indicates that the geometry of the complex formed must be substantially different from that of the other complexes.

TABLE 3

Thermodynamic functions for the formation of ternary complexes at 25 °C and $I = 0.1$ mol dm^{-3} (Na[ClO$_4$]), and relative spectral (e.s.r. and electronic) parameters

Reaction	$-\Delta G^{\ominus}$ kJ mol^{-1}	$-\Delta H^{\ominus}$ kJ mol^{-1}	$\Delta S^{\ominus}$ J K^{-1} mol^{-1}
$Cu^{2+} + bipy + mal^{2-} \rightleftharpoons [Cu(bipy)(mal)]$	76.5(3)	42.7(4)	113.8(1.7)
$Cu^{2+} + bipy + succ^{2-} + \rightleftharpoons [Cu(bipy)(succ)]$	62.3(3)	42.7(8)	65.7(2.9)
$Cu^{2+} + bipy + H^{+} + succ^{2-} \rightleftharpoons [Cu(bipy)(succ)H]^{+}$	91.2(3)	33.0(1.3)	195.8(4.5)
$Cu^{2+} + bipy + male^{2-} \rightleftharpoons [Cu(bipy)(male)]$	67.8(1)	34.7(1.3)	112.1(4.2)
$Cu^{2+} + bipy + pht^{2-} \rightleftharpoons [Cu(bipy)(pht)]$	67.7(1)	33.8(1.3)	113.8(4.2)
$Cu^{2+} + bipy + H^{+} + pht^{2-} \rightleftharpoons [Cu(bipy)(pht)H]^{+}$	87.4(3)	43.9(1.3)	146.0(4.5)

Complex	E.s.r. spectra g_{iso}	A_{iso}	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$g_{\perp}'$ [a]	$A_{\perp}$	$A_{\perp}'$ [a,b]	Electronic spectra (10^3 cm^{-1})
[Cu(bipy)(ox)] [d]			2.258	183	2.063		24		
[Cu(bipy)(mal)]	2.127	67	2.256	174	2.069	2.063	10	14	15.9(50)
[Cu(bipy)(succ)]	2.135	70	2.264	167	2.065	2.071	15	22	15.4(83)
[Cu(bipy)(male)]	2.135	65	2.262	174	2.074	2.072	17	11	15.6(51)
[Cu(bipy)(pht)]	2.138	73	2.264	174	2.071	2.075	19	23	15.9(68)

[a] $g_{\perp}' = \frac{1}{2}(3\,g_{iso} - g_{\parallel})$, $A_{\perp}' = \frac{1}{2}(3\,A_{iso} - A_{\parallel})$. [b] All the hyperfine coupling constants have units of 10^4 cm^{-1}. [c] Values in parentheses are the molar absorption coefficients in dm^3 mol^{-1} cm^{-1}. [d] F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, 1972, **11**, 2756.

The points for the cyclic complexes also lie on a straight line, indicating that the members of this series all have the same geometry. The different gradient of this line can undoubtedly be attributed to the greater effect of the release of water molecules, probably a result of the presence of the aliphatic ring.

Mixed Complexes.—The e.s.r. and electronic spectroscopic parameters do not differ much in this series of ternary complexes. The only exception is [Cu(bipy)(succ)] which, by comparison with the other mixed complexes, has a greater value of ε and a smaller value of $A_{\parallel}$ (Tables 3). Table 3 also contains the $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ values for the formation of the mixed neutral complexes. As has previously been found in systems containing the same arrangement of donor atoms around Cu^{II},[1] these ternary complexes are also stabilised by negative enthalpies and positive entropies. The mixed complexes [Cu(bipy)(mal)] and [Cu(bipy)(succ)] both have the same $-\Delta H^{\ominus}$ value but the $\Delta S^{\ominus}$ value of the former is almost twice as large as that of the latter. Moreover, considering the equilibrium $[Cu(bipy)]^{2+} + L^{2-} \rightleftharpoons [Cu(bipy)L]$, the $-\Delta H^{\ominus}$ value of 48.6 kJ mol^{-1} for L = mal is similar to that found for a cyclic dicarboxylate, whereas the value of 54 kJ mol^{-1} for L = succ is markedly higher. Some new factor, either steric or geometric, must therefore be present in the [Cu(bipy)(succ)] complex. This may well be the fact that [Cu(bipy)(succ)], unlike the mixed complexes previously studied[1] and unlike [Cu(bipy)(mal)], has a strong interaction with solvent molecules in the two axial co-ordination positions. On the other hand, from the structural data on the mutual separations of the oxygen-donor atoms,[14,15] [Cu(mal)] with its six-membered chelate ring should give rise to a greater charge neutralisation than [Cu(succ)] with its seven-membered ring. Consequently, the identical values of $\Delta H^{\ominus}$ are undoubtedly the result of an energy balance between the endothermic effect associated with chelate-ring formation, which will be smaller for the six- than for the seven-membered chelate ring (*cf.* the $\Delta H^{\ominus}$ values of the parent complexes), and that associated with removal of solvent molecules by formation of the mixed complex, which will be larger in the case of the six-membered ring. In other words the endothermic effect due to desolvation is greater in the case of [Cu(bipy)(mal)].

The spectroscopic and thermodynamic data taken together lead us to propose a square-pyramidal structure for [Cu(bipy)(succ)]. The existence of this geometry in this complex can be attributed entirely to the geometric characteristics of the succinate anion and does not seem to depend on the structure of the second ligand. In fact a structure different from that of the other complexes had already been proposed for [Cu(succ)] in aqueous solution.[3] We now believe that this too has a square-pyramidal structure.

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[13] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*A*), 1967, 1441.

[14] J. A. Goedkoop and C. H. MacGillary, *Acta Cryst.*, 1957, **10**, 125.

[15] J. D. Morrison and J. M. Robertson, *J. Chem. Soc.*, 1949, 980.

The e.s.r. and electronic-spectral data for the complexes [Cu(bipy)(ox)], [Cu(bipy)(pht)], [Cu(bipy)(mal)], and [Cu(bipy)(male)] are so similar as to indicate an essentially identical structure for all the ternary complexes. This similarity was not so evident in the case of the parent complexes and it can therefore be ascribed to the presence of bipy which must force the dicarboxylic acid anions to adopt the same configuration in all cases.

Protonated Ternary Complexes.—The only species of this type which were found are $[Cu(bipy)(succ)H]^+$ and $[Cu(bipy)(pht)H]^+$. Their thermodynamic parameters are shown in Table 3. The differences between the thermodynamic parameters of these two complexes are so marked that one is inclined to suppose that the complexes must have different protonation sites. However, the differences could also be due to different behaviour towards protonation by the two ternary unprotonated complexes because of their different structures.

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