Thermodynamic and Spectroscopic Properties of Mixed Complexes in Aqueous Solution. Copper(II) Complexes of 2,2′-Bipyridyl and Cycloalkane-1,1-dicarboxylic Acids

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The heats of formation of mixed complexes of copper(II) with 2,2′-bipyridyl and cyclopropane-, cyclobutane-, cyclopentane-, and cyclohexane-1,1-dicarboxylic acids have been determined calorimetrically at 25 °C in 0.1 mol dm^{-3} sodium perchlorate, and have been used to calculate the relative enthalpies. The heats of reaction of Cu^{II} with the acids have also been measured under the same conditions. From the thermodynamic data the relative importance of enthalpy and entropy terms in stabilising mixed complexes is assessed. By assuming the enthalpy of copper(II) complex formation to be related to the strength of the co-ordinate bonds, the e.s.r. and electronic spectral parameters found for aqueous solutions of the complexes have been interpreted and their significance discussed together with that of the thermodynamic values.

MUCH of the work on mixed complexes of copper(II) with bidentate ligands in aqueous solution has only been concerned with the determination of stability constants,[1,2] so that a complete rationalisation of the relative importance of the energy terms involved in the formation of the mixed complex has not been possible. Calorimetric work on mixed complexes of Cu^{II} with various amino-acids has only recently been reported.[3-9] Furthermore it has been claimed on the basis of spectroscopic studies that π bonding is important in the formation of ternary

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complexes of Cu^{II} and 2,2′-bipyridyl (bipy).[10] Some of us have already studied the equilibria involving Cu^{II} with bipy and some dicarboxylic acids by potentiometric measurements.[11-14] The present paper describes a detailed thermodynamic and spectroscopic (e.s.r. and electronic) study of the formation of mixed complexes of Cu^{II} with bipy and some cycloalkane-1,1-dicarboxylic acids [equation (1); L = cyclopropane-, cyclobutane-,

$$Cu^{2+} + \text{bipy} + L^{2-} \rightleftharpoons [Cu(\text{bipy})L] \qquad (1)$$

cyclopentane-, or cyclohexane-1,1-dicarboxylic acid] in aqueous solution at 25 °C and 0.1 mol dm^{-3} $Na[ClO_4]$. The data obtained are compared with those of the corresponding simple and parent complexes measured under the same conditions. Some stability constants have also been remeasured in order to obtain a homogeneous series of data at 25 °C and 0.1 mol dm^{-3} $Na[ClO_4]$.

EXPERIMENTAL

Chemicals.—Cyclobutane-1,1-dicarboxylic acid (cbda) was obtained by boiling the commercial product (Fluka) in benzene. It was then recrystallised from diethyl ether–benzene (1 : 1) containing 5% of light petroleum. Cyclopropane-1,1-dicarboxylic acid (cpda) and cyclopentane-1,1-dicarboxylic acid (cptda) were prepared by basic hydrolysis of the diethyl esters (Fluka), and were recrystallised in the same manner as cbda. Cyclohexane-1,1-dicarboxylic acid (chda) was synthesised by the reaction between the diethyl ester of malonic acid and 1,5-dibromopentane according to Vogel's procedure.[15] The melting points were in agreement with the values reported in the literature.[16] The purity of these acids was checked by (*i*) titration with CO_2-free standard Na[OH], in all cases a purity higher than 99.5% being found, and (*ii*) determination of the pK, the agreement being within ±0.02 and 0.01 logarithmic units for pK_1 and pK_2 respectively.[17] 2,2′-Bipyridyl (Erba RPE) was recrystallised from water–ethanol. The pK_1 value found was in agreement with the value previously determined by us [13] and also with that determined by Irving and Mellor.[18]

The preparation of the solid parent and mixed complexes has been described elsewhere.[19]

Standard Solutions.—All the solutions were prepared with twice-distilled water and their ionic strength was kept at 0.1 mol dm^{-3} by addition of $Na[ClO_4]$. Sodium hydroxide solutions were prepared either from Normex Erba ampoules or from concentrated solutions, previously filtered at low temperature to remove sodium carbonate. The dilute solutions (in the range 0.1—1 mol dm^{-3}) were standardised with potassium hydrogenphthalate (E. Merck; ' Zur Analise ', dried at 120 °C for 2 h). The $HClO_4$ solutions were obtained by dilution of concentrated solutions (Erba, 70% RP) and then standardised with aminotris(hydroxymethyl)methane. Sodium perchlorate was prepared as described by Grenthe and Williams.[20] Stock solutions of $Cu[ClO_4]_2$ were standardised by titration with the disodium salt of ethylenediaminetetra-acetic acid (Erba) as recommended by Flaschka.[21]

E.M.F. Measurements.—The potentiometric measurements were carried out by means of an Orion 801-A potentiometer using a glass electrode (EIL) and a double-junction calomel electrode (Orion model 90-02-00). The system was calibrated by titrating either 0.01 mol dm^{-3} $HClO_4$ or potassium hydrogenphthalate solutions with Na[OH]. For each titration the ionic strength was kept at 0.1 mol dm^{-3}. The vessel was thermostatted at 25 ± 0.1 °C by means of a Colora (NB/DS 997) thermostat. Carbon dioxide was excluded from the solutions by bubbling nitrogen through them. A magnetic stirrer was also employed. Other details were as previously reported.[11-13]

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}-cbda system, the following concentrations were used: (in the titration vessel) $c_{cbda}{}^0 = 0$; $c_{Cu}{}^0 = 2 \times 10^{-3}$—$5 \times 10^{-3}$; $c_H{}^0 = 1 \times 10^{-3}$—$5 \times 10^{-3}$ (in the titrant itself) $c_{cbda} = 5 \times 10^{-2}$; $c_H = 2 \times 10^{-3}$ mol dm^{-3}. Titrations were also performed with Na[OH] using ratios of $[Cu]_T : [cbda]_T = 1 : 1$, 1 : 2, 1 : 3, 2 : 1, and $[Cu]_T = 2 \times 10^{-3}$ mol dm^{-3}.

Calorimetric Measurements.—The calorimetric measurements were made at 25 ± 0.001 °C employing an LKB precision calorimeter (model 8700) and titration vessel (100 cm^3, model 8726-1). The change of thermistor resistance during the titration was recorded by means of a Leeds and Northrup recorder (model Speedomax W). The reproducibility of the system and other details have already been reported.[22,23] In order to determine the formation enthalpies of the ternary and binary complexes, several calorimetric titrations were carried out, at least six 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 in Supplementary Publication No. SUP 21965 (3 pp.).*

Spectroscopic Measurements.—E.s.r. spectra were redorded on a Varian E-9 spectrometer and calibrated with diphenylpicrylhydrazyl (dpph) as a g marker. Glassy spectra were recorded at −140 °C and solution spectra at room temperature. Solutions of the (10^{-2}—10^{-3} mol dm^{-3}) copper(II) salts in methanol–water (1 : 2) were used for the measurement of the spectra. Solutions of the complexes were generally prepared by mixing weighed quantities of copper(II) perchlorate, the dicarboxylic acids, and Na[OH] (solution of known titre) in a flat-bottomed flask (10 cm^3). The concentrations were chosen so as to obtain

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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the maximum percentage of the complex desired in solution.[24] In some cases spectra were recorded of solutions obtained by dissolving the solid [Cu(bipy)L] or [CuL] salt in the methanol–water mixture. No differences were found between the spectra obtained by these two methods. On the other hand, solutions of the solid [CuL] salts in ethylene glycol–water gave e.s.r. spectra characteristic of triplet-state species. This is not surprising in view of the polymeric structure of some of these salts in the solid state.[19] Electronic-absorption spectra in solution were recorded on a Beckmann DK-2A spectrophotometer.

Calculations.—The formation constants of the Cu^{II}–cbda complexes were refined by means of the least-squares computer program SCOGSB.[13,25] 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 made by means of the least-squares computer program ACBA,[26] which refines all the parameters of an acid–base titration. The formation enthalpies of the binary and ternary systems were determined by means of the least-squares program DOEC.[27] Thermodynamic data both for the protonation of the ligands and for the formation of the simple complexes of bipy with Cu^{II} have already been reported.[17,23]

TABLE 1

Thermodynamic functions [a] for the formation of binary complexes at 25 °C and $I = 0.1$ mol dm^{-3} (Na[ClO$_4$])

Reaction	$-\Delta G^\ominus$ / kJ mol^{-1}	$-\Delta H^\ominus$ / kJ mol^{-1}	$\Delta S^\ominus$ / J K^{-1} mol^{-1}
$Cu^{2+} + cpda^{2-} \rightleftharpoons [Cu(cpda)]$	34.2(1) [b]	−3.8(2)	127.8(8)
$[Cu(cpda)] + cpda^{2-} \rightleftharpoons [Cu(cpda)_2]^{2-}$	20.6(1) [b]	−0.3(1)	70.3(4)
$Cu^{2+} + cbda^{2-} \rightleftharpoons [Cu(cbda)]$	28.5(1) [c]	−10.9(4)	132.2(1.7)
$[Cu(cbda)] + cbda^{2-} \rightleftharpoons [Cu(cbda)_2]^{2-}$	19.6(3) [c]	−2.9(4)	74.9(1.7)
$Cu^{2+} + cptda^{2-} \rightleftharpoons [Cu(cptda)]$	27.9(2) [b]	−13.6(4)	139.3(1.7)
$[Cu(cptda)] + cptda^{2-} \rightleftharpoons [Cu(cptda)_2]^{2-}$	16.0(2) [b]	−6.5(8)	75.3(2.5)
$Cu^{2+} + chda^{2-} \rightleftharpoons [Cu(chda)]$	26.4(1) [b]	−14.2(6)	136.0(2.1)
$[Cu(chda)] + chda^{2-} \rightleftharpoons [Cu(chda)_2]^{2-}$	14.9(4) [b]	−7.1(6)	74.1(2.1)
$Cu^{2+} + 2MeCO_2^- \rightleftharpoons [Cu(O_2CMe)_2]$ [d]		−8.6	72.3
$Cu^{2+} + bipy \rightleftharpoons [Cu(bipy)]^{2+}$ [e]	46.3(1)	44.6(2)	5.9(8)
$[Cu(bipy)]^{2+} + bipy \rightleftharpoons [Cu(bipy)_2]^{2+}$ [e]	31.7(1)	25.4(3)	20.5(9)

[a] The figures in parentheses are the standard deviations. [b] E. Roletto, A. Vanni, and G. Ostacoli, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2817. [c] This work. [d] R. Aruga, *Ann. Chim.* (*Italy*), 1974, **64**, 659. [e] Ref. 23.

Simulated e.s.r. spectra for a Lorentzian line shape were obtained using a modified version of Venable's program.[28] The e.s.r. parameters given in Table 2 are the best fits to the final simulation. All the e.s.r. spectra can be fitted using an axial spin Hamiltonian, although it should be borne in mind that small anisotropies in the g values in the xy plane are almost impossible to detect experimentally in solution spectra because of the small in-plane hyperfine coupling constants and the relatively large linewidths.

RESULTS AND DISCUSSION

Simple Complexes.—Table 1 shows the $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ values for the reaction of Cu^{II} with the anions of the cycloalkane-1,1-dicarboxylic acids. All the heats of reaction are endothermic, while the entropies are large and positive, so that the complexes are only stabilised by the entropy contribution. The first step of the reaction involves both the exothermic formation of two new Cu–O$_2$C bonds and the endothermic desolvation processes accompanying the reaction. The desolvation process is a result both of the steric effect of placing the anions adjacent to the cation and of the decrease in the charge from +2 to 0, and is similar for all the complexes studied as can be seen from the $\Delta S^\ominus$ changes which are essentially constant along the series. The breakdown of the solvent lattice around the reacting ion and the consequent release of solvent molecules accounts both for the large positive entropy changes and for the positive $\Delta H^\ominus$ values. The exothermic process of formation of the two new bonds is more than balanced by the more endothermic heat of desolvation. However, if we compare these data with those relative to the equilibrium between Cu^{II} and two acetate ions (Table 1) we see that the formation of our complexes involves: (*i*) larger entropy changes; and (*ii*) more endothermic heats which become progressively larger along the series. These data support the hypothesis that the aliphatic ring also makes a contribution to the desolvation process. However, the e.s.r. parameters for all these complexes are very similar and are consistent with copper(II) complexes containing a CuO'_2O_2 chromophore [29] (O′ = carboxylate oxygen) with a $d_{x^2-y^2}$ ground state (Table 2). The differences observed between the $\Delta H^\ominus$ values, increasingly endothermic from [Cu(cpda)] to [Cu(chda)], correlate well with the different angles between the substituted carbon atom and the carboxylate groups, which are a function of the size of the aliphatic ring, and therefore with the relative planarity of the two ligand groups. The structure of the acid cpda [30] shows that the two carboxylic acid groups are almost coplanar, with a dihedral angle of 6°, and this would account both for a less distorted structure for [Cu(cpda)] and for its larger heat of formation. The differences observed between the electronic spectra can also be correlated with this hypothesis. The enthalpy and entropy values for the introduction of the second dicarboxylate ligand into the

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complex are lower than those for the first step (Table 1). The formation of a doubly charged anionic complex from an uncharged complex involves less desolvation, and consequently lower $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ values. However, the $\Delta H_2^{\ominus}$ values follow the same trend as the $\Delta H_1^{\ominus}$ values.

Mixed Complexes.—The thermodynamic data for the formation of the mixed complexes are summarised in Table 3. For all the complex-formation reactions considered we find large values of $-\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ which explain the high values of the stability constants. From a comparison of the thermodynamic data for the [Cu(bipy)]$^{2+}$ system with those for the [CuL] systems (Table 1) we see that the negative enthalpy contribution for the mixed complexes arises mainly from the formation of the Cu–N(bipy) bonds whilst the positive entropy change is the result of charge neutralisation. Examination of the $\Delta H^{\ominus}$ values reveals a trend similar to that observed for the copper(II)–dicarboxylate series itself, with an increase in the difference between the $\Delta H^{\ominus}$ value for the [Cu(bipy)(cpda)] complex and the values for the other mixed complexes. However, if we consider the reaction [CuL] + bipy $\rightleftharpoons$ [Cu(bipy)L] we find the heats of reaction are essentially constant whatever the dicarboxylate anion (49.8, 47.3, 49.6, and 49.8 kJ mol^{-1}) and they are not very different from the heat of formation for the simple reaction Cu^{2+} + bipy $\rightleftharpoons$ [Cu(bipy)]$^{2+}$. This must mean that steric repulsion between the two ligands is almost absent on all these mixed complexes. These data confirm the hypothesis already put forward on the basis of the values of the stability constants.[11,13]

The electronic spectra of all these mixed complexes are very similar and resemble those observed for some CuN_2O_2 chromophores previously studied;[31-33] moreover the in-plane ligand field is stronger than that observed in the simple [CuL] or [Cu(bipy)]$^{2+}$ complexes (Table 2). This emerges clearly not only from the electronic spectra but also from the e.s.r. spectra, demonstrating once again that the ligand field of the carboxylate group is stronger than that of water.[29] Now in tetragonal copper(II) species low $g_{\parallel}$ values and high $A_{\parallel}$ values are characteristic of a strong in-plane ligand field and a weaker axial ligand field. The lower $g_{\parallel}$ values found for some mixed complexes of bipy have been explained by other workers in terms of a co-operative effect acting between the π systems of the two organic ligands present.[10]

TABLE 2

E.s.r. and electronic-spectral data

Complex	E.s.r. spectra $g_{\text{iso.}}$	$A_{\text{iso.}}$	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$g_{\perp}'$ [a]	$A_{\perp}$	$A_{\perp}'$ [a,b]	Electronic spectra (10^3 cm^{-1}) [c]
[Cu(cpda)]	2.165	55	2.337	158	2.074	2.079	10	4	13.0(42)
[Cu(cbda)]	2.160	57	2.332	155	2.070	2.074	12	8	13.5(44)
[Cu(cptda)]	2.167	50	2.333	152	2.067	2.084	7	1	13.5(44)
[Cu(chda)]	2.160	56	2.331	150	2.071	2.074	12	9	13.5(50)
[Cu(bipy)]$^{2+}$ [d]			2.308	166	2.068			7	11.1—13.6
[Cu(bipy)(cpda)]	2.125	72	2.244	183	2.066	2.065	16	17	16.3(57)
[Cu(bipy)(cbda)]	2.116	71	2.249	184	2.050	2.050	14	14	16.1(87)
[Cu(bipy)(cptda)]	2.114	71	2.249	184	2.047	2.047	19	14	16.1(87)
[Cu(bipy)(chda)]	2.118	72	2.246	182	2.054	2.054	15	17	16.0(72)
[Cu(en)(cpda)]	2.121	75	2.246	183	2.049	2.058	15	21	17.2(50)

[a] $g_{\perp}' = \frac{1}{2}(3g_{\text{iso.}} - g_{\parallel})$, $A_{\perp}' = \frac{1}{2}(3A_{\text{iso.}} - A_{\parallel})$. [b] All hyperfine coupling constants are in units of 10^4 cm^{-1}. [c] The values in parentheses are the molar absorption coefficients in dm^3 mol^{-1} cm^{-1}. [d] Ref. 10.

TABLE 3

Thermodynamic functions [a] for the formation of ternary complexes at 25 °C and $I = 0.1$ mol dm^{-3} (Na[ClO$_4$])

Reaction	$\dfrac{-\Delta G^{\ominus}}{\text{kJ mol}^{-1}}$	$\dfrac{-\Delta H^{\ominus}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta S^{\ominus}}{\text{J K}^{-1}\text{ mol}^{-1}}$
Cu^{2+} + bipy + cpda^{2-} $\rightleftharpoons$ [Cu(bipy)(cpda)]	88.3(3) [b]	46.0(4)	141.8(1.7)
Cu^{2+} + bipy + cbda^{2-} $\rightleftharpoons$ [Cu(bipy)(cbda)]	81.1(3) [b]	36.4(8)	150.2(2.9)
Cu^{2+} + bipy + cptda^{2-} $\rightleftharpoons$ [Cu(bipy)(cptda)]	75.7(1) [b]	36.0(1.3)	130.1(4.2)
Cu^{2+} + bipy + chda^{2-} $\rightleftharpoons$ [Cu(bipy)(chda)]	74.3(1) [c]	35.6(1.3)	129.7(4.2)

[a] The figures in parentheses are the standard deviations. [b] Ref. 11. [c] Ref. 13.

However, we have found e.s.r. parameters for the complex [Cu(en)(cpda)] (en = ethylenediamine) which are very similar to those of the other mixed complexes. What is more, calculation of the bonding parameters, using the equations used by other workers, *i.e.* essentially the equations originally proposed by Maki and McGarvey,[34] yields values of α, the σ-bonding parameter, which are virtually identical for both [Cu(en)(cpda)] and the mixed bipy complexes, and values of β, the in-plane π-bonding parameter, which are slightly lower for the bipy complexes. If we assume, as have most previous workers, that with saturated aliphatic amines as ligands the amount of metal–ligand π bonding is negligible, then we expect a value of β for [Cu(en)(cpda)] of close to unity. However, the value of β found using the Maki–McGarvey equations is lower for [Cu(en)(cpda)] than the value of α. This implies that π bonding is more important than σ bonding in the binding of aliphatic amines to Cu$^{\text{II}}$ and

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this is clearly not so. Two of us have already pointed out [35] that the use of the Maki–McGarvey equations for the evaluation of bonding parameters is suspect, precisely because they consistently lead to estimates of large amounts of in-plane π bonding for complexes of saturated aliphatic amines. We are therefore forced to the conclusion that, on the available evidence, it is not possible to say whether or not metal–ligand π bonding is important in some mixed bipy complexes. We believe that, while the e.s.r. parameters undoubtedly indicate stronger overall bonding in the mixed complexes than in the simple [CuL] and $[Cu(bipy)]^{2+}$ complexes, to attribute this to the importance of in-plane π bonding, using the above equations, is very questionable.

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