Complex Formation between Squarate ($C_4O_4^{2-}$) and Cu^{II}L [L = 2,2′-bipyridyl, 2,2′:6′,2″-terpyridyl or bis(2-pyridylcarbonyl)amide anion (bpca)] in Dimethyl Sulphoxide Solution. Crystal Structure of [$Cu_2(bpca)_2(H_2O)_2(C_4O_4)$]†

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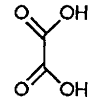
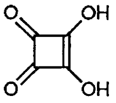
A new dinuclear copper(II) complex [$Cu_2(bpca)_2(H_2O)_2(C_4O_4)$] **1** [bpca = bis(2-pyridylcarbonyl)amide anion and $C_4O_4^{2}$) = dianion of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione)] has been synthesised and characterized by spectroscopy, magnetic and X-ray diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$ with a = 7.222(2), b = 10.272(1), c = 10.362(2) Å, α = 82.85(1), β = 70.89(2), γ = 69.94(2)° and Z = 1. The structure consists of neutral centrosymmetrical squarate-O^1,O^3-bridged dinuclear copper(II) units. The configuration around each copper atom is distorted square pyramidal with the three nitrogen atoms of bpca and one squarato oxygen atom in the basal plane and a water oxygen atom at the apex. Variable-temperature magnetic susceptibility measurements (4.2–300 K) revealed an extremely weak exchange interaction through squarate. The protonation of squarate and its complex formation with Cu^{II}L (L = 2,2′-bipyridyl, 2,2′ : 6′2″-terpyridyl or bpca) have been investigated in dimethyl sulphoxide solution at 25 °C and 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. Co-ordination modes of squarate for this system are discussed on the basis of the thermodynamic and structural parameters and compared to those of the related oxalato complexes.

Squaric acid, $H_2C_4O_4$ (3,4-dihydroxycyclobut-3-ene-1,2-dione), was synthesised for the first time by Cohen *et al.*[1] in 1959. It belongs to the series of cyclic oxocarbons of formula $H_2C_nO_n$ (n = 3–6 for deltic, squaric, croconic and rhodizonic acids, respectively), whose organic chemistry was reviewed recently.[2,3] The similarity between squarate and oxalate (a set of four oxygen donors, planar stereochemistry and π-electron delocalization) is at the origin of the interest on its co-ordinating properties.[4,5] However, the well known chelating and bis(chelating) co-ordination modes of oxalate have not been found for squarato complexes with first-row transition-metal ions. In a recent paper[6] some of us have explained the lack of these co-ordination modes by the large value of the bite parameter in the squarate ion.

As a part of our coupled solution–solid state studies on polynuclear copper(II) complexes with extended bridges,[7–10] we have investigated the formation of complexes between squarate and Cu^{II}L, L being N-donor bidentate [2,2′-bipyridyl (bipy)] and tridentate [2,2′:6′,2″-terpyridyl (terpy) or bis(2-pyridylcarbonyl)amide anion (bpca)] ligands in dimethyl sulphoxide (dmso) solution. The co-ordination of L to copper(II) precludes the precipitation of the insoluble $Cu(C_4O_4){\cdot}2H_2O$ chain compound.[11] The structure of the dinuclear copper(II) complex [$Cu_2(bpca)_2(H_2O)_2(C_4O_4)$] together with its spectral and magnetic characterisation are also reported herein. A thorough discussion on the co-ordination modes of squarate and oxalate complexes with Cu^{II}L is carried out in the light of available thermodynamic and structural data.



$H_2C_2O_4$



$H_2C_4O_4$

Experimental

Materials.—Copper(II) nitrate trihydrate, 2,2′-bipyridyl, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) and dmso were Merck analytical grade reagents, whereas squaric acid and 2,2′:6′,2″-terpyridyl were purchased from Aldrich. Squaric acid was twice recrystallised from hot water and dried at 110 °C in an oven. (2,2′-Bipyridyl)copper(II) nitrate, diaqua[bis(2-pyridylcarbonyl)amido]copper(II) nitrate dihydrate and (2,2′:6′,2″-terpyridyl)copper(II) nitrate monohydrate were prepared by previously reported procedures[9,10,12] and used as copper(II) salts for the solution studies. Carbonate-free solutions of tetrabutylammonium hydroxide in dmso (freshly prepared from BDH reagent, 40% aqueous solution) and [NBu^n_4][ClO_4] (from Fluka) were used as titrant and supporting electrolyte, respectively.

Synthesis of [$Cu_2(bpca)_2(H_2O)_2(C_4O_4)$] **1**.—This compound was obtained as needle-like dark green crystals by slow evaporation of aqueous solutions of [$Cu(bpca)(H_2O)$]$NO_3{\cdot}2H_2O$ and lithium squarate in a 2:1 molar ratio. The crystals were filtered off, washed with water and ethanol and stored over calcium chloride (Found: C, 46.20; H, 2.95; N, 11.35. Calc. for $C_{28}H_{20}Cu_2N_6O_{10}$: C, 46.25; H, 2.75; N, 11.55%).

Single crystals of **1** were grown from slow evaporation of aqueous solutions of [Cu(bpca)]$^+$ containing a large excess of squarate.

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† μ-3,4-Dihydroxycyclobut-3-ene-1,2-dionato(2−)-κO^1:κO^3-bis-[aquabis(2-pyridylcarbonyl)amido-κ^3N,N',N''-copper(II)].

Supplementary data available (No. SUP 56837, 3 pp.): magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

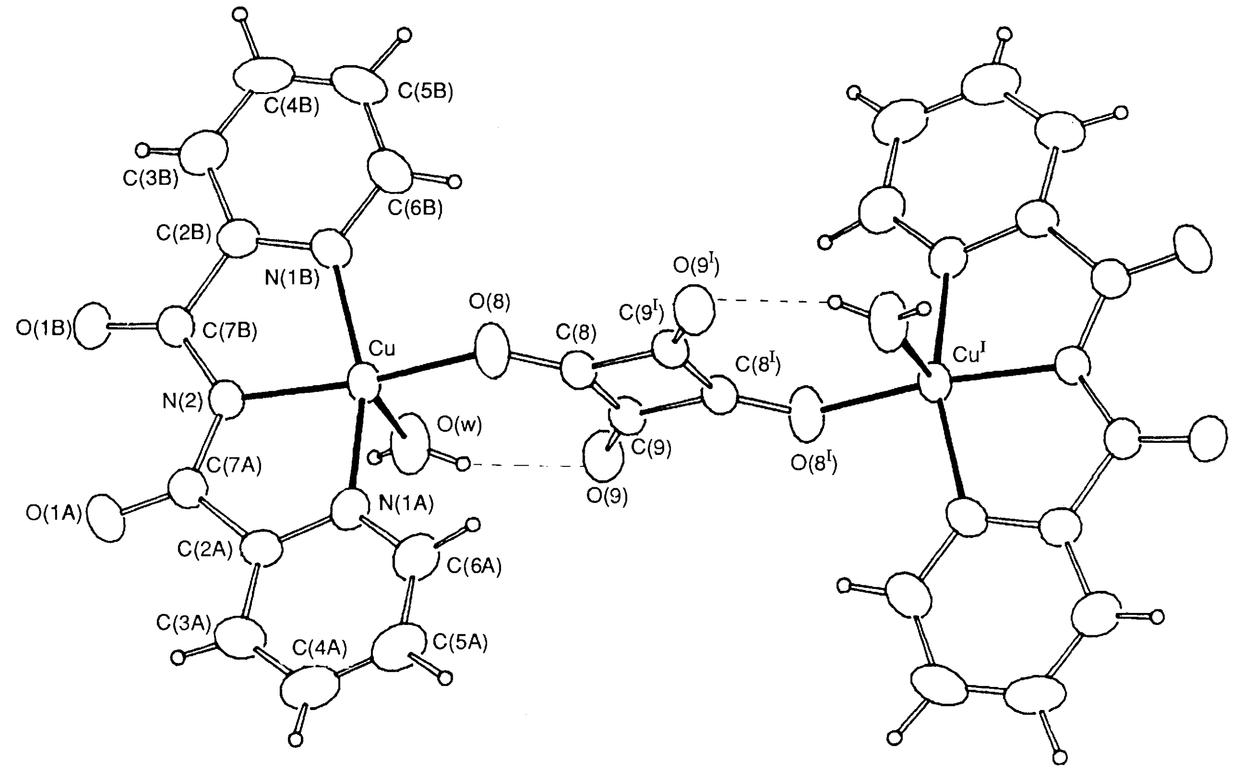

Fig. 1 ORTEP drawing of $[Cu_2(bpca)_2(H_2O)_2(C_4O_4)]$ **1** showing the atom-numbering scheme and 50% probability thermal ellipsoids. Hydrogen atoms are given an arbitrary radius

Physical Techniques.—Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer for KBr discs in the 4000–250 cm^{-1} region and X-band ESR spectra of powdered samples on a Brüker ER 200D spectrometer equipped with a helium continuous-flow cryostat. Magnetic susceptibility measurements of powdered samples were carried out with a SQUID Métronique Ingénierie magnetometer in the temperature range 4.2–300 K. The apparatus was calibrated with $Gd_2(SO_4)_3 \cdot 8H_2O$ and the experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants.

Potentiometric titrations were carried out with a previously described titration assembly[8] at 25.0 ± 0.1 °C and at constant ionic strength (0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$). The equilibrium constants for the reaction of $Cu^{II}L$ and squarate were determined by titrating dmso solutions of $Cu^{II}L$ as nitrate salts and $H_2C_4O_4$ with $[NBu^n_4][OH]$. The deprotonation equilibria of squaric acid in dmso were investigated by using the same procedure. Electromotive force data from different experiments on each system were merged and treated simultaneously by the computer program SUPERQUAD[13] to determine the acidity constants of squaric acid and the stability constants concerning the complex formation between $Cu^{II}L$ and squarate.

Crystal Structure Determination and Refinement.—Diffraction data were collected at 293 K with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Information dealing with conditions for crystallographic data collection and structure refinement is summarised in Table 1. The unit-cell parameters were determined by least-squares refinement of 25 well centred reflections ($12 \leqslant \theta \leqslant 24°$). Three reference reflections monitored throughout the data collection showed no significant sign of crystal deterioration. The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by the successful refinement of the structure. Intensity data were corrected for Lorentz and polarization effects and correction for absorption was done by an empirical method.[14]

The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were localized in a Fourier difference map, and were included in the refinement with isotropic thermal parameters. The refinement converged at $R = 0.040$ and $R' = 0.042$. All calculations were carried out on a MICROVAX II computer with the Enraf-Nonius structure determination programs.[15] Atomic scattering factors were taken from ref. 16. Positional parameters of non-hydrogen atoms are given in Table 2 and selected bond lengths and bond angles as well as non-bonded distances are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Molecular Structure of Complex **1**.—The structure is built of discrete dinuclear units, $[Cu_2(bpca)_2(H_2O)_2(C_4O_4)]$, where a squarate dianion is bridging two centrosymmetrically related copper atoms (Fig. 1). The bis(2-pyridylcarbonyl)amido groups function as tridentate outer ligands, co-ordinating to copper through the nitrogen atoms. Squarate oxygen and bpca-nitrogen atoms constitute the equatorial plane in the distorted square-pyramidal copper co-ordination geometry, the axial position being occupied by a water molecule. The Cu–N(pyridyl) distances are 2.007(2) and 2.004(2) Å and Cu–N(amide) is 1.922(2) Å, all in agreement with those observed in other bis(2-pyridylcarbonyl)amido-containing copper(II) complexes.[8,12,17] The Cu–O(squarate) distance is 1.923(2) Å, and the axial bond is relatively strong, Cu–O(water) being 2.178(3) Å. The basal atoms [N(1A), N(1B), N(2) and O(8)] are coplanar within ±0.027 Å and the copper atom is displaced by 0.246 Å from this least-squares plane towards the axial ligand. The angles N(1A)–Cu–N(1B) and N(2)–Cu–O(8) in the basal plane are

Table 1 Summary of crystal data, intensity-data collection, and structure refinement for complex **1**

Formula	$C_{28}H_{20}Cu_2N_6O_{10}$
M	727.59
Crystal symmetry	Triclinic
Space group	$P\bar{1}$ (No. 2)
a/Å	7.222(2)
b/Å	10.272(1)
c/Å	10.362(2)
α/°	82.85(1)
β/°	70.89(2)
γ/°	69.94(2)
U/Å^3	682.2(2)
Z	1
D_c/g cm^{-3}	1.771
μ(Mo-Kα)/cm^{-1}	16.33
F(000)	368
Range of transmission factors	0.80–1.01
Crystal size/mm	0.19 × 0.11 × 0.10
Scan type	ω
Scan range $\Delta\omega$/°	$1.1 + 0.35 \tan\theta$
Scan speed/° min^{-1}	2
2θ range/°	0–50
No. of reflections measured	2411
No. of unique reflections[a]	1858
No. of variables refined	248
$R[=[\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert]$	0.040
$R'\{=[\Sigma w(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$[b]	0.042

[a] $\geqslant 3.0\sigma(I)$. [b] $w = 1/\sigma^2_F$; $\sigma_F = \sigma_I(IL_p)^{-\frac{1}{2}}$; $\sigma_I = [\sigma^2_C + (0.002N_{net})^2]^{\frac{1}{2}}$ where N_{net} is the net count of each reflection.

Table 2 Final atomic coordinates with estimated standard deviations (e.s.d.s.) in parentheses for complex **1**

Atom	X/a	Y/b	Z/c
Cu	0.596 99(8)	0.277 65(5)	0.321 44(5)
O(w)	0.406 2(5)	0.196 7(3)	0.250 1(3)
O(1A)	0.828 3(5)	−0.080 0(3)	0.506 3(3)
O(1B)	0.463 3(5)	0.099 3(3)	0.692 8(3)
O(8)	0.597 4(4)	0.429 5(3)	0.192 6(3)
O(9)	0.348 5(5)	0.332 2(3)	0.022 6(3)
N(1A)	0.875 0(5)	0.147 9(3)	0.221 3(3)
N(1B)	0.370 4(5)	0.390 7(3)	0.475 1(3)
N(2)	0.630 7(5)	0.144 9(3)	0.467 0(3)
C(2A)	0.930 7(6)	0.030 1(4)	0.292 0(4)
C(2B)	0.340 5(6)	0.320 0(4)	0.594 2(4)
C(3A)	1.111 3(7)	−0.075 0(5)	0.237 8(5)
C(3B)	0.191 2(7)	0.379 1(5)	0.710 8(4)
C(4A)	1.236 4(7)	−0.059 3(5)	0.108 9(5)
C(4B)	0.069 0(7)	0.515 7(5)	0.706 6(5)
C(5A)	1.182 8(7)	0.060 2(5)	0.036 8(5)
C(5B)	0.098 5(7)	0.588 2(5)	0.586 0(5)
C(6A)	0.999 8(7)	0.162 0(5)	0.096 6(4)
C(6B)	0.251 2(6)	0.523 2(4)	0.472 5(4)
C(7A)	0.791 5(6)	0.023 5(4)	0.434 4(4)
C(7B)	0.484 4(6)	0.174 1(4)	0.591 9(4)
C(8)	0.541 8(6)	0.465 7(4)	0.085 8(4)
C(9)	0.431 4(6)	0.422 9(4)	0.011 4(4)

Table 3 Main bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **1**[a]

Environment of copper atoms			
Cu–N(1A)	2.007(2)	Cu–O(8)	1.923(2)
Cu–N(1B)	2.004(2)	Cu–O(w)	2.178(3)
Cu–N(2)	1.922(2)		
N(1A)–Cu–N(1B)	158.8(1)	N(2)–Cu–O(8)	166.7(1)
N(1A)–Cu–N(2)	82.2(1)	N(1A)–Cu–O(w)	98.2(1)
N(1B)–Cu–N(2)	81.8(1)	N(1B)–Cu–O(w)	97.4(1)
N(1A)–Cu–O(8)	97.0(1)	N(2)–Cu–O(w)	97.0(1)
N(1B)–Cu–O(8)	95.4(1)	O(8)–Cu–O(w)	96.3(1)
Squarate bridge			
O(8)–C(8)	1.268(3)	C(8)–C(9)	1.467(4)
O(9)–C(9)	1.245(4)	C(8)–C(9^I)	1.449(4)
O(8)–C(8)–C(9)	138.0(3)	O(9)–C(9)–C(8)	137.5(3)
O(8)–C(8)–C(9^I)	130.3(3)	O(9)–C(9)–C(8^I)	134.2(3)
C(9)–C(8)–C(9^I)	91.7(3)	C(8)–C(9)–C(8^I)	88.3(3)

Hydrogen bonds

A[b]	D[c]	H	A···D	A···H–D
O($1A^{II}$)	O(w)	H(w1)	2.919(4)	144(4)
O($1B^{II}$)	O(w)	H(w1)	2.904(4)	134(4)
O(9)	O(w)	H(w2)	2.664(4)	156(5)

[a] Symmetry operations: I $1 - x$, $1 - y$, $-z$; II $1 - x$, $-y$, $1 - z$. [b] Acceptor atom. [c] Donor atom.

158.8(1) and 166.7(1)°, respectively. The deviation of the values of the angles N(1A)–Cu–N(2) [82.2(1)°] and N(1B)–Cu–N(2) [81.8(1)°] from the ideal value of 90° is due to the small bite size of the ligand.

The pyridyl rings of the bpca ligand are planar but the dihedral angle between them is 12.5°. The bpca ligand is best described by two pyridylcarbonyl halves noted A and B that make a dihedral angle of 11.4°. Another point to note is the value of the angles around the carbonyl-carbon atoms [110.9(2) and 110.6(2)° for C(2A)–C(7A)–N(2) and C(2B)–C(7B)–N(2)] that show significant deviations from the expected value of 120° for sp^2 hybridization. The formation of short metal–nitrogen bonds causes this angular strain which in the case of Cu^{II}–tptz promotes the metal-assisted hydrolysis of tptz.[12,17,18]

The squarate dianion is planar within experimental errors (largest deviation from the mean plane 0.005 Å). The dihedral angle between the equatorial copper plane and the plane of the squarate ligand is 94.35°. The C(8)–O(8) bond length [1.268(3) Å] is somewhat longer than the C(9)–O(9) distance [1.245(4) Å] as expected from O(8)···Cu co-ordination. Slight differences are also observed between the carbon–carbon bond lengths [1.449(4) and 1.467(4) Å for C(8)–C(9^I) and C(8)–C(9) respectively]; they are close to the values found in other squarato complexes[6,19,20] or in the free acid,[21] although smaller than those reported for $Ni(C_4O_4)\cdot 2H_2O$.[22] The range of the values of the O–C–C angles [138.0(3)–130.3(3)°] is similar to the ones reported for squaric acid and squarate complexes with transition-metal ions but different from those observed (141.0–128.3 Å) when squarate acts as a chelating or bis(chelating) ligand.[23] The C–C–C angles are close to 90° as expected.

Of particular interest in the structure is the presence of intra- and inter-molecular hydrogen bonds (Fig. 1). The relevant data are reported at the end of Table 3. The co-ordinated water molecule, O(w), forms a hydrogen bond to the unco-ordinated squarate carbonyl-oxygen atom within a dinuclear unit, and a bifurcated hydrogen bond to the bpca carbonyl oxygen atoms of another unit.

The intramolecular Cu···Cu^I separation across the squarato bridge is 7.833(1) Å, the intermolecular copper–copper distances being shorter [5.740(1), 6.710(1) and 7.222(2) Å for Cu···Cu^{III}, Cu···Cu^{II} and Cu···Cu^{IV}, respectively, where III and IV refer to the equivalent $1 - x$, $1 - y$, $1 - z$ and $1 + x$, y, z relative to the reference molecule at x, y, z].

Infrared and ESR Spectra.—The IR spectrum of the dinuclear complex exhibits absorptions typical of a co-ordinated bis(2-pyridylcarbonyl)amido ligand in the range 3100–350 cm^{-1}. The most important of them is the sharp and intense band located at 1710 cm^{-1} which has been assigned to the ν_{asym}(C=O) vibration of the imide group of bpca.[18] Absorptions at 1780w and 1510–1570s cm^{-1} correspond to ν(C=O) and ν(C–C + C–O) bands of squarate. The weak peak at higher energy is consistent with the presence of localised C=O bonds, whereas the strong and broad

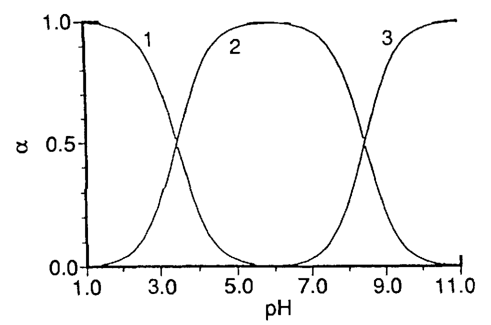

Fig. 2 Distribution diagram of α *versus* pH for squaric acid; α is the ratio between the concentration of each species and the initial concentration of $H_2C_4O_4$. Curves 1, 2 and 3 correspond to $H_2C_4O_4$, $HC_4O_4^-$ and $C_4O_4^{2-}$, respectively

feature centred at 1540 cm^{-1} has been observed for other squarato-O^1,O^3-bridged copper(II) complexes[6] and provides evidence that the symmetry of the C–O parts of the molecule is lower than D_{4h} as shown by the above reported structure of **1**. A continuous absorption at 3600–3200 cm^{-1} with sharp maxima at 3500 and 3300 cm^{-1} is attributable to the presence of an aqua ligand[24] with extensive hydrogen bonding. Bands which may be assigned to ν(Cu–O) (490 and 420 cm^{-1}) and ν(Cu–N) (350 cm^{-1}) are clearly detectable in the far-IR region.

The X-band ESR spectrum of complex **1** recorded on a polycrystalline sample at room temperature appears as a non-resolved asymmetric feature centred at *ca.* $g = 2.10$. However, it is nicely resolved upon cooling and looks like an axial doublet with $g_{\parallel}$ and $g_{\perp}$ values of 2.178 and 2.043, respectively at 7.2 K (average value, $g_{av} = \frac{1}{3}g_{\parallel} + \frac{2}{3}g_{\perp}$, 2.088). The pattern $g_{\parallel} > g_{\perp} > 2.0$ is indicative of a copper(II) $d_{x^2-y^2}$ orbital ground state in agreement with the square-pyramidal geometry of copper in complex **1**. In addition, a weak half field transition is observed at both room and liquid-helium temperatures. Its occurrence is indicative of exchange interaction and most likely corresponds to a $\Delta M_s = 2$ forbidden transition within the triplet state of the dinuclear complex. Another possible origin for the half-field transition is the intermolecular interactions. However, this explanation can be ruled out because the intermolecular pathway involves a through-space δ overlap between the magnetic orbitals, which are separated by at least 5.7 Å, making such a pathway very unlikely. Both dipolar interaction ($|D_{dip}| = 1.55 \times 10^{-2}$ cm^{-1}) and anisotropic exchange[25] are expected to be small, which explains the lack of fine structure in the spectrum.

Magnetic Properties.—Variable-temperature magnetic susceptibility measurements have been performed down to 4.2 K for complex **1**. The value of μ_{eff} per dimer is 2.56 at room temperature and it remains practically constant (2.54) when cooling to 4.2 K. This magnetic behaviour corresponds to two uncoupled copper(II) ions and it can readily be understood by considering the weak overlap between the $d_{x^2-y^2}$ magnetic orbitals through the 1,3-bis(monodentate) squarate bridge.[6] In the approximation where $J \propto S^2$ (ref. 26) (J and S being the singlet–triplet energy gap and the overlap integral between the magnetic orbitals, respectively), a very small coupling is predicted.

Solution Study.—Studies of complex formation between squaric acid and metal ions have been carried out by potentiometric,[27] polarographic,[27] spectrophotometric,[27–29] chromatographic[27] and ionic exchange[27,30] methods. All these studies have been carried out in aqueous solution and only 1:1 and 1:2 metal ion–squarate complexes were formed. The values of the stability constants are much smaller than the corresponding ones for the related oxalato complexes[31] suggesting that the squarate dianion does not act as a chelating ligand. It is worthwhile noting that before X-ray data on squarato complexes were available the low values of their stability constants were attributed to the aromatic character of the squarate.[27]

As deprotonation of squaric acid and its complex formation with metal ions occur in the same pH range in aqueous solution, it is necessary to know accurately the acidity constants of squaric acid when attempting to determine the complex stability constants. A survey of the reported values for the acidity constants of squaric acid determined by potentiometry shows that (*i*) it behaves as a strong acid for the first dissociation and moderately strong for the second and (*ii*) both pK_{a_1} and pK_{a_2} values exhibit a great dispersion.[1,27,32] The relatively large uncertainties in the pK_a values are due to the difficulties inherent in the potentiometric method as applied to a fairly strong acid with a limited solubility in water. The use of other adequate techniques such as conductance[33] or spectrophotometry[27] reinforces the dispersion. These difficulties are overcome when working in a non-aqueous solvent such as dmso in which squaric acid behaves as a weak diprotic acid (see below) and its solubility is much increased. Recently, the use of this aprotic solvent allowed us to make accurate studies of the deprotonation equilibria of oxalic acid and its complex formation with some transition-metal ions.[8–10,34]

Acidity Constants of Squaric Acid.—Series of dmso solutions of 10^{-2} mol dm^{-3} squaric acid were titrated with 5×10^{-2} mol dm^{-3} $[NBu^n{}_4][OH]$ and the electromotive force data from three different sets were processed by SUPERQUAD. This procedure allowed us to determine the values of the overall proton association constants, 8.459(3) and 11.900(4) for log β_{j1} and log β_{j2}, respectively (maximum standard deviation in the last significant digit given in parentheses). Throughout the data treatment, 150 experimental points were used covering the range pH 2.9–8.3. The unsatisfactory response of the electrode at higher pH values precludes the exploration of more basic media. The distribution diagram of α *versus* pH for squaric acid is depicted in Fig. 2. The only species existing at pH $\leqslant 2$ is $H_2C_4O_4$ whereas $HC_4O_4^-$ is the main species in the range pH 3.5–8.4 and $C_4O_4^{2-}$ is predominant at pH $\geqslant 9$. As far as this last species is concerned, our measurements extend only up to a 40% extent of formation.

The greater values of log β_{j1} and log β_{j2} for oxalic acid in dmso [8.551(3) and 14.242(3), respectively][34] when compared to the ones for squaric acid under the same conditions indicate that oxalate dianion exhibits a higher affinity for hydrogen ions. Consequently, oxalato complexes will be more stable than squarato ones in cases where identical co-ordination modes are operative as shown hereunder.

Stability Constants of $Cu^{II}L$*–Squarate Complexes.*—Series of dmso solutions of $Cu^{II}L$ and squaric acid [$c_M = (5.0$–$10) \times 10^{-3}$ mol dm^{-3} and $c_{H_2C_4O_4} = (5.1$–$10) \times 10^{-3}$ mol dm^{-3}] were titrated with $[NBu^n{}_4][OH]$ in order to investigate the formation of squarato complexes. Data processing by SUPERQUAD of 237 (bipy), 159 (terpy) and 193 (bpca) experimental points from three different experiments for each system, belonging to the ranges pH 2.8–5.2 (bipy), 2.9–6.6 (terpy) and 2.7–6.1 (bpca), provided the stability constants listed in Table 4. Only the mono- and di-nuclear squarato complexes given therein fitted well the experimental data in the pH ranges investigated. The distribution diagrams of α *versus* pH for the $Cu^{II}L$–squarate systems are given in Fig. 3 [L = bipy (*a*) or terpy (*b*)]. The distribution diagram for bpca is very close to that for terpy because the same equilibrium scheme occurs with nearly identical values of the stability constants of the complexes involved. The complex $[Cu(bipy)(HC_4O_4)]^+$ exists at lower pH values reaching a degree of formation of 49% at *ca.* pH 4.3, whereas the dinuclear $[Cu_2(bipy)_2(C_4O_4)]^{2+}$ and mononuclear $[Cu(bipy)(C_4O_4)]$ species coexist in the range pH 4.5–8.0 achieving degrees of formation of 23 (pH 5.8) and 31% (pH 6.5), respectively. The complex $[Cu(bipy)(C_4O_4)_2]^{2-}$ is

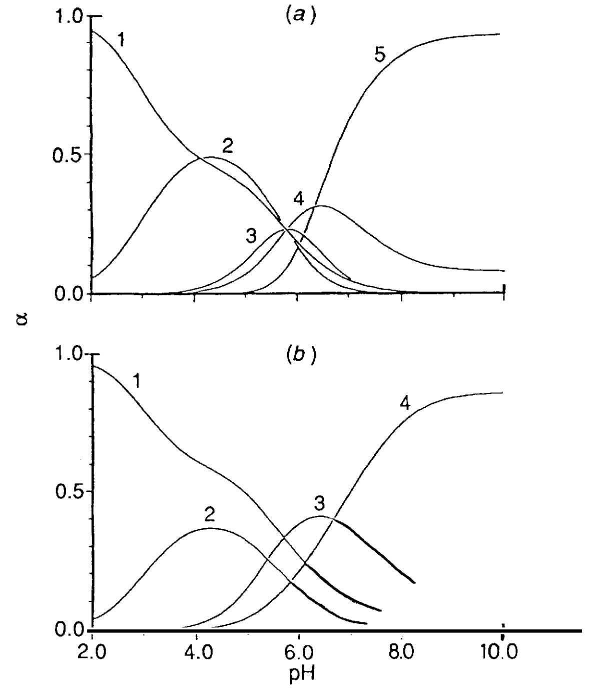

Fig. 3 Distribution diagram of α *versus* pH for (*a*) $[Cu(bipy)]^{2+}$–$H_2C_4O_4$ and (*b*) $[Cu(terpy)]^{2+}$–$H_2C_4O_4$ systems. Curves 1, 2, 3, 4 and 5 in (*a*) refer to $[Cu(bipy)]^{2+}$, $[Cu(bipy)(HC_4O_4)]^+$, $[Cu_2(bipy)_2(C_4O_4)]^{2+}$, $[Cu(bipy)(C_4O_4)]$ and $[Cu(bipy)(C_4O_4)_2]^{2-}$, whereas 1, 2, 3 and 4 in (*b*) are for $[Cu(terpy)]^{2+}$, $[Cu(terpy)(HC_4O_4)]^+$, $[Cu_2(terpy)_2(C_4O_4)]^{2+}$ and $[Cu(terpy)(C_4O_4)]$, respectively. Molar fractions are referred to total $[Cu(bipy)]^{2+}$ ($c_M = 5 \times 10^{-3}$ mol dm^{-3} and $c_{H_2C_4O_4} = 10^{-2}$ mol dm^{-3}) (*a*) and to total $[Cu(terpy)]^{2+}$ ($c_M = c_{H_2C_4O_4} = 10^{-2}$ mol dm^{-3}) (*b*)

predominant at higher pH values. It is not formed in the other two systems. The complexes $[Cu(terpy)(HC_4O_4)]^+$ (maximum degree of formation 37% at pH 4.3), $[Cu_2(terpy)_2(C_4O_4)]^{2+}$ (maximum degree of formation 41% at pH 6.4) and $[Cu(terpy)(C_4O_4)]$ are formed successively, the latter being predominant at pH >7.

The values of the stability constants for complexes with the same stoichiometry are very similar. This strongly suggests that squarate co-ordinates to $Cu^{II}L$ in the same manner for each family of complexes. Moreover, the small values of β_{110}, K_{111} and β_{210} when compared to the corresponding values for the related oxalato complexes (see Table 5) leads us to assume the occurrence of monodentate (first two constants) and bis(monodentate) (last constant) co-ordination modes of squarate. The known structural data validate this assumption: squarate acts as a monodentate ligand in $[Cu(bipy)(H_2O)(C_4O_4)]\cdot H_2O$,[6] and as a bis(monodentate) bridge in $[Cu_2(bipy)_2(H_2O)_2(C_4O_4)][NO_3]_2$,[6] $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)][ClO_4]_2$[6] and **1** whereas chelating and bis(chelating) modes have been observed for the related $Cu^{II}L$–oxalate complexes.[5e,h,8–10]

As far as squarate complexes are concerned, the analogous species to $[Cu(bipy)(C_4O_4)_2]^{2-}$ do not exist in the terpy and bpca systems. This fact is easily explained taking into account the existence of only two (bipy) and one (terpy, bpca) equatorial sites occupied by solvent molecules which can be replaced by squarate ligands.

A comparison of the log K_{111} values, which can be considered as a measure of the strength of $HC_2O_4^-$ and $HC_4O_4^-$ as monodentate ligands towards $Cu^{II}L$, shows that the monohydrogenoxalato complexes are more stable than the monohydrogensquarato ones, as expected according to their different basicities.

Table 4 Thermodynamic parameters[a] concerning complex formation between squaric acid and $[Cu^{II}L]$ (L = bipy, terpy or bpca)

	L		
Reaction[b]	bipy	terpy	bpca
$M + sq + H \xrightleftharpoons{\beta_{111}} M(Hsq)$	10.669(4)	10.533(2)	10.349(2)
$2M + sq \xrightleftharpoons{\beta_{210}} M_2(sq)$	7.52(3)	7.235(4)	7.118(5)
$M + sq \xrightleftharpoons{\beta_{110}} M(sq)$	4.87(1)	4.700(2)	4.466(3)
$M + 2sq \xrightleftharpoons{\beta_{120}} M(sq)_2$	9.34(1)		
$M + Hsq \xrightleftharpoons{K_{110}} M(Hsq)$	2.24[c]	2.07[c]	1.89[c]
$M(sq) + M \xrightleftharpoons{K_{210}} M_2(sq)$	2.65[c]	2.535[c]	2.652[c]

[a] Values correspond to the logarithms of the stability constants determined at 25 °C and 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$ in dmso solution. [b] Charges have been omitted for clarity; M and sq denote $Cu^{II}L$ and squarate(2−) respectively. [c] Calculated by combination of the appropriate β_{pqr} and β_{ji}.

Table 5 Thermodynamic parameters[a] concerning complex formation between oxalic acid and $[Cu^{II}L]$ (L = bipy, terpy or bpca)

	L		
Reaction[b,c]	bipy	terpy	bpca
$M + ox + H \xrightleftharpoons{\beta_{111}} M(Hox)$		12.397(5)	12.22(5)
$2M + ox \xrightleftharpoons{\beta_{210}} M_2(ox)$	13.185(5)	10.621(6)	10.2(1)
$M + ox \xrightleftharpoons{\beta_{110}} M(ox)$	11.165(1)	7.394(2)	7.0(1)
$M + Hox \xrightleftharpoons{K_{110}} M(Hox)$		3.855[c]	3.94[c]
$M(ox) + M \xrightleftharpoons{K_{210}} M_2(ox)$	2.02[c]	3.227[c]	3.2[c]

[a] Values correspond to the logarithms of the stability constants determined at 25 °C and 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$ in dmso solution. [b] Charges have been omitted for clarity; M and ox denote $Cu^{II}L$ and oxalate(2−) respectively. [c] Calculated by combination of the appropriate β_{pqr} and β_{ji}.

Conclusion

We have synthesised and characterised by spectroscopic, magnetic and X-ray diffraction methods the dinuclear copper(II) complex $[Cu_2(bpca)_2(H_2O)_2(C_4O_4)]$. This solid-state study has been complemented with an investigation of the complex formation between squaric acid and $Cu^{II}L$ (L = bipy, terpy or bpca) in dmso solution. A comparison of the obtained results from the solution and solid-state studies for the related squarate and oxalate systems allows us to demonstrate that the analogy between squarate and oxalate as ligands is purely formal. This work shows that complementary solution and solid-state studies constitute one of the best tools to obtain knowledge of complex formation.

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