Complex Formation between Croconate ($C_5O_5{}^{2-}$) and $Cu^{II}L$ [L = 2,2'-bipyridine(bipy), 2,2':6',2"-terpyridine or bis(2-pyridylcarbonyl)amide anion] in Dimethyl Sulfoxide Solution. Crystal Structure of [Cu(bipy)(C$_5$O$_5$)(H$_2$O)]†

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A new mononuclear complex of formula [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] [bipy = 2,2'-bipyridine, $C_5O_5{}^{2-}$ = dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)] has been synthesised and characterized by spectroscopic and X-ray diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$, with a = 7.1016(9), b = 9.3392(9), c = 11.8911(7) Å, α = 68.939(6), β = 84.665(7), γ = 68.974(9)° and Z = 2. The stucture consists of neutral monomeric [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] entities. The co-ordination geometry around each copper(II) ion is distorted square pyramidal with the two nitrogen atoms of bipy and two croconate oxygen atoms in the basal plane and a water oxygen atom at the apex. The protonation of croconate and its complex formation with $Cu^{II}L$ [L = bipy, 2,2':6'2"-terpyridine or bis(2-pyridylcarbonyl)amide anion] have been investigated in dimethyl sulfoxide solution at 25 °C and with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as background electrolyte. The co-ordination modes of croconate for this system are discussed in the light of both thermodynamic and structural parameters and compared to those of the related oxalato and squarato (3,4-dihydroxycyclobut-3-ene-1,2-dionato) complexes.

In previous work we have characterized the co-ordination modes of oxalate ($C_2O_4{}^{2-}$) and squarate ($C_4O_4{}^{2-}$ = dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione) toward copper(II) in the system $Cu^{II}L$ [L = 2,2'-bipyridine (bipy), 2,2':6',2"-terpyridine (terpy) or bis(2-pyridylcarbonyl)amide anion (bpca)] both in solution and in the solid state.[1,2] Bi- and tri-dentate N-donor ligands (L) were used in order to avoid the formation of the insoluble one-dimensional copper(II) oxalate[3] and squarate[4] chains. These coupled solution and solid-state studies have revealed that the similarity between oxalate and squarate (identical charge, a set of four oxygen donors, planar stereochemistry and π-electron delocalization) is purely formal. In fact oxalate behaves as a chelating or bis(chelating) ligand, whereas squarate acts as a unidentate or poly(unidentate) group. Geometrical constraints (bite parameter)[2b] are at the origin of their different co-ordination properties. The relative values of stability constants for the oxalato- and squarato-copper(II) complexes agree with their co-ordination modes which have been characterized in the solid state.

Croconate [$C_5O_5{}^{2-}$ = dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)] is a member of the series of cyclic oxocarbons of formula $C_nO_n{}^{2-}$ [n = 3–6 for deltate (2,3-dihydroxycycloprop-2-en-1-onate), squarate, croconate and rhodizonate (5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetronate) anions, respectively] whose co-ordination chemistry has been scarcely investigated. Only six structures of croconato complexes with first-row transition-metal ions are known to us: [M(C$_5$O$_5$)(H$_2$O)$_3$] (M = Cu^{II}, Zn^{II}, or Mn^{II}),[5,6] [Mn(C$_5$O$_5$)(Him)$_2$(H$_2$O)$_2$] (Him = imidazole),[7] [Cu(terpy)(C$_5$O$_5$)][Cu(terpy)(C$_5$O$_5$)(H$_2$O)]·4H$_2$O[8] and [Cu$_2$(bpca)$_2$(C$_5$O$_5$)]·3H$_2$O.[9] Keeping in mind the analogies between croconate and oxalate and squarate, we are making a systematic study of the
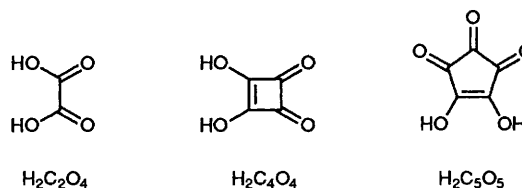
co-ordinating behaviour of croconate toward the $Cu^{II}L$ system.[8,9] In the present publication we report on the complex formation between croconate and $Cu^{II}L$ in dimethyl sulfoxide (dmso) solution. The crystal structure of the first symmetrically croconato-O^1,O^2-bonded copper(II) complex, [Cu(bipy)(C$_5$O$_5$)(H$_2$O)], is also presented.

H₂C₂O₄   H₂C₄O₄   H₂C₅O₅

Experimental

Materials.—(2,2'-Bipyridine)copper(II) nitrate, (2,2':6',2"-terpyridine)copper(II) nitrate monohydrate and diaqua[bis(2-pyridylcarbonyl)amido]copper(II) nitrate dihydrate were prepared by previously reported procedures[1c,d,10] and used as copper(II) salts for the solution studies. Anhydrous potassium croconate was prepared according to the literature.[11] As this salt is insoluble in dmso, we prepared the tetraphenylphosphonium derivative (see below) which is highly soluble in this solvent. This compound was used as the croconate source 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.

Preparation of [PPh$_4$]$_2$[C$_5$O$_5$]·3.5H$_2$O.—This compound was obtained by metathesis (reaction of aqueous solutions of potassium croconate and tetraphenylphosphorium chloride in

a 1:2 molar ratio). The crystals were filtered off, washed with small amounts of cold water and stored in vacuum over silica gel (Found: C, 72.15; H, 5.00. Calc. for $C_{53}H_{47}O_{8.5}P_2$: C, 72.20; H, 5.35%).

Preparation of [Cu(bipy)(C$_5$O$_5$)(H$_2$O)].—This compound was obtained as a green powder by reaction of stoichiometric amounts of (2,2′-bipyridine)copper(II) nitrate and potassium croconate in aqueous solution. The product was filtered off, washed with water and ethanol and stored over calcium chloride. It is insoluble in common solvents (water, methanol, ethanol, acetone, acetonitrile, nitromethane) and soluble in dmso and dimethylformamide (dmf) (Found: C, 47.70; H, 2.65; N, 7.40. Calc. for $C_{15}H_{10}CuN_2O_6$: C, 47.40; H, 2.45; N, 7.70%). Single crystals of this compound were obtained by slow diffusion of aqueous solutions of [Cu(bipy)][NO$_3$]$_2$ and K$_2$C$_5$O$_5$ in an H-double-tube glass vessel.

Physical Techniques.—The infrared spectrum was taken on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–225 cm^{-1} region. Variable-temperature X-band ESR spectra were recorded on polycrystalline samples with a Bruker ER 200D spectrometer equipped with a nitrogen cryostat.

Potentiometric titrations were performed using the equipment (burette, stirrer, electrode, pH meter, microcomputer, *etc.*) and following the experimental procedure described elsewhere.[1b] The equilibrium constants for the reaction of Cu^{II}L and croconate were determined by titrating dmso solutions of Cu^{II}L [(0.5–5) × 10^{-3} mol dm^{-3}], tetraphenylphosphonium croconate, [(1–5) × 10^{-3} mol dm^{-3}] and toluene-*p*-sulfonic acid, [(4–17) × 10^{-3} mol dm^{-3}] with [NBu$^n_4$][OH] (4 × 10^{-2} mol dm^{-3}). The sets of electromotive force data from different experiments for each system, carried out in the range pH 2.0–5.0, were merged and treated simultaneously by the computer program SUPERQUAD[12] to determine the croconate stability constants (see below). The deprotonation of croconic acid (acidified dmso solutions of 8.0 × 10^{-3} mol dm^{-3} tetraphenylphosphonium croconate) was investigated by using the same procedure. Electromotive force data from the range pH 2.3–7.9 were used to determine the acidity constants of croconic acid.

Crystal Structure Determination and Refinement.—Diffraction data for [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] were collected at 294 K with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystal parameters and refinement results are listed in Table 1. The unit-cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range 32–52°. A total of 3131 unique reflections were recorded in the range 2 < 2θ < 55°. Three reference reflections monitored throughout the data collection showed no sign of crystal deterioration. Based on the intensity distribution the space group P$\bar{1}$ was assumed throughout the structure analysis, and was confirmed by the successful refinement of the structure. The usual corrections for Lorentz and polarization effects were carried out. Correction for absorption was done by the Gaussian integration method.[13]

The structure was solved by direct methods and refined by the full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a Fourier difference map and were refined isotropically. The final full-matrix least-squares refinement, minimizing $\Sigma[w(F_o - F_c)^2]$, including 2885 reflections with $I \geqslant 2\sigma(I)$, converged at R = 0.028, R' = 0.035 and s = 2.58. All calculations were carried out on a MICRO-VAX II computer with the Enraf-Nonius Structure Determination Programs.[14] The scattering curves, with anomalous scattering terms included, were those of Cromer and Mann.[15] The final atomic coordinates for non-hydrogen atoms are given in Table 2 and selected bond lengths and angles in Table 3.

Table 1 Summary of crystallographic data for the complex [Cu(bipy)(C$_5$O$_5$)(H$_2$O)]

Formula	$C_{15}H_{10}CuN_2O_6$
M	377.80
Crystal system	Triclinic
Space group	P$\bar{1}$ (no. 2)
a/Å	7.1016(9)
b/Å	9.3392(9)
c/Å	11.8911(7)
α/°	68.939(6)
β/°	84.665(7)
γ/°	68.974(9)
U/Å^3	686.4(1)
Z	2
D_c/Kg m^{-3}	1.828
μ(Mo-Kα)/mm^{-1}	16.29
$F(000)$ (incl. anomalous scattering)	382.71
Range of transmission factors	0.79–0.63
Crystal size/mm	0.28 × 0.19 × 0.18
Scan type	ω
Scan range $\Delta\omega$/°	1.00 + 0.34 tan θ
Scan speed/° min^{-1}	1.6
2θ range/°	2–55
No. of unique reflections collected	3131
No. of reflections in the refinement,^{a} N_o	2885
No. of variables refined, N_v	257
$R\{ = [\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|]\}$	0.028
$R'\{ = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$	0.035
s^b	2.58
k^c	0.02
Maximum, minimum electron density/e Å^{-3}	0.58, −0.62
Maximum final shift/e.s.d.	0.02

^{a} $I \geqslant 2.0\sigma(I)$. ^{b} $s = [\Sigma w(\|F_o\| - \|F_c\|)^2/(N_o - N_v)]^{\frac{1}{2}}$. ^{c} $w = 4F_o^2/[\sigma_c^2 + (kF_o^2)^2]$, where σ_c is the standard deviation in F^2 based on counting statistics alone.

Table 2 Final atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for the complex [Cu(bipy)(C$_5$O$_5$)(H$_2$O)]

Atom	X/a	Y/b	Z/c
Cu	0.539 60(3)	0.178 79(2)	0.127 65(2)
O(1)	0.535 6(2)	0.197 5(1)	−0.046 1(1)
O(2)	0.342 5(2)	0.404 4(1)	0.073 9(1)
O(3)	0.062 5(2)	0.720 8(2)	−0.096 4(1)
O(4)	0.065 3(2)	0.671 2(2)	−0.328 4(1)
O(5)	0.384 2(2)	0.354 2(2)	−0.307 5(1)
O(6)	0.317 8(2)	0.043 3(2)	0.175 9(1)
N(1)	0.559 2(2)	0.177 2(2)	0.292 5(1)
N(2)	0.780 4(2)	−0.023 3(2)	0.188 1(1)
C(1)	0.710 6(3)	0.049 9(2)	0.364 0(1)
C(2)	0.738 1(3)	0.030 2(2)	0.482 9(2)
C(3)	0.608 6(3)	0.144 8(2)	0.528 7(2)
C(4)	0.453 7(3)	0.275 3(2)	0.455 1(2)
C(5)	0.432 9(3)	0.287 6(2)	0.337 8(2)
C(6)	0.835 9(3)	−0.064 5(2)	0.304 0(2)
C(7)	0.999 7(3)	−0.202 2(2)	0.359 8(2)
C(8)	1.111 1(3)	−0.297 4(2)	0.293 6(2)
C(9)	1.054 1(3)	−0.255 4(2)	0.175 4(2)
C(10)	0.887 8(3)	−0.118 9(2)	0.125 9(2)
C(11)	0.402 8(3)	0.336 7(2)	−0.100 9(1)
C(12)	0.302 4(3)	0.445 5(2)	−0.038 3(1)
C(13)	0.163 4(3)	0.596 7(2)	−0.119 1(2)
C(14)	0.169 9(3)	0.573 4(2)	−0.238 0(2)
C(15)	0.329 5(3)	0.410 3(2)	−0.227 0(2)

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 [Cu(bipy)(C$_5$O$_5$)(H$_2$O)].—The structure consists of neutral monomeric [Cu(bipy)(C$_5$O$_5$)-

Table 3 Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for the complex [Cu(bipy)(C$_5$O$_5$)(H$_2$O)]

Copper environment

Cu–O(1)	2.012(1)	Cu–N(1)	1.973(1)
Cu–O(2)	1.972(1)	Cu–N(2)	1.985(1)
Cu–O(6)	2.270(1)		

O(1)–Cu–O(2)	85.89(3)	O(2)–Cu–N(1)	92.09(4)
O(1)–Cu–O(6)	92.15(4)	O(2)–Cu–N(2)	166.50(4)
O(1)–Cu–N(1)	173.85(4)	O(6)–Cu–N(1)	93.89(4)
O(1)–Cu–N(2)	98.93(3)	O(6)–Cu–N(2)	94.23(4)
O(2)–Cu–O(6)	98.21(4)	N(1)–Cu–N(2)	81.80(4)

Croconate ligand

O(1)–C(11)	1.276(1)	C(11)–C(12)	1.421(2)
O(2)–C(12)	1.278(1)	C(11)–C(15)	1.463(2)
O(3)–C(13)	1.233(1)	C(12)–C(13)	1.447(2)
O(4)–C(14)	1.224(1)	C(13)–C(14)	1.500(2)
O(5)–C(15)	1.219(1)	C(14)–C(15)	1.506(2)

Cu–O(1)–C(11)	105.95(7)	O(3)–C(13)–C(14)	126.7(1)
Cu–O(2)–C(12)	107.14(7)	C(12)–C(13)–C(14)	105.7(1)
O(1)–C(11)–C(12)	120.4(1)	O(4)–C(14)–C(13)	125.8(1)
O(1)–C(11)–C(15)	129.5(1)	O(4)–C(14)–C(15)	126.1(1)
C(12)–C(11)–C(15)	110.0(1)	C(13)–C(14)–C(15)	108.1(1)
O(2)–C(12)–C(11)	120.4(1)	O(5)–C(15)–C(11)	128.3(1)
O(2)–C(12)–C(13)	128.9(1)	O(5)–C(15)–C(14)	126.5(1)
C(11)–C(12)–C(13)	110.7(1)	C(11)–C(15)–C(14)	105.3(1)
O(3)–C(13)–C(12)	127.6(1)		

Hydrogen bond

A^a	D^b	H	A···D	A···H–D
O(1^{II})^c	O(6)	H(62)	3.007(2)	173(3)
O(3^{III})	O(6)	H(61)	2.784(2)	162(2)

^{a} Acceptor atom. ^{b} Donor atom. ^{c} Symmetry operations: II 1 – x, –y, –z; III –x, 1 – y, –z.

Fig. 1 An ORTEP drawing of [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] showing the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level

co-ordination have been found.[5,8,9] The symmetrical bidentate co-ordination mode has been observed in complexes of Zn and Mn where the M–O bonds are longer.[5–7] In the present complex, the O(1)···O(2) bite distance (2.715 Å) has been reduced to accommodate the symmetrical chelation, the O···O distances between unco-ordinated oxygen atoms being 2.954 and 2.953 Å and between one co-ordinated and one unco-ordinated oxygen 3.031 and 3.003 Å. The shortening is reflected in the small O–C–C angles in the chelate ring (120.4°).

The water molecule is hydrogen bonded to croconato groups in neighbouring molecules (see end of Table 3). The shortest intermolecular metal–metal distances are 5.444 and 5.508 Å for Cu···Cu^{II} and Cu···Cu^I, respectively (II refers to the symmetry operation 1 – x, –y, –z).

Infrared and ESR Spectra.—Aiming at establishing a tool to identify the symmetrical bidentate co-ordination mode of croconate, the most relevant features of the IR spectrum of the [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] complex are the carbon–oxygen stretching frequencies of the croconato group. The absorptions observed at 1740, 1730, 1720 and 1710 cm^{-1} are attributed to the unco-ordinated carbonyls of the croconate entity,[18] which exhibits a strong double-bond character, as shown by the structural data. The co-ordinated C–O groups are characterized by medium absorptions at 1680 and 1650 cm^{-1}. The most striking feature of this spectrum is that the vibrational modes representing mixtures of C–C and C–O stretching motions appear as a doublet at 1510 and 1450 cm^{-1}. For asymmetrical chelating and asymmetrical bis(chelating) croconato-containing copper(II) complexes, on the other hand, such vibrational modes are observed as a broad absorption at higher wavenumbers (1600–1500 cm^{-1}).[8,9] These features suggest that the croconato group in [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] exhibits a different co-ordination mode as evidenced by its structure. The presence of co-ordinated water is evidenced by a broad absorption located in the 3600–3300 cm^{-1} region, with two sharp peaks at 3320 and 3480 cm^{-1} (OH stretching frequency) and the occurrence of the ν(HOH) bending at 1620 cm^{-1}.[19]

The X-band ESR spectrum of [Cu(bipy)(C$_5$O$_5$)(H$_2$O)] recorded on a polycrystalline sample at room temperature looks like an axial doublet with $g_\parallel$ and $g_\perp$ values of 2.26 and 2.07, respectively. It remains unchanged upon cooling to liquid-nitrogen temperatures. The observed 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 this complex.[20] No half-field transition is observed at room and liquid-nitrogen temperatures as expected for a mononuclear copper(II) complex with very weak intermolecular interactions.

(H$_2$O)] units linked by hydrogen bonds between the co-ordinated water molecule and croconate oxygen atoms from different units. A perspective view of the mononuclear complex with the atom-numbering scheme is depicted in Fig. 1.

The Cu atom has approximately square pyramidal surroundings with two bipyridyl nitrogen atoms [1.973(1) and 1.985(1) Å for Cu–N(1) and Cu–N(2), respectively] and two croconato oxygen atoms [2.012(1) and 1.972(1) Å for Cu–O(1) and Cu–O(2), respectively] in the basal plane and a water molecule in the apical position [2.270(1) Å for Cu–O(6)]. The sixth position is screened by the proximity of the croconate group of a neighbouring molecule [Cu–O(3^I) 3.234 Å where I refers to the symmetry operation 1 – x, 1 – y, –z]. The copper atom is displaced by 0.16 Å from a least-squares plane defined by O(1), O(2), N(1), N(2), toward the apical ligand.

The pyridyl rings of the bipyridine ligand are planar as expected with deviations from the mean planes not greater than 0.010 Å and the ligand as a whole is quasi-planar (the six-membered rings form a dihedral angle of 1°). These structural features are in agreement with those previously reported for other bipyridine-containing copper(II) complexes.[16] Average carbon–carbon and –nitrogen bond lengths are close to those observed in unco-ordinated 2,2′-bipyridine.[17]

The croconate ion has approximate C_{2v} symmetry with bond lengths consistent with an enediol form. It is approximately planar [the largest deviation is 0.100 Å at O(3)]. The dihedral angles between the equatorial plane and the croconate and bipyridine ligands are 3.7 and 5.8°, respectively. This is, to our knowledge, the first time the croconate ion has been observed to co-ordinate in a symmetrical bidentate fashion to copper. In previous studies asymmetrical bidentate as well as monodentate
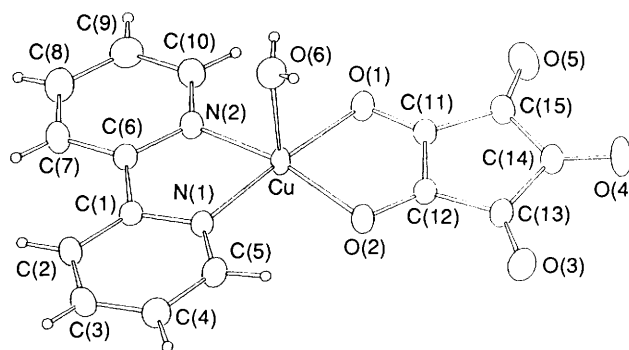
Solution Study.—Although cyclic oxocarbons have been known for more than 150 years,[21] solution studies of complex formation between croconic acid and metal ions are practically non-existent. The only reported example concerns the

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

| | L | | |
Reaction	bipy	terpy	bpca
$Cu^{II}L + C_5O_5^{2-} + H^+ \xrightleftharpoons{\beta_{111}} Cu^{II}L(HC_5O_5)$		9.88(3)	
$Cu^{II}L + C_5O_5^{2-} \xrightleftharpoons{\beta_{110}} Cu^{II}L(C_5O_5)$	8.028(1)	6.976(4)	6.391(1)
$Cu^{II}L + HC_5O_5^- \xrightleftharpoons{K_{110}} Cu^{II}L(HC_5O_5)$		1.42^b	

^{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} Calculated by combination of the appropriate β_{pqr} and β_{ji}.
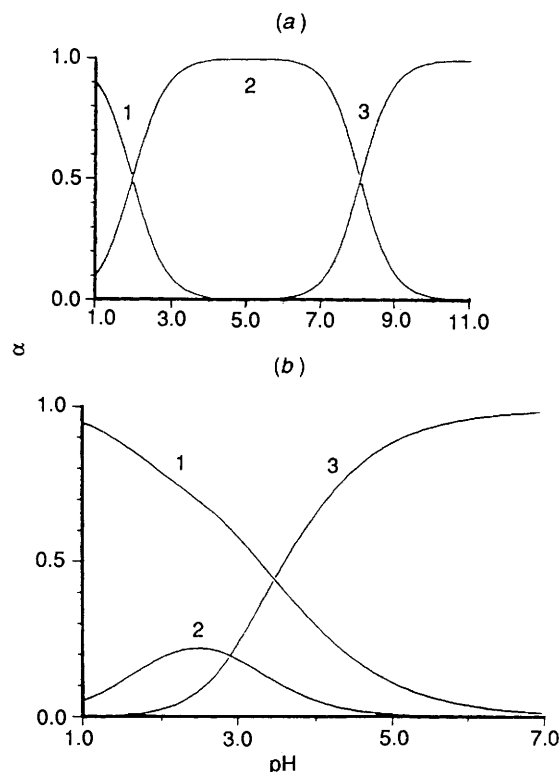
Fig. 2 (*a*) Distribution diagram of α *versus* pH for croconic acid where α is the ratio between the concentration of each species and the initial concentration of $H_2C_5O_5$. Curves 1, 2 and 3 correspond to $H_2C_5O_5$, $HC_5O_5^-$ and $C_5O_5^{2-}$, repectively. (*b*) Distribution diagram α *versus* pH for the $[Cu(terpy)^{2+}]$–$H_2C_5O_5$ system: 1, 2 and 3 refer to $[Cu(terpy)]^{2+}$, $[Cu(terpy)(HC_5O_5)]^+$ and $[Cu(terpy)(C_5O_5)]$, respectively. Molar fractions are referred to total $[Cu(terpy)]^{2+}$ ($c_M = c_L = 1 \times 10^{-2}$ mol dm^{-3})

croconato complexes with some alkaline-earth-metal cations.[22] Croconic acid behaves as a strong acid for the first and relatively strong acid for the second dissociation step, as shown by potentiometric[23] and spectrophotometric[23a] methods. The relatively large uncertainties in the pK_a values (0.36–0.76 and 1.5–2.23 for pK_{a1} and pK_{a2}, respectively) and the low values of pH for which the complex formation would occur prevent the use of the classical potentiometric method in aqueous solution and are the reasons for the paucity of thermodynamic data about the co-ordination chemistry of croconic acid in solution. The use of a non-aqueous solvent such as dmso in which croconic acid is soluble and behaves as a weak acid (see below) allowed us to overcome these difficulties. Analogous accurate studies of the deprotonation equilibria of the related oxalic and squaric acids and their complex formation with first-row transition-metal ions have been carried out in this aprotic solvent.[1b,d,2c,24]

Acidity Constants of Croconic Acid.—Treatment by

SUPERQUAD of electromotive force data from basic titrations of dmso solutions of croconic acid allowed us to determine the values of the overall proton association constants, 8.104(2) and 10.083(2) for log β_{j1} and log β_{j2}, respectively (maximum standard deviation in the last significant digit given in parentheses). The distribution diagram of α *versus* pH for croconic acid is depicted in Fig. 2(*a*). The species $H_2C_5O_5$ and $HC_5O_5^-$ coexist at low pH values; $HC_5O_5^-$ is the main one in the range pH 2–8, and the dianion is the only species existent at pH $\geqslant$ 10.

The smaller values of the overall protonation constants of croconate when compared to those of the related squarate [8.459(3) and 11.900(4) for log β_{j1} and log β_{j2}]^{2c} indicate that the latter is less acidic as a diprotic species. As they can be considered as organic oxoacids of formula $(HO)_2C_mO_m$, their acidity would increase with the formal charge of the nucleus C_m,^{25} that is with the ring size, as is observed.

Stability Constants of $Cu^{II}L$–Croconate Complexes.—Data processing by SUPERQUAD of 203 (bipy), 161 (terpy) and 112 (bpca) experimental points from three different experiments for each system, belonging to the ranges pH 2.0–2.9 (bipy), 2.2–4.6 (terpy) and 2.6–4.7 (bpca), provided the stability constants listed in Table 4. Only the croconato complexes given therein fitted well the experimental data in the pH ranges investigated. The distribution diagram of α *versus* pH for the terpy system is given in Fig. 2(*b*). The mononuclear 1:1 complex, [Cu(terpy)-(C_5O_5)], is predominant at pH > 3.5 and it is the only species in solution at pH > 6.5. At lower pH values a protonated complex also exists (maximum degree of formation 22% at pH 2.5). No binuclear species is formed in solution. The distribution diagrams for the other two systems are similar, but the protonated complex is lacking.

The stability of the complexes $Cu^{II}L(C_5O_5)$ follows the trend bipy > terpy > bpca. In agreement with these thermodynamic data, the structure of the $[Cu(bipy)(C_5O_5)(H_2O)]$ complex, which is reported in this work, shows that the croconate ligand is co-ordinated as a symmetric bidentate ligand, whereas it co-ordinates in an assymmetrical bidentate fashion in the parent $[Cu(terpy)(C_5O_5)(H_2O)]$ and $[Cu-(terpy)(C_5O_5)]$ complexes.[8] This co-ordination mode is expected also for $[Cu(bpca)(C_5O_5)]^-$. All the attempts to isolate this complex were unsuccessful, and they led to the $[Cu_2(bpca)_2(C_5O_5)]\cdot3H_2O$ binuclear species[9] whose formation in solution has not been observed under our experimental conditions. In such a complex the croconate anion behaves as a very asymmetric bis(bidentate) ligand.

On the Behaviour of Croconate as a Ligand.—It is interesting to compare the stability of the $Cu^{II}L(C_5O_5)$ complexes with those of the corresponding oxalato and squarato species (see Table 5). Oxalate binds usually as a bidentate ligand occupying two equatorial positions (two short bonds) in the co-ordination sphere of copper(II), as observed in [Cu(bipy)-(C_2O_4)],[1a,c,26] a very stable complex in dmso solution. When the copper(II) ion has three co-ordination sites occupied by a tridentate ligand such as terpy or bpca only one additional

Table 5 Stability constants* of the 1:1 complexes between $Cu^{II}L$ (L = bipy, terpy or bpca) and oxalate, squarate and croconate ligands

$Cu^{II}L$	$\log \beta_{110}$		
	$C_2O_4^{2-}$	$C_4O_4^{2-}$	$C_5O_5^{2-}$
$[Cu(bipy)]^{2+}$	11.2	4.9	8.0
$[Cu(terpy)]^{2+}$	7.4	4.7	7.0
$[Cu(bpca)]^{+}$	7.0	4.5	6.4

* Rounded values to the first decimal point are given.

short bond is possible (Jahn–Teller effect) and, therefore, the oxalate anion is forced to be co-ordinated to copper(II) in an asymmetrical bidentate fashion. In this case, the stability of the resulting oxalato complex is much decreased. On the other hand, the squarate ligand is always monodentate. The squarato complexes are much less stable and their stability is independent of the bi- or tri-dentate character of the other ligand present in the co-ordination sphere of copper(II). As reported elsewhere, the bite parameter of the squarate ion is causing this difference in the co-ordinating behaviour.[2b]

Although $C_4O_4^{2-}$ and $C_5O_5^{2-}$ belong to the same family of cyclic oxocarbon dianions, the co-ordinating behaviour of croconate resembles that of oxalate more than that of squarate. The stabilities of the oxalato and croconato complexes are very similar when the ligands are co-ordinated in the asymmetric fashion, but quite different in the symmetric one, the oxalato complex being much more stable. This greater stability of the oxalato complex is related to the shorter Cu–O(oxalate) distance (1.91–1.95 Å) in $[Cu(bipy)(C_2O_4)]^{1c,26}$ as compared to the average Cu–O(croconate) one (1.99 Å) in $[Cu(bipy)-(C_5O_5)(H_2O)]$. In the case of the bidentate asymmetric co-ordination, the short Cu–O(oxalate) (1.93 Å)[1d] and Cu–O(croconate) (1.94 Å)[8] are nearly equal. There is only a small difference in the stability of the two co-ordination modes of the croconato complexes, and thus it is not surprising that the symmetrical mode may be observed in the crystalline state. However, the intrinsic tendency of croconate to co-ordinate as an asymmetric bidentate ligand is reflected in the structure of $[Cu(C_5O_5)(H_2O)_3]^5$ where it forms only one short bond to copper while three water molecules occupy the other equatorial positions, and in the quasi-symmetrical bidentate croconatometal complex where slight but significant differences in the length of the short croconate to metal bonds are observed.

Acknowledgements

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