Complex Formation between Oxalate and (2,2′:6′,2″-Terpyridyl)-copper(II) in Dimethyl Sulphoxide Solution. Synthesis and Crystal Structures of Mono- and Di-nuclear Complexes‡

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The crystal and molecular structures of two new complexes $[\{Cu(terpy)(H_2O)\}_2(ox)][\{Cu(terpy)\}_2(ox)][ClO_4]_4 \cdot 2H_2O$ **1** and $[Cu(terpy)(H_2O)(ox)] \cdot 4H_2O$ **2** (terpy = 2,2′:6′,2″-terpyridine and ox = oxalate) have been determined by X-ray diffraction. Crystals of **1** are monoclinic, space group $P2_1/c$, with $Z = 2$, $a = 13.443(2)$, $b = 23.183(4)$, $c = 12.394(1)$ Å and $\beta = 116.29(1)°$, whereas those of **2** are triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 10.192(2)$, $b = 12.319(2)$, $c = 8.397(3)$ Å, $\alpha = 86.65(3)$, $\beta = 96.80(3)$ and $\gamma = 106.14(1)°$. The structure of **1** contains two different centrosymmetrical copper(II) dinuclear dicationic units, unco-ordinated perchlorate groups and lattice water. In both dinuclear units the terpyridyl group is terminal and the oxalate acts as an asymmetrical bis(chelating) bridge. However, the copper atom is five-co-ordinate in one dinuclear unit and six-co-ordinate in the other. The structure of **2** consists of neutral mononuclear $[Cu(terpy)(H_2O)(ox)]$ entities and unco-ordinated water molecules. The copper atom is in a six-co-ordinate, tetragonally elongated, octahedral environment. The stability constants of the oxalato complexes of $[Cu(terpy)]^{2+}$ [equations (i)–(iii)]

$$[Cu(terpy)]^{2+} + ox^{2-} + H^+ \overset{\beta_{111}}{\rightleftharpoons} [Cu(terpy)(Hox)]^+ \quad \text{(i)}$$

$$2[Cu(terpy)]^{2+} + ox^{2-} \overset{\beta_{210}}{\rightleftharpoons} [\{Cu(terpy)\}_2(ox)]^{2+} \quad \text{(ii)}$$

$$[Cu(terpy)]^{2+} + ox^{2-} \overset{\beta_{110}}{\rightleftharpoons} [Cu(terpy)(ox)] \quad \text{(iii)}$$

were determined by potentiometry in dimethyl sulphoxide solution: $\log \beta_{111} = 12.397(4)$, $\log \beta_{210} = 10.621(6)$ and $\log \beta_{110} = 7.394(2)$ (25 °C, 0.1 mol dm^{-3} $[NBu_4][ClO_4]$). The co-ordination modes of oxalate in the $Cu^{II}L$–ox^{2-} system (L being tri- or bi-dentate N-donor ligands) are discussed in the light of available thermodynamic and structural parameters.

It is well known that oxalate (ox) can co-ordinate to metal ions as a quadri-,[1] bi-,[1e,h,2] or uni-dentate ligand.[3] In the first case the ligand is particularly able to propagate electronic effects as evidenced by recent studies on the magnetic properties of oxalate-bridged copper(II),[1c,g,h,4] nickel(II)[1k,5] and iron(III)[6] complexes. Although the preparation and chemistry of oxalato complexes with transition-metal ions have been thoroughly investigated,[2a] thermodynamic studies on the co-ordination modes of oxalate are scarce. As far as the oxalate-containing copper(II) complexes are concerned all the above-mentioned co-ordination modes are found because the plasticity of the co-ordination sphere of this metal ion allows it to adopt different stereochemistries. Bi- and tri-dentate N-donor ligands have to be used as terminal ligands in order to avoid the formation of the insoluble one-dimensional copper(II) oxalate chain.

As a part of our coupled solution–solid state studies on oxalato complexes with first-row transition-metal ions,[2f,5b–d,7–10] we report here on the complex formation between oxalate and $[Cu(terpy)]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) in dimethyl sulphoxide (dmso) solution. The syntheses and crystal structures of the dinuclear $[\{Cu(terpy)(H_2O)\}_2(ox)][\{Cu(terpy)\}_2(ox)][ClO_4]_4 \cdot 2H_2O$ **1** and mononuclear $[Cu(terpy)(H_2O)(ox)] \cdot 4H_2O$ **2** complexes are also presented.

Experimental

Materials.—Copper(II) nitrate trihydrate, 2,2′:6′,2″-terpyridine, oxalic acid dihydrate, lithium hydroxide monohydrate and dmso were Merck analytical grade reagents and were used as received. Copper(II) perchlorate hexahydrate and tetra butylammonium perchlorate were purchased from Aldrich and Fluka, respectively. (2,2′:6′,2″-Terpyridyl)copper(II) nitrate monohydrate separates as a blue-turquoise crystalline powder when mixing concentrated ethanolic solutions of terpy and copper(II) nitrate in a 1:1 molar ratio. The product was filtered

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Summary of crystal data and data collection details for complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{64}H_{52}Cl_4Cu_4N_{12}O_{28}$	$C_{17}H_{21}CuN_3O_9$
M	1833.17	474.91
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	13.443(2)	10.192(2)
b/Å	23.183(4)	12.319(2)
c/Å	12.934(1)	8.397(3)
α/°	90.0	86.65(3)
β/°	116.29(1)	96.80(3)
γ/°	90.0	106.14(1)
U/Å^3	3614	1005
Z	2	2
D_c/g cm^{-3}	1.68	1.57
F(000)	1856	492
μ(Mo-Kα)/cm^{-1}	14.5	11.9
Scan width	0.60 + 0.35 tan θ	0.90 + 0.35 tan θ
Scan type	ω	θ–2θ
Scan speed/° min^{-1}	$\leqslant$6.7	$\leqslant$10
Maximum Bragg angle/°	25.5	32
Reflections collected	6920	6996
No. of unique reflections*	3346	4853
No. of variables	308	271
R [$=(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$]	0.045	0.044
R'\{$=[\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$\}	0.063	0.052
Weighting factor, w	$0.8656/[\sigma^2(F) + 0.0037\,F_o^2]$	$1/\sigma^2(F)$
Max. electron density/e Å^{-3}	0.90	0.96
Maximum final shift/e.s.d.	0.12	0.20

* $I \geqslant 2.0\sigma(I)$ for complex **1**, $\geqslant 3.0\sigma(I)$ for **2**.

off, washed with cold ethanol and diethyl ether, and stored over silica gel. Carbonate-free solutions of tetrabutylammonium hydroxide in dmso (freshly prepared from BDH reagent, 40% aqueous solution) were used as titrant in the potentiometric study; 0.1 mol dm^{-3} [NBu_4][ClO_4] was used as background electrolyte.

Synthesis of the Complexes.—[{Cu(terpy)(H_2O)}$_2$(ox)][{Cu(terpy)}$_2$(ox)][ClO_4]$_4$·2H_2O **1**. A blue greenish solution was obtained by mixing copper(II) perchlorate hexahydrate (2 mmol) and terpy (2 mmol) in water (300 cm^3) after gentle boiling with stirring for *ca.* 30 min. This solution became dark green after addition of an aqueous solution (10 cm^3) of lithium oxalate (1 mmol). The colour change is due to complex formation between oxalate and [Cu(terpy)]$^{2+}$. Evaporation of solvent at room temperature produced blue greenish plate-like crystals of complex **1** (Found: C, 41.85; H, 2.80; Cl, 8.00; Cu, 14.00; N, 9.20. Calc. for $C_{64}H_{52}Cl_4Cu_4N_{12}O_{28}$ **1**: C, 41.95; H, 2.85; Cl, 7.75; Cu, 13.85; N, 9.15%).

[Cu(terpy)(H_2O)(ox)]·4H_2O **2**. A green solution was obtained when adding an ethanolic solution (10 cm^3) of terpy (1 mmol) to an aqueous suspension (10 cm^3) of Cu(ox)·0.33H_2O (1 mmol)[11] with continuous stirring at room temperature. Slow evaporation of solvent nearly to dryness at room temperature yielded green rhombohedral crystals of complex **2** (Found: C, 42.90; H, 4.20; Cu, 13.05; N, 8.75. Calc. for $C_{17}H_{21}CuN_3O_9$ **2**: C, 43.00; H, 4.40; Cu, 13.40; N, 8.85%). This procedure is the most suitable to obtain **2** in pure form. All our attempts to synthesise it using commercially available ionic copper(II) salts led to mixtures of mono- and di-nuclear oxalate-containing copper(II) complexes, even in the presence of an excess of oxalate. The high solubility of the neutral complex **2** demonstrates that cationic dinuclear species separate first in the presence of suitable counter ions.

Physical Techniques.—Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–250 cm^{-1} region. Electromotive force (e.m.f.) measurements were carried out at 25 °C by using equipment and following an experimental procedure described in detail elsewhere.[8] For convenience, pH instead of $-\log[H^+]$ will be used throughout the text. Series of dmso solutions of (2,2′:6′,2″-terpyridyl)copper(II) nitrate and oxalic acid [$c_M = 2.98 \times 10^{-3}$, $c_L = (2.86–7.13) \times 10^{-3}$ mol dm^{-3}] were titrated with [NBu_4][OH] in order to investigate the formation of oxalato complexes. The computer program SUPERQUAD[12] was used to process e.m.f. data and to determine the stability constants of the interaction between [Cu(terpy)]$^{2+}$ and ox^{2-}.

Crystal Structure Determination and Refinement.—Diffraction data were collected at 293 K for both compounds with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The crystal and refinement data are given in Table 1. The unit-cell parameters and orientation matrix were derived from the setting angles of 25 well centred reflections ($11 \leqslant \theta \leqslant 18°$ and $8 \leqslant \theta \leqslant 23°$ for **1** and **2**, respectively). Examination of three standard reflections monitored every hour showed no significant intensity decay in both cases. The data were corrected for Lorentz and polarization effects, but not for absorption. Independent reflections with $I \geqslant 2\sigma(I)$ and $I \geqslant 3\sigma(I)$ were used for the structure refinement of complexes **1** and **2**, respectively. The data collection for **1** showed systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with the monoclinic space group $P2_1/c$ (no. 14). The space group $P\bar{1}$ was assumed for **2** and this choice was later confirmed by the successful refinement of the structure.

The structures of complexes **1** and **2** were solved by Patterson synthesis followed by alternating cycles of full-matrix least-squares refinements and electron-density calculations by means of Fourier and Fourier-difference synthesis. Anisotropic thermal parameters were given to all the non-hydrogen atoms. The positions of the terpyridyl hydrogen atoms were calculated and introduced as fixed contributors (C–H 0.97 Å) with isotropic thermal parameters equal to those of the atoms to which they were attached. The hydrogen atoms of four water

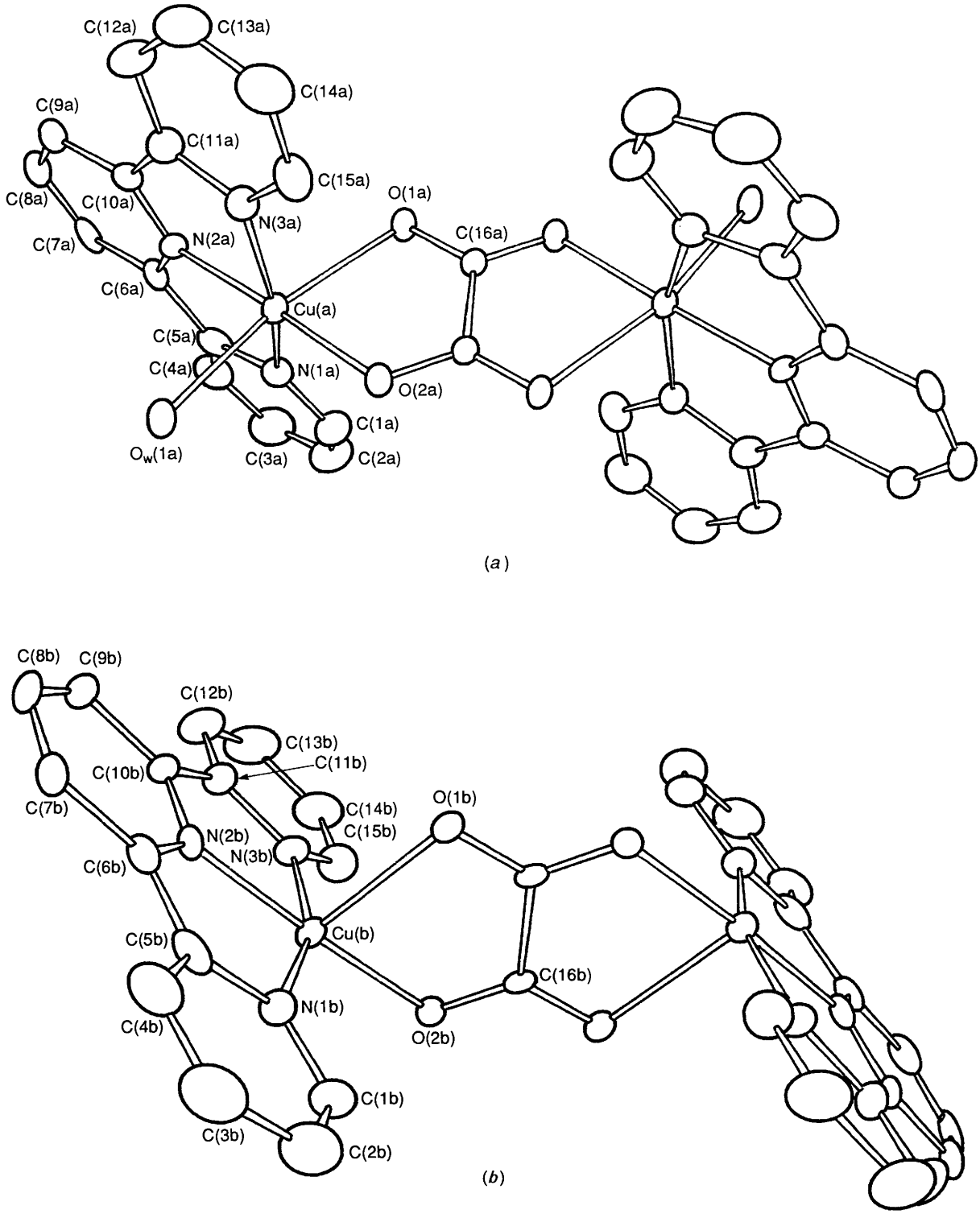

Fig. 1 ORTEP view of the cationic centrosymmetric dinuclear $[\{Cu(terpy)(H_2O)\}_2(ox)]^{2+}$ (*a*) and $[\{Cu(terpy)\}_2(ox)]^{2+}$ (*b*) units of complex **1** along with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity

molecules in complex **2** and none of complex **1** could be located on a Fourier-difference map. They were treated as the previous ones. In all structure-factor calculations the atomic scattering factors were taken from ref. 13. The effect of anomalous dispersion was included for all non-hydrogen atoms. The values of f' and f'' used were those given in ref. 14. The final values of R and R' are given in Table 1. The final Fourier difference maps showed no significant features. All calculations were carried out using the SHELX 76,[15] SDP[16] and ORTEP[17] programs on a DECVAX 11-730 computer. The final atomic coordinates for non-hydrogen atoms of complexes **1** and **2** are given in Tables 2 and 3 respectively.

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 of complex **1** is made up of two different cationic oxalato-bridged

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*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(a)	0.446 40(6)	0.604 87(3)	0.563 88(6)	C(3a)	0.058 9(7)	0.609 1(5)	0.310 1(8)
Cu(b)	0.509 94(6)	0.449 59(3)	0.813 65(6)	C(4a)	0.125 4(7)	0.658 6(4)	0.342 6(7)
Cl(1)	0.875 8(2)	0.393 37(9)	0.277 7(2)	C(5a)	0.234 2(5)	0.653 8(3)	0.417 9(6)
Cl(2)	0.803 5(2)	0.838 34(9)	0.520 3(2)	C(6a)	0.314 8(6)	0.701 9(3)	0.455 2(5)
Ow(1a)	0.409 3(4)	0.621 6(2)	0.725 6(4)	C(7a)	0.291 4(7)	0.760 5(3)	0.424 8(6)
Ow(2)	0.932 0(8)	0.250 3(3)	0.443(1)	C(8a)	0.379 6(7)	0.797 7(3)	0.462 1(6)
O(1a)	0.476 0(4)	0.561 9(2)	0.417 3(4)	C(9a)	0.487 0(7)	0.779 7(3)	0.524 3(6)
O(2a)	0.475 9(4)	0.524 9(2)	0.616 2(4)	C(10a)	0.504 4(6)	0.721 4(3)	0.553 5(5)
O(1b)	0.510 1(3)	0.426 0(2)	0.986 2(3)	C(11a)	0.611 0(6)	0.692 5(3)	0.618 1(6)
O(2b)	0.491 8(3)	0.524 8(2)	0.867 3(3)	C(12a)	0.713 8(7)	0.719 1(4)	0.657 8(7)
O(1p1)	0.922 7(6)	0.346 6(3)	0.248 3(8)	C(13a)	0.807 5(8)	0.688 0(5)	0.710 4(8)
O(2p1)	0.953 0(6)	0.437 8(3)	0.314 0(8)	C(14a)	0.800 5(8)	0.630 1(6)	0.725 9(8)
O(3p1)	0.776 8(5)	0.410 7(3)	0.182 1(6)	C(15a)	0.697 8(6)	0.605 2(4)	0.690 2(7)
O(4p1)	0.849 5(7)	0.377 0(5)	0.364 5(7)	C(1b)	0.746 9(6)	0.490 8(3)	0.942 6(7)
O(1p2)	0.867 6(6)	0.879 1(3)	0.500 2(7)	C(2b)	0.859 9(7)	0.482 6(4)	0.998 6(8)
O(2p2)	0.789 6(8)	0.851 2(4)	0.616 5(7)	C(3b)	0.902 4(8)	0.429 4(5)	0.991(1)
O(3p2)	0.698 4(8)	0.834 6(5)	0.430 8(8)	C(4b)	0.831 4(8)	0.385 6(4)	0.929 9(8)
O(4p2)	0.845(1)	0.786 4(4)	0.525(1)	C(5b)	0.719 9(6)	0.395 8(3)	0.877 9(6)
N(1a)	0.279 5(4)	0.602 4(2)	0.461 5(5)	C(6b)	0.632 9(7)	0.352 5(3)	0.812 5(6)
N(2a)	0.418 5(4)	0.685 1(2)	0.517 8(4)	C(7b)	0.651 2(8)	0.295 0(3)	0.794 2(7)
N(3a)	0.604 7(5)	0.635 5(2)	0.636 4(5)	C(8b)	0.562(1)	0.260 5(3)	0.736 3(7)
N(1b)	0.677 1(4)	0.448 9(2)	0.883 5(5)	C(9b)	0.456 3(9)	0.282 4(3)	0.692 4(6)
N(2b)	0.530 6(5)	0.372 5(2)	0.771 9(4)	C(10b)	0.440 9(7)	0.340 4(3)	0.712 1(5)
N(3b)	0.349 6(5)	0.427 3(2)	0.713 9(5)	C(11b)	0.336 3(7)	0.372 8(3)	0.674 8(6)
C(16a)	0.500 6(5)	0.488 7(2)	0.556 9(5)	C(12b)	0.232 3(9)	0.351 3(4)	0.604 7(7)
C(16b)	0.494 7(5)	0.528 5(2)	0.966 6(5)	C(13b)	0.142 8(9)	0.385 7(5)	0.573 9(9)
C(1a)	0.215 5(6)	0.554 9(3)	0.429 7(7)	C(14b)	0.156 7(7)	0.441 0(4)	0.613 4(8)
C(2a)	0.107 3(8)	0.557 9(5)	0.356 2(8)	C(15b)	0.261 8(6)	0.460 6(3)	0.683 0(6)

Table 3 Final atomic coordinates with e.s.d.s in parentheses for complex **2**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.343 87(4)	0.204 78(3)	0.281 03(5)	C(7)	0.276 5(4)	−0.109 8(3)	0.521 7(4)
O(1)	0.555 2(2)	0.223 5(2)	0.209 5(3)	C(8)	0.205 3(4)	−0.183 2(3)	0.403 4(5)
O(2)	0.401 0(2)	0.365 5(2)	0.232 8(3)	C(9)	0.177 8(4)	−0.142 0(3)	0.248 3(4)
O(3)	0.582 0(3)	0.511 7(2)	0.200 4(4)	C(10)	0.221 2(3)	−0.026 6(3)	0.215 9(4)
O(4)	0.734 6(3)	0.369 1(3)	0.161 9(4)	C(11)	0.198 8(3)	0.033 7(3)	0.060 0(4)
Ow(1)	0.123 0(3)	0.230 2(3)	0.369 9(3)	C(12)	0.135 7(3)	−0.021 6(3)	−0.079 1(4)
N(1)	0.414 1(3)	0.200 7(2)	0.523 3(3)	C(13)	0.114 9(4)	0.044 5(4)	−0.216 1(4)
N(2)	0.289 2(3)	0.044 1(2)	0.330 2(3)	C(14)	0.156 8(4)	0.159 4(4)	−0.212 5(4)
N(3)	0.241 8(3)	0.147 4(2)	0.063 3(3)	C(15)	0.222 1(4)	0.209 8(3)	−0.070 2(4)
C(1)	0.481 0(4)	0.288 3(3)	0.612 4(4)	C(16)	0.613 5(3)	0.326 5(3)	0.193 1(4)
C(2)	0.536 5(4)	0.273 2(3)	0.769 8(4)	C(17)	0.528 4(3)	0.410 2(3)	0.209 1(4)
C(3)	0.522 3(4)	0.165 3(3)	0.833 1(4)	Ow(2)	0.197 1(3)	0.466 8(2)	0.079 5(3)
C(4)	0.451 6(3)	0.073 6(3)	0.743 6(4)	Ow(3)	−0.045 6(3)	0.291 5(2)	0.106 6(4)
C(5)	0.397 9(3)	0.094 8(3)	0.587 8(3)	Ow(4)	0.096 4(4)	0.550 2(3)	0.330 9(4)
C(6)	0.319 0(3)	0.004 6(3)	0.480 9(4)	Ow(5)	0.154 1(4)	0.411 4(3)	0.602 7(4)

centrosymmetrical copper(II) dinuclear units, $[\{Cu(terpy)(H_2O)\}_2(ox)]^{2+}$ [Fig. 1(*a*)] and $[\{Cu(terpy)\}_2(ox)]^{2+}$ [Fig. 1(*b*)], two sets of two independent unco-ordinated perchlorate anions and water of crystallization. Main bond lengths and angles involving non-hydrogen atoms are listed in Table 4.

The co-ordination geometry around each copper(II) ion in $[\{Cu(terpy)(H_2O)\}_2(ox)]^{2+}$ is distorted elongated-tetragonal octahedral [*i.e.* a copper(II) '4 + 1 + 1' co-ordination mode]. The N(1a), N(2a) and N(3a) nitrogen atoms of the terpy ligand occupy three of the basal sites whereas the O(1a) and O(2a) oxygen atoms of oxalate fill the remaining basal and one of the axial positions. A water oxygen atom [Ow(1a)] achieves the octahedral co-ordination. The two nitrogen atoms of the terminal pair of pyridine rings in the terpy ligand form bonds of equal lengths to the copper(II) ion [2.040(5) and 2.037(5) Å for Cu(a)–N(1a) and Cu(a)–N(3a)] whereas the nitrogen atom of the central pyridine ring is at a significantly shorter distance [1.939(5) Å for Cu(a)–N(2a)]. This pattern is due to geometrical constraints and had been previously observed in other terpyridyl-containing copper(II) complexes.[18–22] The distances between copper(II) and the closest neighbouring atoms [N(1a), N(2a), N(3a) and O(2a)] range from 1.94 to 2.04 Å. They form a slightly tetrahedrally distorted square with deviations from the least-squares plane lower than ±0.07 Å. The copper atom departs by 0.014(8) Å from this mean plane towards the oxalate O(1a) atom distant by 2.33 Å, opposite to the water molecule Ow(1a) at 2.39 Å. The values of the angles N(1a)–Cu(a)–N(2a) [79.6(2)°] and N(2a)–Cu(a)–N(3a) [80.0(2)°] deviate significantly from the ideal value of 90° because of the small bite size of the five-membered planar chelate rings.

The individual pyridine rings of the terpy ligand are highly planar [maximum deviation 0.021 Å at C(14a)]. However, the ligand as a whole is far from being planar showing dihedral angles of 8.1 and 5.5° between its two outer rings [N(1a), C(1a), C(2a), C(3a), C(4a), C(5a) and N(3a), C(11a) C(12a), C(13a), C(14a), C(15a)] and the central ring [N(2a), C(6a), C(7a), C(8a), C(9a), C(10a)]. Such a dihedral twist motion is perfectly normal for a co-ordinated terpy ligand. Average C–C bond lengths within the rings (1.37 Å), C–N bonds (1.34 Å) and C–C bonds (inter-ring) (1.47 Å) compare well with previously reported ones.[18–22] Although the mean angle within the individual

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **1** *

Copper environment			
Cu(a)–N(1a)	2.040(5)	Cu(b)–N(1b)	2.016(5)
Cu(a)–N(2a)	1.939(5)	Cu(b)–N(2b)	1.924(5)
Cu(a)–N(3a)	2.037(5)	Cu(b)–N(3b)	2.029(5)
Cu(a)–O(1a)	2.327(5)	Cu(b)–O(1b)	2.297(5)
Cu(a)–O(2a)	1.952(4)	Cu(b)–O(2a)	1.932(4)
Cu(a)–Ow(1a)	2.387(6)		
O(1a)–Cu(a)–O(2a)	78.1(2)	O(1b)–Cu(b)–O(2b)	79.2(2)
O(1a)–Cu(a)–N(1a)	89.7(2)	O(1b)–Cu(b)–N(1b)	92.4(2)
O(1a)–Cu(a)–N(2a)	103.9(2)	O(1b)–Cu(b)–N(2b)	96.5(2)
O(1a)–Cu(a)–N(3a)	90.2(2)	O(1b)–Cu(b)–N(3b)	95.8(2)
O(2a)–Cu(a)–N(1a)	101.2(2)	O(2b)–Cu(b)–N(1b)	98.2(2)
O(2a)–Cu(a)–N(2a)	177.8(2)	O(2b)–Cu(b)–N(2b)	175.6(2)
O(2a)–Cu(a)–N(3a)	99.3(2)	O(2b)–Cu(b)–N(3b)	101.0(2)
N(1a)–Cu(a)–N(2a)	79.6(2)	N(1b)–Cu(b)–N(2b)	81.2(2)
N(1a)–Cu(a)–N(3a)	159.0(2)	N(1b)–Cu(b)–N(3b)	160.4(2)
N(2a)–Cu(a)–N(3a)	80.0(2)	N(2b)–Cu(b)–N(3b)	80.2(2)
Ow(1a)–Cu(a)–O(1a)	163.9		
Ow(1a)–Cu(a)–O(2a)	86.5(2)		
Ow(1a)–Cu(a)–N(1a)	88.7(2)		
Ow(1a)–Cu(a)–N(2a)	91.5(2)		
Ow(1a)–Cu(a)–N(3a)	97.0(2)		
Oxalato bridge			
O(1a)–C(16a)	1.222(7)	O(1b)–C(16b^{II})	1.235(7)
O(2a)–C(16a^{I})	1.277(8)	O(2b)–C(16b)	1.271(9)
C(16)–C(16a^{I})	1.555(14)	C(16b)–C(16b^{II})	1.550(11)
O(1a)–C(16a)–O(2a^{I})	124.8(7)	O(1b^{II})–C(16b)–O(2b)	124.9(5)
O(1a)–C(16a)–C(16a^{I})	118.3(8)	O(1b^{II})–C(16b)–C(16b^{II})	117.7(8)
O(2a^{I})–C(16a)–C(16a^{I})	116.9(6)	O(2b)–C(16b)–C(16b^{II})	117.4(6)

* Symmetry translations: I $1-x, 1-y, 1-z$; II $1-x, 1-y, 2-z$.

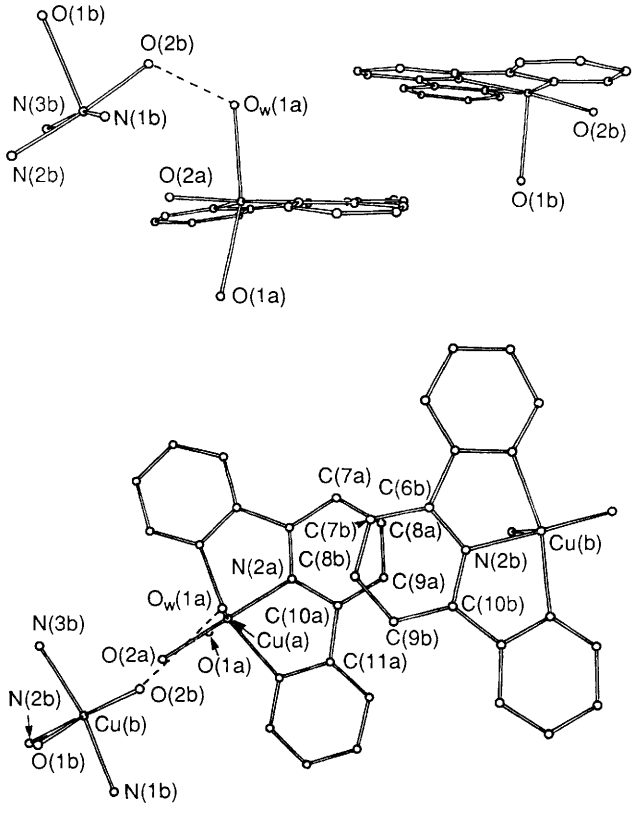

Fig. 2 An illustration of interactions between next-neighbouring units (a) and (b) in complex **1**. The top view emphasizes the presumed hydrogen bond between units having a Cu ··· Cu separation of 4.656(1) Å.The bottom view shows the partial overlap of the central terpyridyl rings. For the sake of clarity not all the atoms are included

pyridine rings is the expected 120.0°, significant deviations from this angle are observed for angles such as C(6a)–C(5a)–N(1a) [113.7(5)°] and N(2a)–C(10a)–C(11a) [112.7(5)°].

The oxalate dianion is planar, the copper atom being 0.076 Å out of this plane. It bridges in an asymmetrical bis(bidentate) fashion between two aqua(terpyridyl)copper(II) units. The dihedral angle between the oxalate plane and the mean plane of the terpy ligand is 89.2°, slightly larger than the dihedral angle between oxalate and the N(1a), N(2a), N(3a) and O(2a) mean plane (88.2°). The bite angle at the copper atom of the oxalate ligand is 78.1°. Such a value as well as the bond lengths and angles in the oxalate ion are in the expected range and very similar to those observed in other asymmetrical oxalato-bridged copper(II) complexes.[1b–g,8]

Each copper atom in $[\{Cu(terpy)\}_2(ox)]^{2+}$ is in a five-co-ordinate square-planar surrounding: the N(1b), N(2b) and N(3b) nitrogens occupy three of the basal sites whereas the O(1b) and O(2b) oxalate oxygen atoms fill the remaining basal and apical positions respectively. The copper(II)–ligand distances in the basal plane range from 1.924(5) to 2.029(5) Å and they are shorter than the apical bond length [2.297(5) Å for Cu(b)–O(1b)]. Atoms N(1b), N(2b), N(3b) and O(2b) are not as coplanar [maximum deviation from the mean plane −0.108 Å at N(2b)] as in the above-described dinuclear unit, but the copper atom does not deviate significantly (0.001 Å) from their mean plane. Again the values of the terpyridylcopper(II) angles are significantly smaller than the ideal value of 90° [81.2(2) and 80.2(2)° for N(1b)–Cu(b)–N(2b) and N(2b)–Cu(b)–N(3b), respectively]. It is worth underlining that in the (b) unit the oxalate ligand acts also as a centrosymmetrically bis(bidentate) bridge between the terpyridylcopper(II) entities in an asymmetrical fashion on each side. There are no unusual bond distances and angles in the terpyridyl and oxalate groups. The terpy ligand is more planar in (b) than in (a) [maximum deviations 0.245 Å at C(3a) and 0.109 Å at C(13b)]. The two outer pyridine rings and the central one form dihedral angles of 2.8 and 5.0°, somewhat smaller than those in the (a) unit. The oxalato bridge is planar, the copper atom being 0.112 Å out of this plane. The oxalate and terpyridyl mean planes are perpendicular to each other (84.2°). In this case the bite angle at the copper atom of the oxalate ligand is 79.2(2)°.

The intramolecular copper–copper separations are 5.528(2) Å in (a) and 5.469(2) Å in (b). Two shorter intermolecular copper–copper distances are observed between neighbouring units (a) and (b), 5.322(1) and 4.656(1) Å, which otherwise show a separation of 2.796(5) Å between the co-ordinated water molecule Ow(1a) and the oxalate oxygen atom O(2b) (Fig. 2), presumably a hydrogen-bond interaction [the H atoms bound to Ow(1a) could not be located]. The angle between the corresponding equatorial copper planes is 36.8°. Intermolecular interaction between neighbouring (a) and (b) units may be also inferred from the partial overlap of their central terpyridyl rings, as shown in Fig. 2: the dihedral angle between the rings is 5.5°, and interatomic distances ranging from 3.25 to 3.60 Å are observed (Table 4).

The two sets of two crystallographically independent perchlorate counter ions do not exhibit any disorder and their geometries are quite satisfactory, with the mean O–Cl–O angle and the Cl–O bond length found to be 109.5° and 1.38 Å, as expected. A screening of interatomic distances up to 3 Å revealed no intermolecular hydrogen bonds from the water molecule Ow(1a). However, the oxygen atom of the un-co-ordinated water molecule, Ow(2), is at 2.97(2) Å from the perchlorate oxygen atom O(4p2).

Molecular Structure of Complex **2**.—The structure of complex **2** consists of neutral mononuclear $[Cu(terpy)(H_2O)(ox)]$ units and water of crystallization linked by an extensive

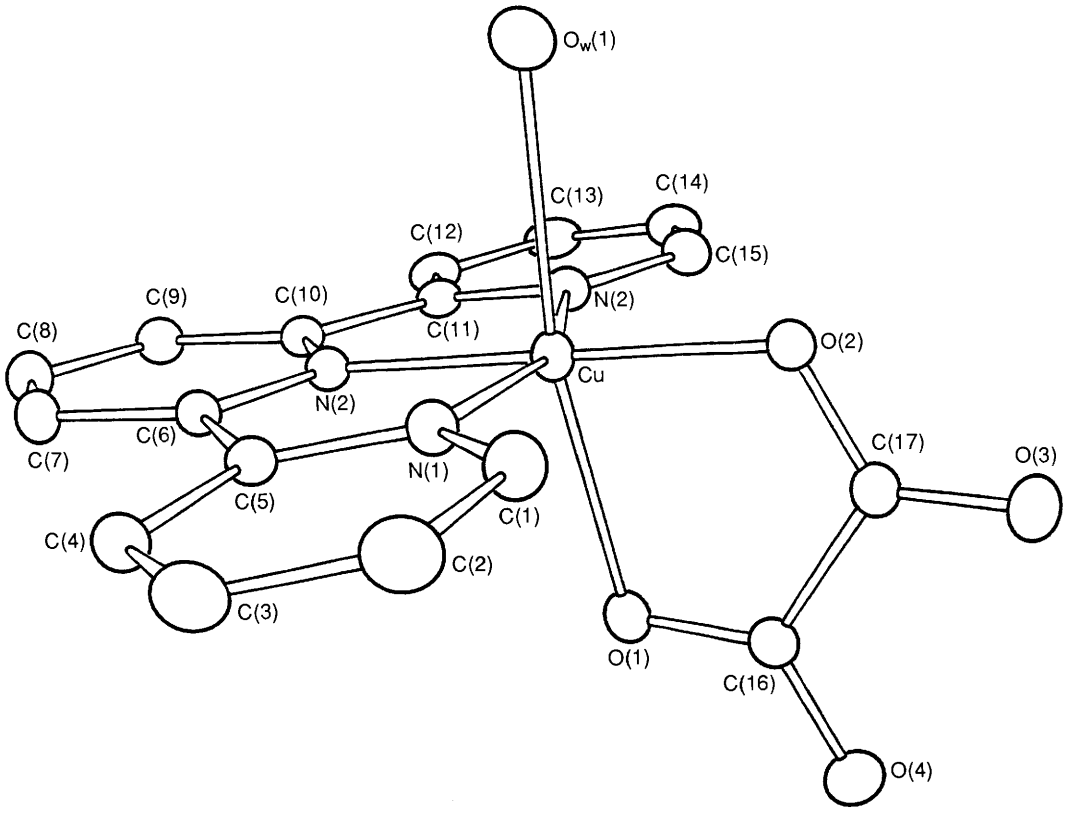

Fig. 3 ORTEP view of complex **2** with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are not included

Table 5 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

Copper environment			
Cu–N(1)	2.077(2)	Cu–O(1)	2.249(2)
Cu–N(2)	1.928(2)	Cu–O(2)	1.928(2)
Cu–N(3)	2.065(2)	Cu–Ow(1)	2.559(3)
O(1)–Cu–O(2)	79.64(9)	O(2)–Cu–Ow(1)	88.39(10)
O(1)–Cu–N(1)	91.68(10)	N(1)–Cu–N(2)	79.66(10)
O(1)–Cu–N(2)	99.71(10)	N(1)–Cu–N(3)	158.89(1)
O(1)–Cu–N(3)	95.24(10)	N(1)–Cu–Ow(1)	86.52(10)
O(1)–Cu–Ow(1)	167.41(9)	N(2)–Cu–N(3)	79.52(10)
O(2)–Cu–N(1)	99.93(10)	N(2)–Cu–Ow(1)	92.23(10)
O(2)–Cu–N(2)	179.24(10)	N(3)–Cu–Ow(1)	90.82(10)
O(2)–Cu–N(3)	100.93(10)		
Oxalate ligand			
O(1)–C(16)	1.247(4)	O(3)–C(17)	1.218(4)
O(2)–C(17)	1.294(4)	O(4)–C(16)	1.250(4)
C(16)–C(17)	1.543(5)		
Cu–O(1)–C(16)	108.2(2)	O(4)–C(16)–C(17)	116.2(3)
Cu–O(2)–C(17)	117.5(2)	O(2)–C(17)–C(16)	116.0(3)
O(1)–C(16)–C(17)	117.5(3)	O(2)–C(17)–O(3)	123.9(4)
O(1)–C(16)–O(4)	126.3(4)	O(3)–C(17)–C(16)	120.1(3)

network of hydrogen bonds. A perspective view of the neutral [Cu(terpy)(H_2O)(ox)] entity is given in Fig. 3. Bond lengths and non-bonded distances and angles are listed in Table 5.

This copper(II) complex displays the same geometry as the corresponding part of the dication (a) in complex **1**. Each copper atom has a six-co-ordinate CuN_3O_3 chromophore with a tetragonally elongated octahedral structure. It is linked to the three terpy nitrogen atoms [N(1), N(2) and N(3)] and an oxalate oxygen atom [O(2)] in the equatorial plane, the bond distances ranging from 1.93 to 2.08 Å. The copper atom lies only 0.021 Å out of the N(1), N(2), N(3), O(2) mean plane toward the axially semi-co-ordinated oxalate oxygen atom [O(1)] [Cu–O(1) 2.249(2) Å]. An oxygen atom [Ow(1)] of a water molecule occupies the sixth co-ordination position at a longer distance [Cu–Ow(1) 2.559(3) Å]. Again, significant deviations from the ideal value of 90° are observed for the angles N(1)–Cu–N(2) [79.66(10)°] and N(2)–Cu–N(3) [79.52(10)°] because of the constrained geometry of the co-ordinated terpyridyl group. The terpy ligand in **2** is more planar than in the related (a) unit in **1** as indicated by the smaller dihedral angles between outer and central pyridine rings [6.9 and 5.2° in **2** and 8.1 and 5.5° in **1** (a)]. The oxalate anion is co-ordinated to the copper atom in an asymmetrical bidentate fashion. It is essentially planar, but the metal ion lies 0.244 Å out of its plane. Carbon–oxygen bond lengths in the C(16) moiety are practically identical [1.247(4) and 1.250(4) Å] whereas they are unequal in the C(17) moiety [1.294(4) and 1.218(4) Å for C(17)–O(2) and C(17)–O(3), respectively]. The strong co-ordination of oxalate to copper through O(2) and its weak co-ordination through O(1) are at the origin of this structural feature. The C(16)–C(17) bond length [1.543(5) Å] is equal to the classical value (1.54 Å) and in accord with previously reported values for neutral oxalates.

The lattice water molecules display hydrogen bonding to each other and to the unco-ordinated and one co-ordinated oxalate-oxygen atoms as well as to the weakly co-ordinated water molecule. The shortest copper–copper separation is 7.242(1) Å.

Infrared Spectra.—The most relevant feature of the IR spectra of complexes **1** and **2** concerns the carbon–oxygen stretching frequencies of the oxalato group because they can be diagnostic of the occurrence of asymmetrical bis(bidentate) (complex **1**) and bidentate (complex **2**) co-ordination modes of the oxalate ligand. The ν_{asym}(OCO) and ν_{sym}(OCO) bands for

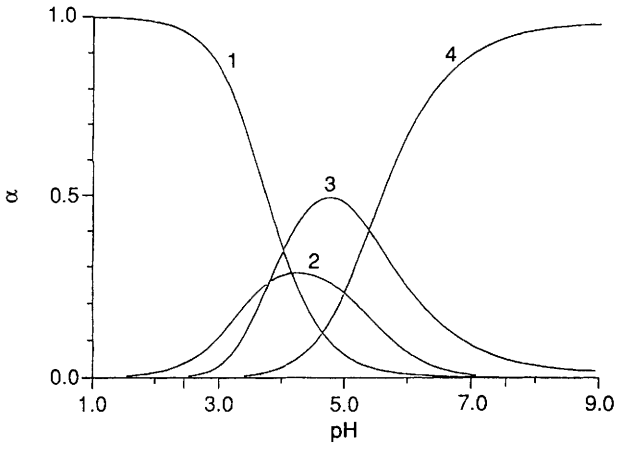

Fig. 4 Distribution diagram of α *vs.* pH for dmso solutions of $[Cu(terpy)]^{2+}$ and oxalic acid. Species: 1, $[Cu(terpy)]^{2+}$; 2, $[Cu(terpy)(Hox)]^{+}$; 3, $[\{Cu(terpy)\}_2(ox)]^{2+}$; and 4, [Cu(terpy)(ox)], respectively. Molar fractions are referred to total $[Cu(terpy)]^{2+}$ ($c_M = c_L = 10^{-2}$ mol dm^{-3})

complex **1** are found as doublets at 1640s and 1600s cm^{-1} for the former and at 1335m and 1305m for the latter; the δ(OCO) vibration is located at 780 cm^{-1} as a sharp and strong band. However, for complex **2** only single absorption peaks are observed for ν_{asym}(OCO) and ν_{sym}(OCO) at 1605s(br) and 1315s cm^{-1} respectively, whereas the δ(OCO) vibration again appears as a sharp and strong band at 785 cm^{-1}. The differences observed between the antisymmetric and symmetric (O–C–O) stretching bands of oxalate in complexes **1** and **2** are clearly attributable to its different co-ordinating role as illustrated by the above-described structures. A continuous absorption at 3600–3200 cm^{-1} in the IR spectra of both compounds is due to the simultaneous presence of aqua ligand and lattice water, and the bands of co-ordinated terpy appear at 3060–3030w, 1580(sh), 1565(sh), 1500m, 1475m, 1450m, 1405m, 1260m, 1165m, 1050w, 1035w, 1025m, 835w and 735m cm^{-1}. The slight splitting of the ν_3 (1100 cm^{-1}) and ν_4 (630 cm^{-1}) perchlorate bands in the spectrum of complex **1** is consistemt with the presence of weakly co-ordinated perchlorate anions[23] as evidenced by the existence of a distance shorter than 3 Å between Ow(1a) and O(4p2).

Solution Study.—The difficulties associated with potentiometric investigations of oxalato complexes in aqueous solution can be overcome by using dmso as solvent.[8–10] The acid strength of H_2ox in water contrasts with its weak acidity in dmso and a satisfactory response of the glass electrode towards hydrogen-ion concentration is also obtained in this latter solvent. Electromotive force data from potentiometric titrations of several $[Cu(terpy)]^{2+}$ and H_2ox mixtures in dmso (see Experimental section) which were performed in the pH range 3.3–5.7 were processed by the program SUPERQUAD. The data analysis allowed us to determine the equilibrium constants of equations (1)–(3): log β_{111} = 12.397(4), log β_{110} = 7.394(2)

$$[Cu(terpy)]^{2+} + ox^{2-} + H^{+} \overset{\beta_{111}}{\rightleftharpoons} [Cu(terpy)(Hox)]^{+} \quad (1)$$

$$[Cu(terpy)]^{2+} + ox^{2-} \overset{\beta_{110}}{\rightleftharpoons} [Cu(terpy)(ox)] \quad (2)$$

$$2[Cu(terpy)]^{2+} + ox^{2-} \overset{\beta_{210}}{\rightleftharpoons} [\{Cu(terpy)\}_2(ox)]^{2+} \quad (3)$$

and log β_{210} = 10.621(6) (values in parentheses refer to the standard deviation on the last significant digit). Several models involving $[Cu(terpy)]^{2+}$: oxalate molar ratios other than 1:1 and 2:1 as well as the corresponding protonated complexes were tested but all were discarded by the SUPERQUAD computer program and only the above-mentioned species fitted well the experimental data in the pH range investigated. The speciation curves, α *versus* pH, for the $[Cu(terpy)]^{2+}$–ox^{2-} system in dmso solution are depicted in Fig. 4. The formation of the oxalato complexes takes place in the pH range 2.50–7.50, *i.e.* where oxalate is present as H_2ox and Hox^{-}. The neutral mononuclear oxalato species is completely formed at pH ≥ 7.50 whereas the dinuclear one and the mononuclear containing co-ordinated Hox^{-} coexist in the pH range 3.0–7.0. The last two species exhibit formation maxima at pH 4.60 and 4.25, with extent of formation of 50 and 28% respectively.

For Hox^{-} as a ligand, a value of log K_1 = 3.855 is easily computed for equilibrium (4) by combination of equilibrium (1)

$$[Cu(terpy)]^{2+} + Hox^{-} \overset{K_1}{\rightleftharpoons} [Cu(terpy)(Hox)]^{+} \quad (4)$$

and that corresponding to the first proton-association constant of oxalate.[10] This value is about three orders of magnitude smaller than that corresponding to equilibrium (2), and can be understood in the light of the above reported structural data for complex **2**. The value of log β_{110} certainly corresponds to an asymmetrical bidentate co-ordination of oxalate, whereas the small value of log K_1 may be associated with a unidentate co-ordination of monohydrogenoxalate.

Some considerations on the values of the thermodynamic parameters for the bis(chelating) oxalate are also in order. Since the dimerization equilibrium 5 may be written in terms of

$$[Cu(terpy)(ox)] + [Cu(terpy)]^{2+} \overset{K_2}{\rightleftharpoons} [\{Cu(terpy)\}_2(ox)]^{2+} \quad (5)$$

equilibria (2) and (3), K_2 may be expressed as β_{210}/β_{110}, from which a value of log K_2 = 3.227 is calculated. *A priori*, this small value seems anomalous keeping in mind the much greater value for log β_{110} [7.394(2)]. It can be explained in terms of the crystallographic data for complexes **1** and **2**. The co-ordination of oxalate in an asymmetrical bidentate fashion leads to a shortening of the terminal carbon–oxygen distance (average 1.235 in **2** and 1.26 Å in free oxalate[24]). Consequently, the double-bond character of the terminal carbonyl group is reinforced leading to a decrease in the basic character of the carbonyl-oxygen atom. Such a situation is much more accentuated in systems like $[Cu(bipy)]^{2+}$–ox^{2-} (bipy = 2,2′-bipyridine) in which oxalate can act in symmetrical bidentate and bis(bidentate) fashions (log β_{110} and log K_2 being 11.165 and 2.02 respectively).[9]

We would like to complete this discussion with some comments on the known values of solution (dmso) and solid-state data for $Cu^{II}L$–oxalate complexes in order to correlate the co-ordination modes of oxalate with the values of the corresponding stability constants (Table 6). It can be seen that the values of log β_{110} and log β_{210} for L = bipy are greater than the corresponding ones for L = bis(pyridine-2-carbonyl)-amide (bpca) or terpy complexes. This is consistent with the fact that oxalate acts in symmetrical bidentate and bis(bidentate) fashions in the former case, whereas asymmetrical bidentate and bis(bidentate) co-ordination modes are observed in the last two cases according to structural data. The values of the stability constants for each set of *p*, *q* and *r* indices for the oxalato complexes of $[Cu(bpca)]^{+}$ and $[Cu(terpy)]^{2+}$ are similar as expected because identical co-ordination modes of the oxalate are present in each case, the terminal groups being tridentate N-donor ligands which form five-membered chelate rings around the metal ion. However, somewhat greater values are exhibited by the terpyridyl complexes. The π-acceptor character of the terpyridyl ligand[25] which enhances the Lewis-acid character of the metal ion is likely to be at the heart of this trend. Finally, the non-existence of the $[Cu(bipy)(Hox)]^{+}$ complex contrasts with the occurrence of the corresponding species in the other two systems. The availability of two *cis* positions in the

Table 6 Thermodynamic parameters[a] and solid-state data concerning the interaction of oxalic acid and $Cu^{II}L$

	$\log \beta_{pqr}$			
L	$p = q = r = 1$	$p = q = 1, r = 0$	$p = 2, q = 1, r = 0$	Products isolated[b]
bipy		11.165(1)	13.185(5)	$[Cu_2(bipy)_2(H_2O)_2(ox)]X\cdot[Cu(bipy)(ox)]$[c] $[Cu(bipy)(ox)]\cdot nH_2O$ ($n = 2$, chain; $n = 3$, mononuclear)
bpca	12.22(5)	7.0(1)	10.2(1)	$[Cu_2(bpca)_2(ox)]$
terpy	12.397(4)	7.394(2)	10.621(6)	**1** (dinuclear), **2** (mononuclear)

[a] Determined at 25 °C in 0.1 mol dm^{-3} $[NBu_4][ClO_4]$–dmso solution. Subscripts *p,q,r* correspond to $Cu^{II}L$, ox^{2-} and H^+ respectively. [b] Characterized by X-ray diffraction methods. [c] $X = SO_4^{2-}$ or $2NO_3^-$.

equatorial plane of the complex $[Cu(bipy)]^{2+}$ precludes formation of this species because of the high affinity of copper(II) for symmetrical bidentate co-ordination of oxalate.

Acknowledgements

Thanks are due to the Comisión Interministerial de Ciencia y Tecnología (Spain) (Proyecto PB88-0490) for partial financial support. One of us (I. C.) acknowledges the Conselleria de Cultura, Educació i Ciència for a grant. Thanks are also due to the Centro de Cálculo de la Universitat de València for computer facilities.

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Received 24*th October* 1990; *Paper* 0/04805D