Study of the interaction between $[Cu(bipy)]^{2+}$ and oxalate in dimethyl sulfoxide. Crystal structure of $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$

Isabel Castro, Juan Faus, Miguel Julve*, M. Carmen Muñoz**

Departament de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot, València (Spain)

Wladimiro Diaz

Departament de Química Física, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot, València (Spain)

and **Xavier Solans**

Departament de Cristal.lografia, Mineralogía i Dipòsits Minerals, Facultat de Geología de la Universitat de Barcelona, 08028 Barcelona (Spain)

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Abstract

A study of complex formation between $[Cu(bipy)]^{2+}$ and ox^{2-} (bipy and ox^{2-} being 2,2′-bipyridyl and the dianion of oxalic acid), has been carried out by potentiometry in dimethyl sulfoxide solution. The constants of the equilibria $[Cu(bipy)]^{2+}+ox^{2-}\xrightleftharpoons{\beta_{110}}[Cu(bipy)ox]$ and $2[Cu(bipy)]^{2+}+ox^{2-}\xrightleftharpoons{\beta_{210}}[Cu_2(bipy)_2ox]^{2+}$ are $\log\beta_{110}=11.165(1)$ and $\log\beta_{210}=13.185(5)$ at 25 °C and 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate. The high values of these constants are consistent with the symmetrical bidentate and bis-bidentate modes of oxalate in [Cu(bipy)ox] and $[Cu_2(bipy)_2ox]^{2+}$ units, respectively, as shown by X-ray diffraction studies. Well-formed single crystals of $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$ were grown from aqueous solutions and characterized by X-ray diffraction. The system is monoclinic, space group $C2/c$, with $a=22.706(5)$, $b=10.485(3)$, $c=16.172(4)$ Å, $\beta=92.63(3)°$, $V=3846(3)$ $Å^3$, $Z=4$, $D_x=1.670$ g cm^{-3}, $\mu(Mo\ K\alpha)=18.38$ cm^{-1}, $F(000)=1956$ and $T=298$ K. A total of 3214 reflections was collected over the range $2\leqslant\theta\leqslant25°$; of these, 1099 (independent and with $I\geqslant2.5\sigma(I)$ were used in the structural analysis. The final R and R_w residuals were 0.067 and 0.070, respectively. The structure is made up of cationic centrosymmetric $[Cu_2(bipy)_2ox]^{2+}$ dinuclear units, neutral axiosymmetric [Cu(bipy)ox] mononuclear entities and SO_4^{2-} as a counterion. Each copper atom of the dinuclear unit shows a square-pyramidal environment with the two nitrogen atoms of 2,2′-bipyridyl and two oxygen atoms of oxalato bridge building the basal plane and an oxygen atom of a water molecule filling the apical position. The copper atom of the mononuclear unit is bound to two oxygen atoms of oxalate and two nitrogen atoms of 2,2′-bipyridyl forming a four-fold surrounding slightly deviating from planarity. In these complexes, copper coordination is 4+1+1 (dinuclear unit) or 4+2 (mononuclear unit) because of the weak binding of the sulfate group in a bis-monodentate fashion linking alternately dinuclear and mononuclear entities. This is a rare case where the two copper(II) complexes bound to the same ligands, that have been observed in solution, are found in the same compound in the solid state.

Introduction

A lot of work has been devoted to the study of mixed-ligand complexes because of their key role in biological processes [1–3]. Of these, ternary copper(II) complexes are the best studied group. It is well known that complexes containing π-acceptor ligands such as 2,2′-bipyridyl (bipy) often afford very stable ternary species in solution [4]. The π back-bonding from the metal ion to the aromatic amine is at the origin of this stability. Ternary complexes of the copper(II) ion with 2,2′-bipyridyl and 1,10-phenanthroline (phen) ligands and the oxalate (ox) ion exhibit a complex solid state chemistry. A similar polymorphism, which is characterized by marked colour changes, is present in both systems [5, 6].

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*Author to whom correspondence should be addressed.

**Also affiliated to Departamento de Física Aplicada, Universidad Politécnica de València, València, Spain.

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Structural evidence for the polymorphic phases has been obtained by means of spectral and X-ray diffraction studies [5–9]. In the light of these investigations the coordination at copper seems to fall into two classes: the first one corresponds to a N_2O_2 chromophore of one oxalate and one bipy/phen coordinated nearly square planar to the metal ion (axially coordinated water may or may not be present), whereas the second one consists of an axially elongated N_2O_4 chromophore made by one aromatic amine and two catena bridging oxalates.

In spite of the emphasis on the preparation, characterization and solid-state reactivity of the mixed-ligand complexes of oxalate and L (L = bidentate N-donor ligand) with copper(II), only a few constants of formation of complexes between $[CuL]^{2+}$ and oxalate have been determined [4d, 10, 11]. As a part of our thermodynamic studies of the coordination modes of oxalate [12–14], we have investigated the formation of complexes between $[Cu(bipy)]^{2+}$ and oxalic acid in dimethyl sulfoxide (DMSO) solution as well as in the solid state. The formation of the mononuclear [Cu(bipy)ox] and dinuclear $[Cu_2(bipy)_2ox]^{2+}$ species has been observed in solution and the crystal structure of the compound of formula $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$, in which both complexes coexist, has been solved by X-ray diffraction methods.

Experimental

Reagents

Copper(II) nitrate trihydrate, copper(II) sulfate pentahydrate, oxalic acid dihydrate and 2,2′-bipyridyl were Merck analytical grade reagents and were used as received. 2,2′-Bipyridylcopper(II) nitrate was obtained as a blue powder when mixing concentrated ethanolic solutions of bipy and copper(II) nitrate in a 1:1 molar ratio. The product was filtered off, washed with cold ethanol and ether and stored over silica gel. Carbonate-free solutions of tetra-n-butylammonium hydroxide ($n\text{-}Bu_4NOH$) in DMSO (freshly prepared from BDH reagent; 40% aqueous solution) were used as titrant in the potentiometric study. 0.1 mol dm^{-3} $n\text{-}Bu_4NClO_4$ was used as supporting electrolyte. It was obtained and purified by a previously reported procedure [13].

Preparation of single crystals of $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$

A blue solution was obtained when 0.067 g of Na_2ox (0.5 mmol) dissolved in a minimum amount of water was added to 100 cm^3 of a warm aqueous solution containing 0.249 g of $CuSO_4\cdot5H_2O$ (1 mmol) and 0.156 g of bipy (1 mmol). Four types of crystals were formed by slow evaporation at room temperature: blue plate-like, blue–violet prismatic, blue needle-like and polyhedral dark blue crystals. Analytical data (C, H, N) revealed that the three first correspond to the formulas $[Cu(bipy)ox]\cdot2H_2O$, $[Cu(bipy)(H_2O)ox]\cdot2H_2O$ and $Cu(bipy)SO_4\cdot2H_2O$, respectively. The nature of the last compound, $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$, was elucidated by single crystal X-ray diffraction. This product is obtained in a very low yield and all our attempts to improve it (varying Cu(II):bipy:ox^{2-} molar ratio, concentration of sulfate, temperature) failed. Polycrystalline powdered samples of $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$ complex can be isolated as a dihydrate from a DMSO–H_2O mixture as follows. 0.078 g of bipy (0.5 mmol) dissolved in 5 cm^3 of DMSO was added to a DMSO solution of tetra-n-butylammonium oxalate (1/3 mmol, 10 cm^3). An aqueous solution of 0.124 g of $CuSO_4\cdot5H_2O$ (0.5 mmol, 3 cm^3) was added with slow stirring and a dark blue solid separated in a few minutes. The product is filtered, washed with ethanol and ether and dried over silica gel. Analytical results (C, H, N) indicate that the isolated compound corresponds to the formula $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]\cdot2H_2O$.

Physical measurements

IR spectra were taken on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–225 cm^{-1} spectral range. Potentiometric titrations were performed using the equipment (vessel, buret, stirrer, electrode, pHmeter, microcomputer, etc.) and following the experimental procedure which were fully described elsewhere [13]. The reaction vessel was water-thermostated at 25.0 ± 0.1 °C and the electrode had a Nernstian response over the hydrogen ion concentration range we investigated. pH instead of $-\log[H^+]$ will be used throughout the text. Series of DMSO solutions of 2,2′-bipyridylcopper(II) nitrate and oxalic acid ($C_M = 5.7\text{–}11.4\times10^{-3}$ mol dm^{-3}, $C_L = 6.0\times10^{-3}$ mol dm^{-3}) were titrated with $n\text{-}Bu_4NOH$ in order to investigate the formation of oxalato complexes. The computer program SUPERQUAD [15] was used to process e.m.f. data from each experiment and to calculate the stability constants of the interaction between $[Cu(bipy)]^{2+}$ and ox^{2-}.

X-ray structure determination

A prismatic crystal of approximate dimensions 0.10 × 0.10 × 0.20 mm was selected and mounted on a Philips PW-1100 four-circle diffractometer. A summary of the crystallographic data and structure refinement is given in Table 1. Unit-cell dimensions were determined and refined from least-squares fitting of 15 carefully centered reflections in the range $4 \leqslant \theta \leqslant 12°$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed during data collection. The θ range of data collection was 2–25°, the octants of data collected being $\pm h$, $+k$, $+l$. Intensities were corrected for Lorentz and polarization effects but not for absorption. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from ref. 16.

The structure was solved by direct methods using the MULTAN-84 system of computer programs [17] and refined by full-matrix least-squares methods using the SHELX-76 computer program [18]. Three oxygen atoms of sulfate anion (O(11), O(12) and O(13)) were located in disorder positions, each atom being distributed in three peaks to which an occupancy factor of 0.33 was assigned according to the Fourier map height of the respective peak. Hydrogen atoms could not be located. The remaining atoms were refined anisotropically. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where $w=[\sigma^2|F_o|+0.014|F_o|^2]^{-1}$. Final R and R_w factors were 0.067 and 0.070 for all observed reflections. Maximum and minimum peaks in final difference synthesis were 0.3 and -0.3 eÅ^{-3}, respectively. Max. shift/e.s.d. is 0.3 in U_{11} of O(13′). Final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix are given in Table 2. The molecular plots were drawn using the SCHAKAL program [19]. Bond distances and angles concerning copper surroundings and oxalate in the dinuclear and mononuclear entities are listed in Table 3.

TABLE 1. Crystal and refinement data

Molecular formula	$Cu_3C_{36}H_{28}N_6O_{14}S$
Molecular weight	967.33
a (Å)	22.706(5)
b (Å)	10.485(3)
c (Å)	16.172(4)
β (°)	92.63(3)
V (Å^3)	3846(3)
Z	4
Space group	$C2/c$
D_{calc} (g cm^{-3})	1.670
Radiation	graphite monochromated Mo Kα (λ=0.71069 Å)
Temperature (K)	298
μ (cm^{-1})	18.38
Scan technique	ω-scan
Scan speed (° min^{-1})	1.8
Scan width (°)	0.8
Scan range (°)	$2 \leqslant \theta \leqslant 25$
No. collected reflections	3214
Cutoff observed data	$2.5\sigma(I)$
No. observed reflections	1099
No. refined parameters	294
R[a]	0.067
R_w[b]	0.070

[a] $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 2. Final atomic coordinates for non-hydrogen atoms[a] and equivalent isotropic displacement parameters[b]

Atom[c]	x/a	y/b	z/c	B_{eq} (Å^2)
Cu(d)	0.3046(1)	0.1038(1)	0.0995(2)	3.90(22)
C(1d)	−0.3277(6)	−0.1183(16)	0.2000(22)	3.52(159)
N(2d)	−0.3155(5)	−0.0844(10)	0.1222(18)	4.81(140)
C(3d)	−0.3041(5)	−0.1725(12)	0.0551(14)	2.92(114)
C(4d)	−0.3080(6)	−0.3053(18)	−0.0738(21)	4.66(183)
C(5d)	−0.3213(7)	−0.3340(14)	0.1567(22)	4.86(193)
C(6d)	−0.3314(6)	−0.2451(13)	0.2220(16)	3.84(128)
C(7d)	−0.3408(6)	−0.0107(11)	0.2549(22)	5.83(176)
N(8d)	−0.3283(5)	0.1073(11)	0.2212(13)	2.94(113)
C(9d)	−0.3407(7)	0.2150(16)	0.2658(22)	3.21(182)
C(10d)	−0.3621(9)	0.2115(19)	0.3431(22)	3.77(190)
C(11d)	−0.3734(7)	0.0882(16)	0.3754(19)	6.67(161)
C(12d)	−0.3644(8)	−0.0229(20)	0.3318(21)	5.18(178)
O(wd)	0.6028(3)	0.1489(9)	0.0436(8)	3.87(77)
O(13d)	−0.2749(4)	0.0940(7)	−0.0171(9)	2.63(82)
C(14d)	−0.2492(7)	−0.1963(14)	−0.0306(19)	2.56(165)
O(15d)	−0.2744(5)	0.2819(10)	0.1011(13)	3.52(106)
Cu(m)	0.0000	−0.0107(2)	0.2500(2)	3.65(24)
C(1m)	0.0072(8)	0.2454(12)	0.2046(18)	3.77(271)
N(2m)	0.0169(5)	0.1297(9)	0.1669(19)	2.91(177)
C(3m)	0.0286(10)	0.1105(22)	0.0874(26)	4.09(241)
C(4m)	0.0343(6)	0.2237(14)	0.0381(16)	4.38(134)
C(5m)	0.0286(9)	0.3459(24)	0.0785(30)	8.43(249)
C(6m)	0.0134(8)	0.3555(13)	0.1562(27)	7.10(211)
O(7m)	−0.0220(4)	−0.1454(7)	0.3219(9)	3.58(77)
C(8m)	−0.0133(5)	−0.2531(11)	0.2933(17)	3.94(171)
O(9m)	−0.0252(4)	−0.3549(8)	0.3260(10)	4.90(82)
S(s)	−0.1327(8)	0.0503(15)	0.1089(26)	9.20(192)
O(1s)	−0.1033(4)	0.0256(10)	0.1848(10)	3.15(91)
O(2s)	−0.1277(19)	0.1836(30)	0.0937(35)	0.57(24)
O(2s)′	−0.1429(12)	0.1701(28)	0.0797(31)	1.93(28)
O(2s)″	−0.1107(12)	0.1757(29)	0.0932(30)	1.55(28)
O(3s)	−0.1870(10)	−0.0009(24)	0.1015(33)	2.14(20)
O(3s)′	−0.3050(13)	0.5203(43)	0.3630(37)	1.98(28)
O(3s)″	−0.1908(11)	0.0600(26)	0.1257(38)	1.42(24)
O(4s)	−0.1076(28)	−0.0200(47)	0.0557(46)	1.33(43)
O(4s)′	−0.0948(13)	−0.0132(29)	0.0587(38)	3.77(27)
O(4s)″	−0.1306(16)	−0.0267(43)	0.0422(39)	2.42(35)

[a] e.s.d.s given in parentheses. [b] $B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$. [c] Primed atom denotes disorder position of the noted atom.

Results and discussion

Description of the structure

The structure of the title compound consists of cationic centrosymmetric $[Cu_2(bipy)_2(H_2O)_2ox]^{2+}$ dinuclear units (Fig. 1), neutral axiosymmetric [Cu(bipy)ox] mononuclear entities (Fig. 2) and $SO_4{}^{2-}$ counterions.

TABLE 3. Selected bond distances (Å) and angles (°) for $[Cu_2(bipy)_2(H_2O)_2ox]SO_4\cdot[Cu(bipy)ox]$[a, b]

Dinuclear unit			
Copper environment			
Cu(d)–N(2d)	2.023(12)	Cu(d)–N(8d)	2.064(12)
Cu(d)–O(13d)	2.033(13)	Cu(d)–O(15d)	1.990(13)
Cu(d)–O(wd)	2.301(13)	Cu(d)–O(3s)	2.681(25)
O(wd)–Cu(d)–O(13d)	89.0(8)	O(13d)–Cu(d)–N(2d)	99.6(8)
O(wd)–Cu(d)–O(15d)	96.9(7)	O(13d)–Cu(d)–N(8d)	175.3(8)
O(wd)–Cu(d)–N(2d)	98.9(7)	O(15d)–Cu(d)–N(2d)	163.3(7)
O(wd)–Cu(d)–N(8d)	95.6(7)	O(15d)–Cu(d)–N(8d)	94.3(7)
O(13d)–Cu(d)–O(15d)	86.0(8)	N(2d)–Cu(d)–N(8d)	78.8(7)
Oxalato bridge			
C(14d)–O(13d)	1.245(28)	C(14d)–C(14d)^{i}	1.502(42)
C(14d)–O(15d)^{i}	1.302(28)		
O(13d)–C(14d)–C(14d)^{i}	120.29(25)	Cu(d)–O(13d)–C(14d)	107.33(8)
O(13d)–C(14d)–O(15d)^{i}	121.37(25)	Cu(d)–O(15d)–C(14d)^{i}	107.99(8)
C(14d)^{i}–C(14d)–O(15d)^{i}	117.97(25)		
Mononuclear unit			
Copper environment			
Cu(m)–N(2m)	2.041(22)	Cu(m)–O(1s)	2.555(10)
Cu(m)–O(7m)	1.911(10)		
O(7m)–Cu(m)–O(7m)^{ii}	84.7(4)	O(7m)^{ii}–Cu(m)–O(1s)	96.9(4)
O(7m)–Cu(m)–N(2m)	174.9(6)	N(2m)–Cu(m)–O(1s)	79.5(4)
N(2m)–Cu(m)–O(7m)^{ii}	94.0(6)	N(2m)^{ii}–Cu(m)–O(1s)	88.2(6)
N(2m)–Cu(m)–N(2m)^{ii}	87.7(6)	O(1s)–Cu(m)–O(1s)^{ii}	162.9(4)
O(7m)–Cu(m)–O(1s)	95.8(4)		
Oxalato			
C(8m)–O(7m)	1.240(17)	C(8m)–C(8m)^{ii}	1.551(49)
C(8m)–O(9m)	1.228(18)		
Cu(m)–O(7m)–C(8m)	113.3(14)	O(7m)–C(8m)–C(8m)^{ii}	114.37(25)
O(7m)–C(8m)–O(9m)	126.1(22)	O(9m)–C(8m)–C(8m)^{ii}	119.49(25)

[a] e.s.d.s. are given in parentheses. [b] Symmetry code: (i) $= -x-\frac{1}{2}, \frac{1}{2}-y, -z$; (ii) $= -x, y, \frac{1}{2}-z$.

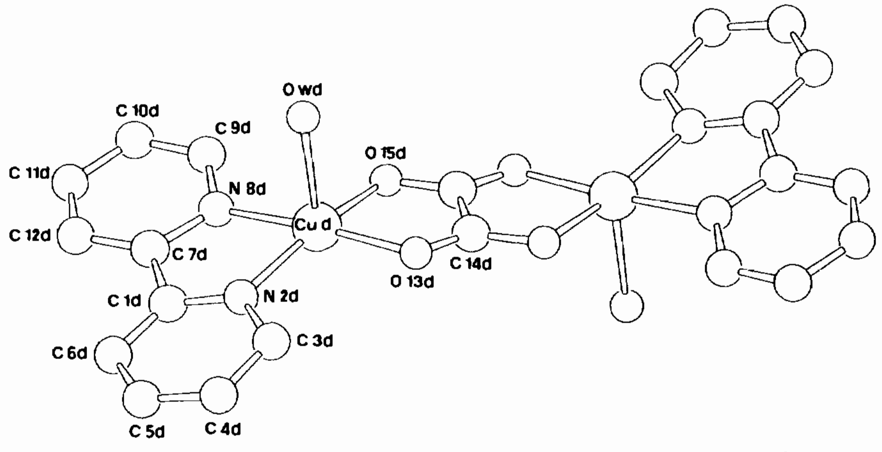

Fig. 1. Perspective view of the cationic centrosymmetric $[Cu_2(bipy)_2(H_2O)_2ox]^{2+}$ dinuclear unit (atoms labelled d in text and tables).

Each copper atom of the dinuclear species (atom labelled d) is in a five coordinate, square-pyramidal environment: the N(2d) and N(8d) nitrogen atoms of the bipyridyl ligand and O(13d) and O(15d) oxygen atoms of the oxalato bridge build the basal plane whereas the O(wd) oxygen atom of a water molecule occupies the apical position. The deviations of N(2d), N(8d), O(13d) and O(15d) atoms from the mean

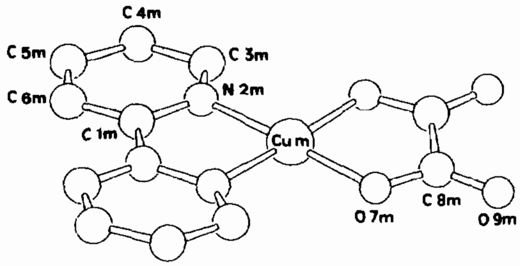

Fig. 2. Perspective view of the neutral axiosymmetric [Cu(bipy)ox] mononuclear entity (atoms labelled m in text and tables).

plane are −0.095, 0.099, 0.090 and −0.094 Å, respectively, and the copper atom is displaced by 0.176 Å from this plane toward the apex. The metal–ligand distances in the equatorial plane range from 1.990(13) to 2.064(12) Å and they are shorter than the apical bond lengths Cu(d)–O(wd) = 2.301(13) Å.

The pyridyl rings of 2,2′-bipyridyl are nearly planar (the largest deviations from the C(1d), N(2d), C(3d), C(4d), C(5d) and C(6d) and C(7d), N(8d), C(9d), C(10d), C(11d) and C(12d) mean planes are 0.009 Å at C(3d) and −0.019 Å at C(9d). The dihedral angle between them is 9.3°. The value of the N(2d)–Cu(d)–N(8d) angle (78.8(7)°) is far from the ideal one of 90° because of the geometry of a bipyridyl ring system. These features are consistent with the previously reported ones for 2,2′-bipyridyl containing copper(II) complexes [7, 20]. The C–C and C–N bond lengths are very close to the reported ones for the non-coordinated 2,2′-bipyridyl [21].

The oxalate anion is essentially planar with the copper atom displaced 0.069 Å from this plane. It bridges in a symmetrical bis-bidentate fashion between two metal centers. The oxalato is situated on a crystallographic center of symmetry, and forms five-membered chelate rings with each of the copper(II) ions. The bite angle at the copper atom of the oxalato ligand is 86.0(8)°. The C–O bond distances range from 1.245(28) to 1.302(28) Å and the length of the C(14d)–C(14d)^{i} bond (1.502(42) Å) is typical of a single C–C bond. Such values are close to the reported ones for other μ-oxalatocopper(II) complexes in which the oxalato bridges in a symmetrical bis-bidentate fashion [20d, 22]. The Cu(d)...Cu(d)^{i} separation through the oxalato bridge is 5.162 Å whereas the shortest intermolecular Cu(d)...Cu(d) distance is 10.315 Å.

As far as the mononuclear species is concerned (atoms labelled m), the Cu(m) atom is in a slightly tetrahedraly distorted square environment formed by two 2,2′-bipyridyl nitrogen atoms and two oxalate oxygen atoms. The deviations of O(7m), O(7m)^{ii}, N(2m) and N(2m)^{ii} atoms from the mean basal plane are −0.087, 0.087, −0.079 and 0.079 Å, respectively, the Cu(m) atom belonging to this plane. The bite angles at the copper atom are normal: 87.7(6) and 84.7(4)° for bipy and oxalate ligands, respectively.

The pyridyl rings of 2,2′-bipyridyl are nearly planar as observed in the previously described dinuclear unit. However, the dihedral angle between them is somewhat smaller (5.4 versus 9.3°). At this point it deserves to be noted that dihedral angles of up to 11° were previously observed for the coordinated bipy ligand [7, 20]. There are no unusual lengths and angles in the bipy ligand.

The oxalate group is practically planar (the largest deviation being −0.022 Å at O(9m)). The dihedral angle between the oxalato plane and the one comprising N(2m), N(2m)^{ii}, O(7m) and O(7m)^{ii} atoms is 4.7° whereas the corresponding one in the dinuclear unit is 10.3° illustrating thus the greater planarity of the Cu(bipy)ox skeleton in the mononuclear unit.

The average C–O bond distances of the oxalate ligand in the mononuclear and dinuclear entities are 1.234 and 1.274 Å, respectively in agreement with its bidentate and bis-bidentate chelating character. The corresponding C–O value observed in the free ligand [23] lies within this range (1.258 Å mean).

The sulfate dianion is weakly coordinated to both species in a bis-unidentate fashion (Cu(d)–O(3s) and Cu(m)–O(1s) distances are 2.681(25) and 2.555(10) Å, respectively) achieving copper coordinations of 5+1 for the dinuclear species and 4+2 for the mononuclear one. This feature leads to a one-dimensional arrangement of mononuclear and dinuclear copper(II)–2,2′-bipyridyl–oxalate units in an alternate fashion through the sulfato bridge. A stereoview of the cell is depicted in Fig. 3 to illustrate such an arrangement. This rare situation in which mononuclear and dinuclear copper(II) units containing the same ligands are present in a single crystal was observed by some of us when using nitrate instead of sulfate [20d]. The same situation has been achieved recently by using tetrafluoroborate or perchlorate as copper(II) salts in a study of the influence of the counterion on the resulting structure and consequently on the magnetic properties [24]. As far as we are aware, for copper(II) only chloro complexes were reported with such a structural property [25].

Infrared spectrum

The carbon–oxygen stretching frequencies of the oxalato group in the IR spectrum of the title complex can serve as a diagnostic of the presence of both bidentate and bis-bidentate oxalato. So, the 1720, 1670 and 1650 cm^{-1} (ν_{as}(CO)), 1415 and 1280 cm^{-1} (ν_s(CO)) and 780 cm^{-1} (δ(OCO)) bands are attributed to bidentate oxalato [26, 8] whereas the

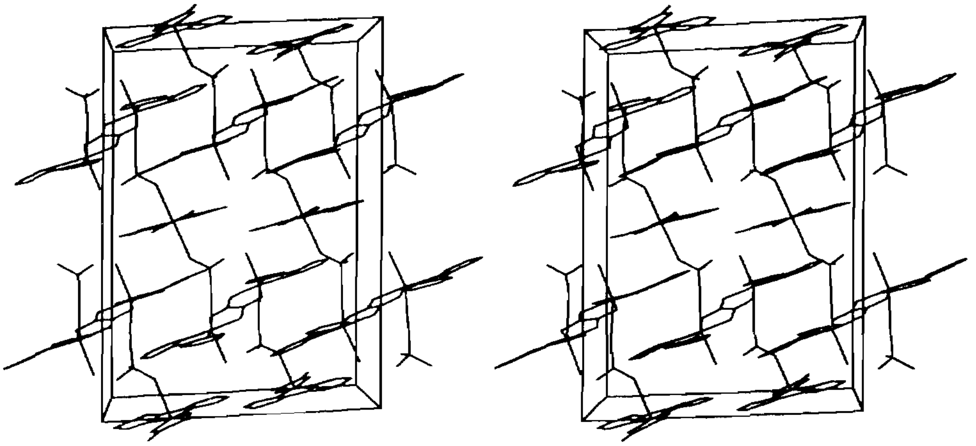

Fig. 3. Stereoscopic view down the *b* axis (*a* axis is vertical) of the molecular packing in $[Cu_2(bipy)_2(H_2O)_2ox]SO_4 \cdot [Cu(bipy)ox]$.

1645 cm^{-1} (ν_{as}(CO)), 1360 and 1315 cm^{-1} (ν_s(CO)) and 800 cm^{-1} (δ(OCO)) features agree with the reported ones for the bis-bidentate oxalato bridge in dinuclear copper(II) complexes [13, 27]. A sharp maximum at 3600 cm^{-1} can be assigned to the OH stretch of the aqua ligand. Sharp bands of medium intensity located at 1610, 1480 and 1450 cm^{-1} correspond to the C–C and C–N ring vibrations of coordinated 2,2′-bipyridyl [28]. These features are observed at higher frequencies for free 2,2′-bipyridyl. In the far infrared region new bands due to Cu–O and Cu–N stretching vibrations are clearly detectable. The symmetry lowering of the sulfate anion from T_d to C_{2v} because of its weak bis-unidentate coordination is evidenced by the splitting of ν_3 (1170–1040 cm^{-1}) and ν_4 (580–530 cm^{-1}) into three bands together with the occurrence of ν_1 (990 cm^{-1}) and ν_2 (460 cm^{-1}) [29].

Solution study

Potentiometric investigations of oxalato complexes in aqueous solution are difficult because oxalic acid behaves as a strong acid for the first dissociation and moderately strong for the second. The low accuracy of its acidity constants [30] together with the fact that deprotonation equilibria and complex formation take place in the same pH range precludes the determination of accurate values of stability constants. However, in contrast to water, DMSO is ideal as solvent to investigate the formation of complexes between oxalate and transition metal ions because in such a non-aqueous solvent oxalic acid behaves as a weak acid [14]. Classical potentiometry can be used to carry out these studies because of the satisfactory response of the glass electrode towards hydrogen ion concentration in DMSO. E.m.f. data from potentiometric titrations of several $[Cu(bipy)]^{2+}$ and H_2ox mixtures in DMSO (see 'Experimental') which were carried out in the 2.0–4.5 pH range were processed by SUPERQUAD. So, the constants of the equilibria (eqns. (1), (2)) were

$$[Cu(bipy)]^{2+} + ox^{2-} \overset{\beta_{110}}{\rightleftharpoons} [Cu(bipy)ox] \qquad (1)$$

$$2[Cu(bipy)]^{2+} + ox^{2-} \overset{\beta_{210}}{\rightleftharpoons} [Cu_2(bipy)_2ox]^{2+} \qquad (2)$$

determined: $\log \beta_{110} = 11.165(1)$ and $\log \beta_{210} = 13.185(5)$. Several models involving hydrogeno-oxalato complexes as well as 1:2 copper:oxalato species were ruled out by SUPERQUAD in the process of refinement and only the two above mentioned copper(II) complexes fitted well the experimental data in the pH range investigated. The speciation curves, α versus pH, for the $[Cu(bipy)]^{2+}$:ox^{2-} system are shown in Fig. 4. The formation of the 1:1 and 2:1 (copper(II):oxalate) complexes occurs at pH $\leqslant$ 4.3,

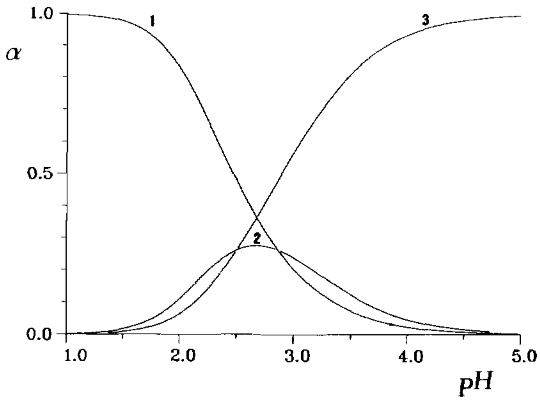

Fig. 4. Distribution diagram α vs. pH for DMSO solutions of $[Cu(bipy)]^{2+}$ and oxalic acid. 1, 2 and 3 correspond to $[Cu(bipy)]^{2+}$, $[Cu_2(bipy)_2ox]^{2+}$ and [Cu(bipy)ox], respectively. Molar fractions are referred to total $[Cu(bipy)]^{2+}$ ($C_M = C_L = 10^{-2}$ mol dm^{-3}).

i.e. in the pH range where oxalate is present as oxalic acid. The mononuclear oxalato species is completely formed at pH = 4 whereas the maximum degree of formation of the dinuclear one is 28% at pH = 2.7. We have not observed the coordination of Hox^- in our experimental conditions. Although examples of coordination of Hox^- have been reported both in solution [13] and in the solid state [31] this coordination mode is rare. In a recent work aimed at characterizing thermodynamically the coordination modes of oxalate [13], we have observed for the first time the coordination of Hox^- as an unidentate ligand. A value of $\log K = 3.94$ was found for eqn. (3)

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + Hox^- \xrightleftharpoons{K} [Cu\{(NC_5H_4CO)_2N\}(Hox)] \quad (3)$$

where $(NC_5H_4CO)_2N^-$ is the bis(2-pyridylcarbonyl)amido ligand. This value is much more smaller than the corresponding one for the formation of the parent $[Cu\{(NC_5H_4CO)_2N\}ox]^-$ complex ($\log \beta_{110} = 7.0(1)$) (eqn. (4)) which in the light of the

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + ox^{2-} \xrightleftharpoons{\beta_{110}} [Cu\{(NC_5H_4CO)_2\}ox]^- \quad (4)$$

structural data of the related dinuclear $Cu_2\{(NC_5H_4CO)_2N\}_2ox]$ species should involve an asymmetrical bidentate oxalato. The three nitrogen atoms of such a tridentate N-donor ligand occupy three of the four equatorial sites of the complex $[Cu\{(NC_5H_4CO)_2N\}]^+$ [32] precluding the symmetrical bidentate coordination of oxalato to copper(II) because of the Jahn–Teller effect. This fact together with the weak acidity of Hox^- favours the formation of the species $[Cu\{(NC_5H_4CO)_2N\}(Hox)]$. The inexistence of analogous species in the Cu(II):bipy system is easily understood taking into account the availability of two *cis*-positions in the equatorial plane of the complex $[Cu(bipy)]^{2+}$.

A comparison of the values of β_{110} for [Cu(bipy)ox] (eqn. (1)) and $[Cu\{(NC_5H_4CO)_2N\}ox]^-$ (eqn. (4)) (11.165(1) and 7.0(1), respectively) illustrates the higher stability of the copper(II)–oxalato complexes in which the oxalate acts in a symmetrical bidentate fashion versus those in which it coordinates as an asymmetrical bidentate ligand. To our knowledge it is the first time that such a comparison has been made in the light of both solution and solid state data of the concerned systems.

Let us comment now on the well known bis-bidentate coordination mode of oxalate. A value of $\log K = 2.02$ is deduced for eqn. (5) by combining eqns. (1) and (2).

$$[Cu(bipy)ox] + [Cu(bipy)]^{2+} \xrightleftharpoons{K} [Cu_2(bipy)_2ox]^{2+} \quad (5)$$

At first sight, such a value seems anomalous taking into account that the value of $\log \beta_{110}$ (11.165(1)) is much greater. This surprising result can be explained in terms of the above reported structural data for the [Cu(bipy)ox] and $[Cu_2(bipy)_2ox]^{2+}$ units. The coordination of oxalate as a bidentate ligand leads to a shortening of the terminal carbon–oxygen distance (C–O values of 1.23 Å in [Cu(bipy)ox] and 1.26 Å in the free oxalate). The double bond character of the terminal carbonyl group is reinforced and consequently the basic character of such a carbonyl oxygen atom decreases. On the other hand, the coordination of oxalate as a bis-bidentate bridge induces a significant lengthening of the Cu–O(oxalate) bond distance (2.01 Å mean value in the dinuclear unit and 1.91 Å in the mononuclear one). So, the strong binding of oxalate to copper as a bidentate ligand undergoes an important decrease of chelating ability of the resulting complex ligand. However, when comparing the values of $\log \beta_{210}$ for $[Cu(bipy)]^{2+}:ox^{2-}$ (13.185(5), eqn. (2)) and $[Cu\{(NC_5H_4CO)_2N\}]^+:ox^{2-}$ (10.2(1), eqn. (6))

$$2[Cu\{(NC_5H_4CO)_2N\}]^+ + ox^{2-} \rightleftharpoons [Cu_2\{(NC_5H_4CO)_2N\}_2ox] \quad (6)$$

a greater stability of the former is observed as expected due to the presence of symmetrical and asymmetrical oxalato bridges, respectively. This trend is also extensive to other oxalato containing copper(II) systems. So, the value of $\log \beta_{210}$ for the $[Cu(terpy)]^{2+}:ox^{2-}$ system (10.621(5)) [33], where terpy is 2,2′:6′,2″-terpiridyl, is somewhat smaller than the one of the related system with bipy.

Supplementary material

Tables of thermal parameters, non-essential bond distances and angles and mean planes (6 pp.) as well as a listing of observed and calculated structure factors (5 pp.) are available from the authors on request.

Acknowledgements

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References

1 (a) H. Sigel, *Angew. Chem., Int. Ed. Engl., 14* (1975) 394; (b) R. B. Martin and R. Prados, *J. Inorg. Nucl. Chem., 36* (1974) 1665; (c) R. F. Bauer and W. M. Smith, *Can. J. Chem., 43* (1965) 2755.

2 H. Sigel and R. B. Martin, *Chem. Rev., 82* (1982) 385.

3 R. Tribolet, R. B. Martin and H. Sigel, *Inorg. Chem., 26* (1987) 638, and refs. therein.

4 (a) H. Sigel, *Inorg. Chem., 19* (1980) 1413; (b) H. Sigel, P. R. Huber, R. Griesser and B. Prijs, *Inorg. Chem., 12* (1973) 1198; (c) R. Griesser and H. Sigel, *Inorg. Chem., 10* (1971) 2229; (d) H. Sigel, P. R. Huber and R. F. Pasternack, *Inorg. Chem., 10* (1971) 2226.

5 (a) P. O'Brien, *Transition Met. Chem., 5* (1980) 314; (b) P. O'Brien, *J. Chem. Soc., Dalton Trans.,* (1981) 1540.

6 P. O'Brien, C. Stafford and Lee Cheng Young, *Inorg. Chim. Acta, 147* (1988) 3.

7 W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. Hathaway and P. O'Brien, *J. Chem. Soc., Dalton Trans.,* (1982) 1117.

8 A. C. Fabretti, G. Franchini, P. Zanini and M. Divaira, *Inorg. Chim. Acta, 105* (1985) 187.

9 (a) W.-L. Kwik, K.-P. Ang, H. S.-O. Chan, V. Chevolu and S. A. Koch, *J. Chem. Soc., Dalton Trans.,* (1986) 2519; (b) S. Musumeci, E. Rizzarell, S. Sammartano and A. Seminara, *Z. Anorg. Allg. Chem., 433* (1977) 297; (c) W.-L. Kwik and K.-P. Ang, *Aust. J. Chem., 31* (1978) 459; (d) K. Stone, S. Utsuno and T. Ogura, *J. Inorg. Nucl. Chem., 31* (1969) 117.

10 (a) R. D. Witt and J. I. Watters, *J. Am. Chem. Soc., 76* (1954) 3810; (b) J. I. Watters, *J. Am. Chem. Soc., 81* (1959) 1560; (c) W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc., 83* (1961) 4699.

11 I. Castro, J. Faus and M. Julve, *Transition Met. Chem., 13* (1988) 455.

12 F. Lloret, M. Julve, M. Mollar, I. Castro, J. Latorre, J. Faus, X. Solans and I. Morgenstern-Badarau, *J. Chem. Soc., Dalton Trans.,* (1989) 728.

13 I. Castro, J. Faus, M. Julve, M. Mollar, A. Monge and E. Gutiérrez-Puebla, *Inorg. Chim. Acta, 161* (1989) 97.

14 M. Mollar, I. Castro, F. Lloret, M. Julve, J. Faus and J. Latorre, *Transition Met. Chem.,* in press.

15 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.,* (1985) 1195.

16 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974, pp. 99–100, 149.

17 P. Main, J. S. Fiske, S. L. Hull, L. Lessinger, G. Germain, S. P. Declercq and M. M. Woollfson, *MULTAN,* an automatic system of computer programs for crystal structure determination from X-ray diffraction data, Universities of York, U.K., and Louvain, Belgium, 1984.

18 G. M. Sheldrick, *SHELX,* a computer program for crystal structure determination, University of Cambridge, U.K., 1976.

19 E. Keller, *SCHAKAL,* a FORTRAN program for the graphic representation of molecular and crystallographic models, University of Freiburg, F.R.G., 1987.

20 (a) B. J. Hathaway, N. Ray, D. Kennedy, N.O'Brien and B. Murphy, *Acta Crystallogr., Sect. B, 36* (1980) 1371 and refs. therein; (b) J. Sletten, *Acta Chem. Scand., Ser. A, 36* (1982) 345; (c) I. Castro, J. Faus, M. Julve, M. Verdaguer, A. Monge and E. Gutiérrez-Puebla, *Inorg. Chim. Acta, 170* (1990) 251, and refs. therein; (d) M. Julve, J. Faus, M. Verdaguer and A. Gleizes, *J. Am. Chem. Soc., 106* (1984) 8306; (e) J. Sletten, A. Sørensen, M. Julve and Y. Journaux, *Inorg. Chem.,* in press.

21 L. L. Merrit and E. D. Schroeder, *Acta Crystallogr., 9* (1956) 801.

22 (a) M. Julve, M. Verdaguer, O. Kahn, A. Gleizes and M. Philoche-Levisalles, *Inorg. Chem., 22* (1983) 368; (b) *23* (1984) 3808; (c) J. Sletten, *Acta Chem. Scand., Ser. A, 37* (1983) 569; (d) A. Bencini, A. C. Fabretti, C. Zanchini and P. Zanini, *Inorg. Chem., 26* (1987) 1445; (e) M. Julve, M. Verdaguer, A. Gleizes, O. Kahn and A. Dworkin, manuscript in preparation.

23 F. S. Stephens, *J. Chem. Soc. A,* (1969) 2493.

24 A. Gleizes, M. Julve, M. Verdaguer, J. A. Real, J. Faus, X. Solans and J. Borrás, manuscript in preparation.

25 R. M. Caly, P. Murray-Rust and J. Murray-Rust, *J. Chem. Soc., Dalton Trans.,* (1973) 595.

26 J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys., 36* (1962) 324, and refs. therein.

27 (a) N. F. Curtis, *J. Chem. Soc. A,* (1968) 1584; (b) K. Nonoyama, H. Ojima, K. Ohki and M. Nonoyama, *Inorg. Chim. Acta, 41* (1980) 155; (c) A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, A. C. Fabretti and G. C. Franchini, *Inorg. Chim. Acta, 86* (1984) 169.

28 A. R. Kratritzky, *Q. Rev. (London), 13* (1959) 353.

29 B. J. Hathaway, in G. Wilkinson, J. McCleverty and R. D. Gillard (eds.), *Comprehensive Coordination Chemistry,* Vol. 2, Pergamon, Oxford, 1987, p. 413.

30 A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vol. III, Plenum, New York, 1977, p. 92.

31 (a) A. C. Villa, A. G. Manfredotti, A. Giacomelli, C. Guastini and A. Indelli, *Inorg. Chem., 14* (1975) 1654; (b) G. M. Miskelly, C. R. Clark, J. Simpson and D. A. Buckingham, *Inorg. Chem., 22* (1983) 3237; (c) J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc., Dalton Trans.,* (1988) 1725.

32 I. Castro, J. Faus, M. Julve, J. M. Amigó, J. Sletten and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.,* (1990) 891.

33 I. Castro, J. Faus, M. Julve and A. Gleizes, manuscript in preparation.