Formation in Solution, Synthesis and Crystal Structure of μ-Oxalatobis[bis(2-pyridylcarbonyl)amido]dicopper(II)

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Abstract

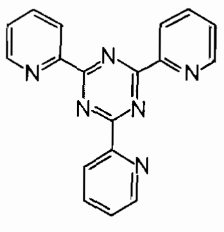
The compound μ-oxalatobis[bis(2-pyridylcarbonyl)amido]dicopper(II), $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$ was synthesized and characterized by spectroscopy, EPR and diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$ with cell constants: $a = 7.6793(6)$, $b = 9.238(2)$, $c = 10.007(2)$ Å, $\alpha = 83.80(1)$, $\beta = 68.37(1)$ and $\gamma = 69.44(1)°$; $V = 617.7(3)$ Å^3, D (calc., $Z = 2$) = 1.80 g cm^{-3}, $M_r = 667.6$, $F(000) = 336$, λ (Mo Kα) = 0.71069 Å, μ (Mo Kα) = 17.895 cm^{-1} and $T = 295$ K. A total of 3587 data were collected over the range of $1 \leqslant \theta \leqslant 30°$; of these, 2391 (independent and with $I \geqslant 2\sigma(I)$) were used in the structural analysis. The final R and R_w residuals were 0.049 and 0.053, respectively.

The structure consists of neutral centrosymmetrical binuclear entities in which $C_2O_4^{2-}$ acts in an asymmetrically bis-bidentate fashion. Each copper atom is in a square-pyramidal environment with the three nitrogen atoms of bis(2-pyridylcarbonyl)amido anion and an oxygen atom of oxalate in the basal plane and another oxygen atom of oxalate occupying the apical position.

The stability constants of the oxalato complexes of bis(2-pyridylcarbonyl)amidocopper(II) have been determined in dimethyl sulphoxide solution: $\log\beta_{111} = 12.22 \pm 0.05$, $\log\beta_{110} = 7.0 \pm 0.1$ and $\log\beta_{210} = 10.2 \pm 0.1$ at 25 °C and 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate. Coordination modes of oxalate for this system are compared in DMSO and water in the light of thermodynamic and structural parameters.

Introduction

Some years ago, Lerner and Lippard [1, 2] reported an interesting copper(II)-assisted hydrolytic reaction of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) (Scheme 1) and the chemically similar 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpmtz). Copper(II) promotes the hydrolysis of these triazines yielding the [bis(arylcarbonyl)amido]copper(II) complexes and free 2-picolinamide (2-pyridylformamide). Very recently, some of us [3] have isolated and characterized by single-crystal X-ray diffraction methods the complexes $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]ClO_4 \cdot H_2O$ and $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ which are the products of the reaction of tptz with copper(II) perchlorate. The most relevant feature of the structure of the former compound is that it contains bis(2-pyridylcarbonyl)amido anion and 2-picolinamide as ligands enabling us to elucidate directly the nature of the two major products of the hydrolytic reaction. On the other hand, the structure of the latter compound has allowed the bis-chelating character of the bis(2-pyridylcarbonyl)amido ligand to be established for the first time. Kinetic and thermodynamic data [4, 5] have shown that the hydrolytic reaction to yield the carboximidate ligand probably occurs via nucleophilic attack at the triazine ring by OH^- or H_2O.



TPTZ

Scheme 1.

As a part of our study on the preparation and characterization of polynuclear compounds of Cu(II) with bis-bidentate C_2XYZW bridges (Scheme 2) such as oxalato (X = Y = Z = W = O) [6], oxamato (X = Y = Z = O; W = N) [7], oxamido (X = W = N;

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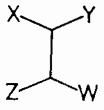

Scheme 2.

Y = Z = O) [7] and 2,2'-bipyrimidine (X = Y = Z = W = N) [8], we have investigated the formation of complexes between the mononuclear complex $[Cu\{(NC_5H_4CO)_2N\}]^+$ and oxalate in solution as well as in the solid state. The present paper deals with the formation in dimethyl sulphoxide (DMSO) solution of the binuclear complex $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$ and the mononuclear ones $[Cu\{(NC_5H_4CO)_2N\}(HC_2O_4)]$ and $[Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]$ which contain bis-bidentate, unidentate and bidentate oxalato respectively. The structure of the binuclear compound is also reported herein together with its electronic and vibrational properties. A similar study has been carried out in aqueous solution for comparison.

Experimental

Reagents

Copper(II) nitrate trihydrate, oxalic acid dihydrate, 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (tptz) and DMSO were Merck analytical grade reagents and were used without further purification. Bis(2-pyridylcarbonyl)amidocopper(II) nitrate tetrahydrate was prepared by a reported procedure [1, 2]. Carbonate-free solutions of tetra-n-butyl-ammonium hydroxide (n-Bu_4NOH) in DMSO, freshly prepared from BDH reagent (40% aqueous solution) were used as titrant in the potentiometry study. Potentiometric measurements were carried out in 0.1 mol dm^{-3} n-Bu_4NClO_4 as ionic medium. n-Bu_4NClO_4 was obtained as a white powder by neutralization of aqueous solutions of n-Bu_4NOH with perchloric acid. It was recrystallized twice from ethanol and dried under vacuum over P_2O_5.

Preparation of $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$

A green suspension was obtained by mixing 0.242 g of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol) and 0.313 g of tptz (1 mmol) in 150 cm^3 of water. Heating at 100 °C with stirring for half an hour yielded a dark blue solution of bis(2-pyridylcarbonyl)amidocopper(II) nitrate. An aqueous solution (10 cm^3) of 0.067 g of $Na_2C_2O_4$ (0.5 mmol) was added, dropwise, at room temperature and a crystalline blue powder of the title compound separated at the end of the addition. The product was filtered off and blue–violet prismatic crystals of the binuclear complex were obtained by slow evaporation of solvent at room temperature. *Anal.* Calc. for $C_{26}H_{16}Cu_2N_6O_8$: C, 46.80; H, 2.40; N, 12.60. Found: C, 46.86; H, 2.60; N, 12.39%.

Physical Measurements

IR spectrum was taken on a Pye Unicam SP 200 spectrometer as KBr pellets in the 4000–200 cm^{-1} spectral range. The electronic spectrum of the solid compound was recorded as nujol mull on filter paper with a UV-V-NIR Perkin-Elmer Lambda 9 spectrophotometer. Polycrystalline powder EPR spectra were recorded at X-band frequency on a Brüker ER 200D spectrometer at room and liquid nitrogen temperatures.

Potentiometric titrations were carried out using a reaction vessel (capacity 70 cm^3) water-thermostated at 25.0 ± 0.1 °C. The titrant was delivered by a Crison-738 burette. A Radiometer PHM 84 pH-mV meter and a 9811 Ingold combined glass electrode were used to perform the potentiometric measurements. The saturated aqueous KCl solution of the reference electrode was replaced with a saturated methanolic KCl one [9]. The electrode was dipped in DMSO for two days before use. Nernst's equation $E = E^{\circ\prime} + 0.0591 \log[H^+]$, was strictly obeyed, at least over the hydrogen ion concentration range we have investigated. As a matter of convenience, pH instead of $-\log[H^+]$ will be used throughout the text. The titration system was controlled by an Apple IIe microcomputer. A BASIC program [10] was used to monitor for each titration point, the e.m.f. values and the volume of titrant added. When the observed e.m.f. value was constant, within user-defined limits, the next volume of titrant was added automatically and the cycle repeated until the predefined total volume of titrant had been added. The computer program SUPERQUAD [11] was used to process data from each experiment and calculate the stability constants of the interaction between bis(2-pyridylcarbonyl)amidocopper(II) and oxalic acid. Average values from three different experiments are given. The estimated values of the errors in the electrode and volume readings, were 0.3 mV and 0.003 cm^3. Accurate concentrations of the basic titrant as well as the $E^{\circ\prime}$ value were determined with toluene-4-sulphonic acid solution in DMSO before each titration series by applying the Gran method. Reliable potential measurements were obtained between five and fifteen minutes after each addition of base solution. The more basic the solution is, the more time is required.

X-ray Data Collection

A prismatic crystal of approximate dimensions 0.30 × 0.30 × 0.40 mm was mounted on a Nonius CAD-4F diffractometer and used for data collection. A summary of the crystallographic data is reported in Table 1. Unit-cell dimensions were determined and refined from least-squares fitting of the setting angles of 25 carefully centered reflections. The crystal became damaged by radiation and intensities were scaled from the variation of three standard

TABLE 1. Crystal and refinement data

Molecular formula	$Cu_2C_{26}H_{16}N_6O_8$
Molecular weight	667.6
a (Å)	7.6793(6)
b (Å)	9.238(2)
c (Å)	10.007(2)
α (°)	83.80(1)
β (°)	68.37(1)
γ (°)	69.44(1)
V (Å^3)	617.7(3)
Z	2
Space group	$P\bar{1}$[a]
D_{calc} (g cm^{-3})	1.80
Radiation	graphite monochromated Mo Kα (λ = 0.71069 Å)
Temperature (°C)	22
μ (cm^{-1})	17.895
Scan technique	$\omega/2\theta$
Scan speed (° m^{-1})	20–1.54
Scan width (°)	0.80 + 0.35 tg θ
Scan range (°)	$1 < \theta < 30$
Total no. independent reflections	3587
Cutoff observed data	$2\sigma(I)$
No. observed reflections	2391
No. refined parameters	190
R[b]	0.049
R_w[c]	0.053

[a] Based on a centric distribution of E values and later confirmed by the structural determination. [b] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [c] $R_w = [\Sigma(|F_o| - |F_c|)^2 / \Sigma(F_o)^2]^{1/2}$ (unit weights).

reflections whose intensities fell to 9% at the end of the data collection. Intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from ref. 12.

Solution and Refinement of the Structure

On the basis of the centric distribution of E values, the $P\bar{1}$ space group was assumed and later confirmed by the successful refinement of the structure. The structure was solved by a three-dimensional Patterson map and Fourier synthesis, which allowed the location of all atoms other than hydrogen. An empirical absorption correction [13] was applied at the end of the isotropic refinement. No trend in ΔF versus F_o or $(\sin \theta)/\lambda$ was observed. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.054$. Final refinement with fixed isotropic temperature factors and coordinates for hydrogen atoms converged at $R = 0.049$ and $R_w = 0.053$. Maximum and average shifts/error were 0.002 and 0.001 respectively. Table 2 reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix.

TABLE 2. Final atomic coordinates[a]

Atom	x/a	y/a	z/a
Cu	0.28245(9)	0.20644(7)	0.22473(7)
O(1)	0.47077(52)	−0.00501(39)	0.18320(37)
O(2)	0.31259(49)	0.17255(38)	−0.00459(36)
C(1)	0.45299(63)	0.05243(50)	−0.05287(49)
O(3A)	0.11005(59)	0.66148(42)	0.30507(47)
N(1A)	0.49128(56)	0.30740(48)	0.17010(43)
C(2A)	0.41545(71)	0.45846(58)	0.20243(50)
C(3A)	0.53057(79)	0.55270(63)	0.17140(58)
C(4A)	0.73513(83)	0.48516(73)	0.10234(66)
C(5A)	0.81436(75)	0.32957(70)	0.06752(63)
C(6A)	0.68993(73)	0.24286(63)	0.10308(59)
C(7A)	0.19021(72)	0.52430(56)	0.27367(52)
O(3B)	−0.21989(55)	0.54996(42)	0.42796(44)
N(1B)	0.03293(60)	0.15558(48)	0.32112(45)
C(2B)	−0.12585(69)	0.28114(55)	0.38602(51)
C(3B)	−0.31282(76)	0.27178(64)	0.45829(59)
C(4B)	−0.33811(83)	0.12930(71)	0.46129(70)
C(5B)	−0.17757(85)	0.00223(65)	0.39245(68)
C(6B)	0.00723(80)	0.01962(59)	0.32422(60)
C(7B)	−0.08714(70)	0.43151(55)	0.37258(51)
N(2)	0.10903(59)	0.41205(46)	0.29473(44)

[a] e.s.d.s given in parentheses.

Most of the calculations were carried out by using XRAY [14]. The molecular plots were produced by the program ORTEP [15].

Results and Discussion

Description of the Structure

The crystal structure of the title compound consists of neutral oxalate-bridged centrosymmetrical copper(II) binuclear units linked by weak van der Waals forces. A perspective view of the binuclear complex is shown in Fig. 1 and bond lengths and angles for the non-hydrogen atoms are listed in Table 3. Each copper atom is in a five coordinate, square-pyramidal environment: the N(1A), N(2) and N(1B) nitrogen atoms of the bis(2-pyridylcarbonyl)amido ligand occupy three of the basal sites whereas the O(1) and O(2) oxygen atoms of oxalate fill the remaining basal and the apical positions respectively. The basal plane, therefore, is comprised of atoms N(1A), N(2), N(1B) and O(1) with the Cu(II) ion only 0.156(1) Å out of this plane. The Cu(II)–ligand distances in the basal plane range from 1.921(4) to 2.009(5) Å and they are shorter than the apical bond length Cu–O(2) = 2.264(4) Å. The angles N(1A)–Cu–N(2) and N(1B)–Cu–N(2) are 82.2(2) and 83.0(2)° respectively. They are smaller than the ideal value of 90° because these angles are part of a five-membered planar chelate ring. The other angles in the chelate ring lie

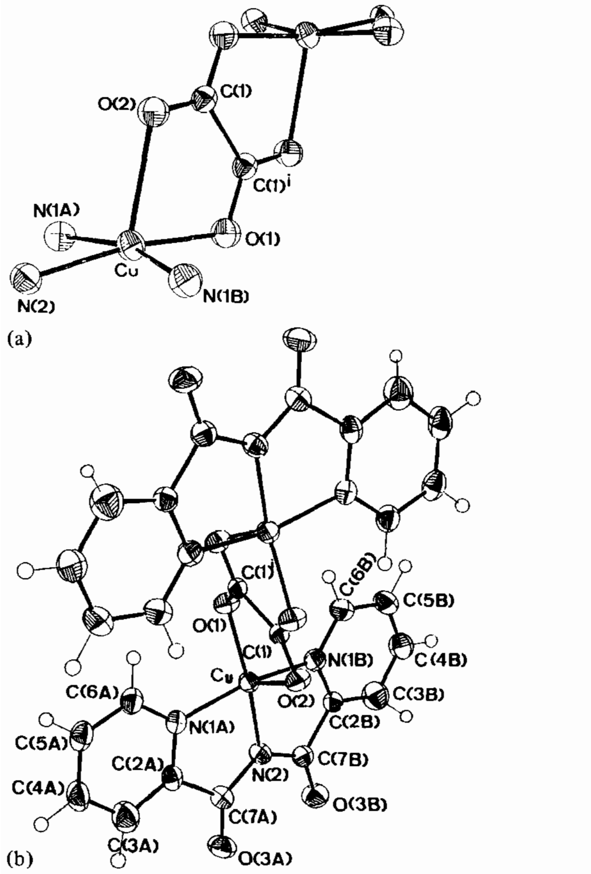

Fig. 1. (a) ORTEP plotting of the inner coordination sphere and oxalato bridge of $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$. (b) ORTEP drawing of $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$ showing the atom labelling scheme with 50% probability ellipsoids.

between 110 and 120° as expected for sp^2-hybridized carbon or nitrogen atoms. Distortion of the angle at the metal atom from 90° is found in related complexes [2, 3, 16, 17].

An approximate mirror plane passes through atoms Cu, O(2), O(1) and N(2) as can be seen by comparing the geometries of the A and B halves of the bis(2-pyridylcarbonyl)amido ligand. The individual pyridine rings show no deviations from planarity greater than 0.009(5) Å. However, the ligand is not planar. The A and B halves show no deviations from planarity greater than 0.019(5) and 0.024(2) Å respectively. The dihedral angle between these two planes is 6.0°, a value which is close to the observed ones for this ligand in other Cu(II) complexes [3, 18].

The average carbon–carbon bond distance within the pyridyl rings and the average intraring carbon–nitrogen bond length are 1.38 and 1.34 Å respectively. These values agree with the reported ones for similar systems [2, 3, 16, 18–20]. The deviation of the angles at the carbonyl–carbon atoms from the expected value of 120° (see Table 3) is caused by the binding of the copper atom. The need for short metal–nitrogen bonds introduces this angular strain. Angular strain is responsible for the copper-promoted hydrolytic reaction of tptz [1–3].

The oxalate dianion is planar. It bridges in an asymmetrical bis-bidentate fashion between two bis(2-pyridylcarbonyl)amidocopper(II) units. The CuC_2O_4Cu network deviates significantly from planarity: the atom-to-plane greater distance is 0.092(4) Å at O(1). The dihedral angle between the mean planes through copper–oxalate and N(1A), N(2), N(1B) and O(1) is 92.0(1)°. The bite angle at the copper atom of the oxalate ligand is 72.3(1)°. Such a value is close to the reported ones for other μ-oxalatocopper(II) complexes in which the oxalato bridges in an asymmetrical bis-bidentate fashion [6, 21a–d]. The Cu···Cu separation through the oxalato bridge inside the binuclear complex is 5.442(1) Å, whereas the shortest intermolecular Cu···Cu distance is 7.493(2) Å.

Infrared, Electronic and EPR Spectra

The IR spectrum of the binuclear compound exhibits absorptions typical of coordinated bis(2-pyridylcarbonyl)amido ligand (3100, 1710, 1600, 1570, 1460, 1440, 1350, 1290, 1250, 1045, 1025, 1000, 820, 760, 700, 650 and 610 cm^{-1}). The sharp intense band located at 1710 cm^{-1} has been assigned to the ν_{as}(CO) vibration of the imide group of this ligand [2]. The ν_{as}(CO) and δ(OCO) bands of the oxalate ligand which are found in the present complex at 1645 and 795 cm^{-1} respectively, agree with the reported ones for the bis-bidentate oxalate bridge in binuclear copper(II) complexes [22a–c]. The ν_{sym}(CO) bands which appear between 1360 and 1300 cm^{-1} are not observed because they are obscured by the strong and broad absorption of the bis(2-pyridylcarbonyl)amido ligand centered at 1350 cm^{-1}. Bands which may be assigned to ν(Cu–O) (490 and 420 cm^{-1}) and ν(Cu–N) (350 cm^{-1}) are clearly detectable in the far infrared region.

Its electronic reflectance spectra consists of a broad band centered at 16 100 cm^{-1} with a shoulder at 12 820 cm^{-1} and a small peak at 23 800 cm^{-1}. This spectra is very similar to that reported for the parent complex [bis(2-pyridylcarbonyl)amido](2-pyridylformamide)copper(II) perchlorate monohydrate [3]. These bands are tentatively assigned as $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz,yz} \rightarrow d_{x^2-y^2}$ electronic transitions respectively according to its square-pyramidal stereochemistry.

The EPR spectrum of a polycrystalline sample of this complex looks like an axial doublet with no hyperfine structure. Features at $g_{\parallel} = 2.23$ and $g_{\perp} = 2.05$ clearly point towards a mainly copper(II) $d_{x^2-y^2}$ orbital ground state as confirmed by its structure. A weak absorption at half field arising

TABLE 3. Bond distances (Å) and angles (°)[a]

Copper environment			
Cu–N(1A)	2.009(5)	Cu–O(1)	1.957(3)
Cu–N(2)	1.921(4)	Cu–O(2)	2.264(4)
Cu–N(1B)	1.997(4)	Cu–Cu^{i}(intra)	5.442(1)
		Cu–Cu^{ii}(inter)	7.493(2)
N(2)–Cu–N(1A)	82.2(2)	N(2)–Cu–N(1B)	83.0(2)
O(2)–Cu–N(1A)	94.8(2)	O(2)–Cu–N(1B)	97.0(2)
O(1)–Cu–N(1A)	95.3(2)	O(1)–Cu–N(1B)	98.2(2)
O(2)–Cu–N(2)	110.4(2)	O(2)–Cu–O(1)	72.3(1)
N(1A)–Cu–N(1B)	163.5(2)	N(2)–Cu–O(1)	170.1(2)
Bis(2-pyridylcarbonyl)amido ligand			
N(1A)–C(2A)	1.334(6)	N(1B)–C(2B)	1.354(5)
C(2A)–C(3A)	1.377(9)	C(2B)–C(3B)	1.370(7)
C(3A)–C(4A)	1.386(7)	C(3B)–C(4B)	1.386(9)
C(4A)–C(5A)	1.377(8)	C(4B)–C(5B)	1.376(7)
C(5A)–C(6A)	1.375(9)	C(5B)–C(6B)	1.385(8)
C(6A)–N(1A)	1.352(5)	C(6B)–N(1B)	1.336(8)
C(2A)–C(7A)	1.523(6)	C(2B)–C(7B)	1.504(8)
C(7A)–O(3A)	1.215(6)	C(7B)–O(3B)	1.214(5)
C(7A)–N(2)	1.349(7)	C(7B)–N(2)	1.374(6)
Cu–N(1A)–C(2A)	113.0(3)	Cu–N(1B)–C(2B)	112.6(3)
Cu–N(1A)–C(6A)	128.6(4)	Cu–N(1B)–C(6B)	128.4(3)
C(2A)–N(1A)–C(6A)	118.4(5)	C(2B)–N(1B)–C(6B)	119.0(5)
N(1A)–C(2A)–C(7A)	115.7(4)	N(1B)–C(2B)–C(7B)	116.1(4)
N(1A)–C(2A)–C(3A)	123.0(5)	N(1B)–C(2B)–C(3B)	121.9(4)
C(7A)–C(2A)–C(3A)	121.3(4)	C(7B)–C(2B)–C(3B)	122.1(5)
C(2A)–C(3A)–C(4A)	118.4(5)	C(2B)–C(3B)–C(4B)	119.0(5)
C(3A)–C(4A)–C(5A)	119.0(6)	C(3B)–C(4B)–C(5B)	119.3(6)
C(4A)–C(5A)–C(6A)	119.5(6)	C(4B)–C(5B)–C(6B)	118.9(5)
C(5A)–C(6A)–N(1A)	121.7(5)	C(5B)–C(6B)–N(1B)	121.9(5)
C(2A)–C(7A)–O(3A)	119.7(5)	C(2B)–C(7B)–O(3B)	121.1(4)
C(2A)–C(7A)–N(2)	110.9(4)	C(2B)–C(7B)–N(2)	111.2(3)
O(3A)–C(7A)–N(2)	129.4(5)	O(3B)–C(7B)–N(2)	127.7(7)
Cu–N(2)–C(7A)	118.2(3)	Cu–N(2)–C(7B)	117.2(3)
Oxalato bridge			
C(1)^{i}–O(1)	1.269(5)	C(1)–O(2)	1.234(4)
C(1)–C(1)^{i}	1.561(7)		
Cu–O(1)–C(1)^{i}	117.1(3)	Cu–O(2)–C(1)	107.5(3)
O(1)–C(1)^{i}–C(1)	116.3(4)	O(2)–C(1)–C(1)^{i}	118.0(4)
O(1)^{i}–C(1)–O(2)	125.7(4)		

[a] Symmetry code: (i) = 1 − *x*, −*y*, −*z*; (ii) = 1 − *x*, −*y*, 1 − *z*.

from a $\Delta M_s = 2$ forbidden transition in the triplet is observed at room temperature and at 100 K.

Solution Study

Oxalic acid acts as a diprotic acid in aqueous solution. The values of its deprotonation constants show that it behaves as a strong acid for the first dissociation and moderately strong for the second as has been shown by different techniques [23]. This behaviour makes the potentiometric investigation of oxalato complexes in aqueous solution difficult. However, oxalic acid behaves as a weak acid in DMSO ($pK_{a1} = 5.87$ and $pK_{a2} = 8.28$ at 25 °C and 0.1 mol dm^{-3} n-Bu_4NClO_4) [24]. This fact allowed us to investigate the formation of oxalato complexes by classical potentiometry. Deprotonation equilibria and complex formation do not occur in the same pH range in DMSO in contrast to what is observed in aqueous solution. A satisfactory response of the glass electrode towards [H^+] is observed in DMSO (see 'Experimental').

Series of DMSO solutions of bis(2-pyridylcarbonyl)amidocopper(II) nitrate and oxalic acid (C_M = 0.99–1.40 × 10^{-3} mol dm^{-3}, $C_L = 2.9 \times 10^{-3}$ mol dm^{-3}) were titrated with n-Bu_4NOH in order to investigate the formation of oxalato complexes.

Data processing by the SUPERQUAD of 50 experimental points from each experiment which were carried out in the 3.7–5.8 pH range allowed us to determine the constants of the equilibria (eqns. (1)–(3)):

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + C_2O_4^{2-} + H^+ \overset{\beta_{111}}{\rightleftharpoons} [Cu\{(NC_5H_4CO)_2N\}(HC_2O_4)] \quad (1)$$

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + C_2O_4^{2-} \overset{\beta_{110}}{\rightleftharpoons} [Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]^- \quad (2)$$

$$2[Cu\{(NC_5H_4CO)_2N\}]^+ + C_2O_4^{2-} \overset{\beta_{210}}{\rightleftharpoons} [Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)] \quad (3).$$

$\log\beta_{111} = 12.22 \pm 0.05$, $\log\beta_{110} = 7.0 \pm 0.1$ and $\beta_{210} = 10.2 \pm 0.1$. Several models involving metal: oxalate 1:2 complexes as well as protonated species were ruled out by the SUPERQUAD computer program in the process of refinement and only the above mentioned species fitted well the experimental data in the pH range studied. The distribution diagram, α versus pH, for the existing species in solution is plotted in Fig. 2. The mononuclear complex $[Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]^-$ is completely formed at pH $\geqslant 7$ whereas it coexists with all other copper(II) complexes in the 3–6 pH range. A value of $\log K$ of 3.94 for eqn. (4) is deduced from eqn.

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + HC_2O_4^- \overset{K}{\rightleftharpoons} [Cu\{(NC_5H_4CO)_2N\}(HC_2O_4)] \quad (4)$$

(1) and the one corresponding to the second deprotonation of oxalic acid. This value is much smaller than the one corresponding to eqn. (2). In the light of the above structural data for the binuclear complex, it can be assumed that β_{110} and β_{210} correspond to asymmetric bidentate and bis-bidentate chelating modes of the oxalate whereas the small value of K can be associated to a unidentate coordination of $HC_2O_4^-$. Complexes where the oxalate behaves as a bis-bidentate [6, 21a–d, 25a–g] and bidentate [21c, 25c, 26a–f] are well known. Its unidentate character is rarer but not unknown [27a–c].

Although the preparation and chemistry of the oxalato complexes of transition metal ions have been extensively investigated, thermodynamic studies of the coordination modes of the oxalate, i.e. its unidentate and chelating ability, are still lacking. This paper is, as far as we are aware, one of the first contributions to this field. To our knowledge, it is the first time that the ability of the oxalate ligand to bridge two copper(II) ions has been studied on the same complex both in solution and in the solid state.

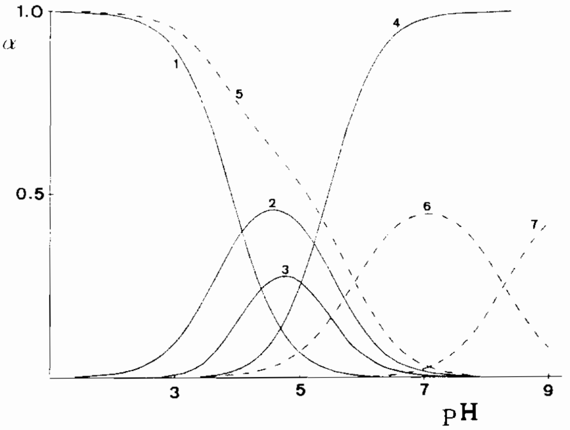

Fig. 2. Distribution diagram α vs. pH for DMSO solutions of $[Cu\{(NC_5H_4CO)_2N\}]^+$ and oxalic acid. 1, 2, 3, 4, 5, 6 and 7 refer to $[Cu\{(NC_5H_4CO)_2N\}]^+$, $[Cu\{(NC_5H_4CO)_2N\}(HC_2O_4)]$, $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$, $[Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]^-$, $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$. Molar fractions are referred to total $[Cu\{(NC_5H_4CO)_2N\}]^+$ ion (1–4) and to total oxalate (5–7).

In order to study the role of the solvent on the complex formation scheme, and in spite of the above mentioned experimental difficulties, we have investigated the same system in aqueous solution (25 °C, 0.1 mol dm^{-3} $NaNO_3$). We could not follow the usual procedure (solutions containing equimolar amounts of copper(II) complex and oxalic acid were titrated with sodium hydroxide) because the degree of formation of the binuclear copper(II) complex is too high and, moreover, it precipitates as a crystalline powder due to its low solubility. These difficulties are avoided when using oxalic acid as the titrant. The proton association constants of oxalic acid, 3.80(1) and 4.8(1) for $\log\beta_{011}$ and $\log\beta_{012}$, respectively, were determined previously [28] (values in parentheses refer to the standard deviation on the last significant digit). Data processing by the SUPERQUAD of 108 experimental points from different experiments, ($C_M = 1.25 \times 10^{-3}$ mol dm^{-3}, $C_L = 10^{-2}$ mol dm^{-3} and a 4.0–3.0 pH range), allowed us to determine the constants of eqns. (2) and (3) together with the protonation equilibria (eqn. (5))

$$[Cu\{(NC_5H_4CO)_2N\}]^+ + H^+ \overset{\beta_{101}}{\rightleftharpoons} [Cu\{(NC_5H_4CO)_2NH\}]^{2+} \quad (5)$$

Values of 3.67(3), 6.3(2) and *c.* 2 were obtained for $\log\beta_{110}$, $\log\beta_{210}$ and $\log\beta_{101}$, respectively. Only these species fitted well the experimental data in the short pH range studied. As far as we know, the neutral complexes $[Cu(en)C_2O_4]$ and $[Cu(bipy)C_2O_4]$ (en = ethylenediamine and bipy = 2,2′-bipyridine) are the only mixed-ligand complexes with oxalate for which the stability constant has been determined: $\log\beta = 4.83$ [29a–c] and 5.78(2) [28] respectively. These values are greater than the one corresponding to $[Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]^-$ (eqn. (2)). The tridentate character of the bis(2-pyridylcarbonyl)amido ligand leads to an asymmetrical bidentate coordination of oxalate which explains its lower stability constant.

The bis(2-pyridylcarbonyl)amido anion is easily protonated in aqueous solution leading to the neutral monoprotic acid which has been isolated only very recently [30]. H NMR and IR data reveal that the proton is bound to the basic imide-nitrogen atom. However, the basicity of this nitrogen atom is much decreased when it is bound to copper(II) (Cu–N(2) bond distance is significantly shorter than the other three basal distances) as the low value of β_{101} reveals. Indeed, $[Cu\{(NC_5H_4CO)_2NH\}]^{2+}$ is formed only at low pH values.

When comparing our results in DMSO and water, three points deserve to be noted: (i) the mononuclear and binuclear oxalato complexes $[Cu\{(NC_5H_4CO)_2N\}(C_2O_4)]^-$ and $[Cu_2\{(NC_5H_4CO)_2N\}_2(C_2O_4)]$ exist in both solvents but they exhibit a higher stability in DMSO; (ii) the complex containing $HC_2O_4^-$, $[Cu\{(NC_5H_4CO)_2N\}(HC_2O_4)]$, has not been observed in aqueous solution in our experimental conditions; (iii) the protonation reaction (eqn. (5)) does not occur in DMSO solution. Dealing with the latter point, it is well known that cationic acids are usually stronger in DMSO than in water, whereas the neutrals and anionic ones exhibit smaller acidity constants.

Supplementary Material

Tables of thermal parameters, calculated positions of hydrogen atoms and mean planes (4 pages) as well as a listing of observed and calculated structure factors (24 pages) are available from the authors on request.

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