Synthesis, structure and properties of aquabis(2,4'-bipyridine)di(propionato-O)copper(II)

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The title complex has been synthesized and characterized by elemental and thermal analysis, IR and electronic spectroscopy, conductivity studies and X-ray crystallography. In the crystal, the complex has two-fold symmetry and the copper atom adopts square pyramidal coordination. Bond valences for Cu were computed. $Cu-O_{(propionate)}$ bonds are slightly stronger than the Cu–N bonds, and the $Cu-O_{(water)}$ bond is distinctly weaker. Molecules are linked by O–H$\cdots$O hydrogen bonds to form infinite hydrogen-bonded chains along the y axis.

1. Introduction

Copper(II) ions and their complexes play a very important role in a number of different biological processes. Recently [1], it was stated that copper(II) propionate complexes are very promising as new non-steroid anti-inflammatory agents. Copper(II) propionate has been described in the literature in terms of its preparation, X-ray structure [2–4], thermal behaviour [5] and biological activity [1]. Several studies have been carried out on mixed ligand copper(II) complexes with isomers of bipyridine [4,4′-bipyridine (4-bpy) and 2,4′-bipyridine (2,4′-bpy)] and anions of monocarboxylic acids [6–9]. Interest in mixed ligand complexes of Cu(II) with such ligands is not only due to their important role in biological systems but also because they may exist in different structural forms producing different properties. Among complexes of Cu(II) with propionate only the 4-bpy–propionate system has been studied. Japanese researchers [10] have reported the preparation, characterization and X-ray studies of the chain structures of $[Cu_2(4\text{-bpy})(C_2H_5COO)_4]_n$ and $[Cu_2(4\text{-bpy})(C_2H_5COO)_2(OCH_3)_2 (CH_3OH)_2]_n \cdot 2nCH_3OH$ which were obtained from ethanol and methanol solutions,

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respectively. The X-ray structure analyses show that open, cubane, tetranuclear units or bridged dinuclear units are linked by bidentate ligands to form infinite chains. Czakis-Sulikowska *et al.* [11] have synthesized and characterized the complex $Cu(4\text{-}bpy)_{0.5}$ $(C_2H_5COO)_2 \cdot H_2O$. Analysis of the IR spectra of this compound indicates that propionate is attached to copper(II) probably with bidentate chelating bonds. To the authors' knowledge, no data on the copper(II)–propionate–2,4′-bpy system have been presented in the literature. Therefore, we report the preparation, characterization and structural investigation of a Cu(II) complex with propionate and 2,4′-bpy.

2. Experimental

2.1. *Synthesis of the complex*

A solution of copper propionate was obtained by reaction of 30 mmol of $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ with $20 \, cm^3$ of $3 \, mol \, dm^{-3}$ aqueous propionic acid. The mixture was filtered and in the resulting solution (pH ≈ 4–5) Cu(II) was determined chelatometrically. The complex was prepared by treating a solution containing 60 mmol of 2,4′-bipy in $5.7 \, cm^3$ of water plus $0.3 \, cm^3$ of 96% EtOH with a solution of 3.0 mmol of copper propionate in $14.0 \, cm^3$ of water. The mixture was stirred and heated at 80°C for $\sim$10 min and then allowed to cool. During several hours a fine, dark blue crystalline compound was obtained. The solid product was filtered off, washed with water and ethanol–diethyl ether (1 : 1) and dried at room temperature. Anal. for $Cu(H_2O)(C_{10}N_2H_8)_2 (C_2H_5COO)_2$ Calc./Found (%): Cu, 11.76/12.15; C, 57.82/57.52; H, 5.23/5.21; N, 10.37/10.03.

2.2. *Crystal structure determination*

A blue, rectangular, prismatic crystal was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector. X-ray intensity data were collected with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \, \text{Å}$) at 293.0(2) K, with the ω scan mode. A 30 s exposure time was used and a whole Ewald sphere was collected up to $2\theta = 50.20°$. Unit cell parameters were determined from least-squares refinement of the setting angles of the 4473 strongest reflections. Details concerning crystal data and refinement are given in table 1. Examination of two reference frames monitored after each 20 frames measured showed a 2.8% loss of total intensity. During data reduction the decay correction was taken into account. Lorentz, polarization, and numerical absorption [12] corrections were applied. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All hydrogen atoms were found from a difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with an individual isotropic temperature factor equal to 1.2 times the value of the equivalent temperature factor of the parent atom. SHELXS97 [13], SHELXL97 [14] and SHELXTL [15] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs. Interatomic bond distances and angles are listed in table 2. Atomic coordinates and equivalent isotropic displacement parameters are listed in table 3.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{26}H_{28}CuN_4O_5$
Formula weight	540.06
Temperature/K	293.0(2)
λ(Mo $K\alpha$)/Å	0.71073
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions/Å,°	$a = 23.8028(14)$
	$b = 5.8036(3)$
	$c = 19.7781(11)$
	$\beta = 110.447(5)$
Volume/Å^3	2560.0(2)
Z, Calculated density/Mg m^{-3}	4, 1.401
Absorption coefficient/mm^{-1}	0.896
$F(000)$	1124
Crystal size/mm	$0.079 \times 0.107 \times 0.122$
θ range for data collection/°	3.31 to 25.10
Index ranges	$-28 \leq h \leq 26, -6 \leq k \leq 6, -23 \leq 1 \leq 23$
Reflections collected/unique	12158/2274 [$R_{(int)} = 0.033$]
Completeness to $2\theta = 25.11°$	95.3%
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.791 and 0.854
Data/restraints/parameters	2274/0/166
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0332, wR2 = 0.0815$
R indices (all data)	$R1 = 0.0388, wR2 = 0.0845$
Largest diff. peak and hole/e Å^{-3}	0.332 and -0.268

Tables of crystal data and structure refinement details, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre (No. CCDC239518).

2.3. *Other measurements*

Elemental determinations were carried using a Carbo-Erba C, H, N analyzer. Copper(II) contents was estimated by EDTA titration after decomposition of the complex in dilute HCl. Molar conductivity (χ_M) of 10^{-3} mol dm^3 solutions (in methanol, DMF and DMSO) were measured at $25 \pm 0.05°$C.

IR spectra (4000–400 cm^{-1}) were recorded on a Shimadzu spectrophotometer using KBr pellets. The electronic spectrum for the polycrystalline sample (in Nujol mull) was recorded on a Specord 40 spectrophotometer. Thermal decomposition studies were carried out on a derivatograph (type Q-1500) over the temperature range 20–1000°C, at a heating rate of $10°$C min^{-1}, in air. The sample mass was 100 mg; α-Al$_2$O$_3$ served as the reference. Analysis of solid decomposition products was performed using derivatographic curves, analytical data and X-ray powder methods in conjunction with the Powder Diffraction File [16].

3. Results and discussion

The complex is air stable and fairly soluble in water. Low molar conductance in methanol and DMSO (15.7 and 6.1 Ω^{-1}cm^{2}mol^{-1}, respectively) indicates that the

Table 2. Selected structural data for the complex. Distances in Å, angles in deg.

Cu(1)–O(11)#1	1.9458(16)	C(4)–C(5)	1.373(3)
Cu(1)–O(11)	1.9458(16)	C(6)–N(2)	1.337(3)
Cu(1)–N(1)	2.0237(19)	C(6)–C(10)	1.368(4)
Cu(1)–N(1)#1	2.0237(19)	N(2)–C(7)	1.337(4)
Cu(1)–O(1)	2.213(2)	C(7)–C(8)	1.370(5)
N(1)–C(1)	1.334(3)	C(8)–C(9)	1.355(5)
N(1)–C(5)	1.337(3)	C(9)–C(10)	1.376(4)
C(1)–C(2)	1.375(3)	O(11)–C(11)	1.270(3)
C(2)–C(3)	1.387(3)	O(12)–C(11)	1.221(3)
C(3)–C(4)	1.387(3)	C(11)–C(12)	1.512(3)
C(3)–C(6)	1.488(3)	C(12)–C(13)	1.433(5)
O(11)#1–Cu(1)–O(11)	179.68(11)	N(2)–C(6)–C(10)	122.0(2)
O(11)#1–Cu(1)–N(1)	89.35(7)	N(2)–C(6)–C(3)	115.8(2)
O(11)–Cu(1)–N(1)	90.62(7)	C(10)–C(6)–C(3)	122.2(2)
O(11)#1–Cu(1)–N(1)#1	90.62(7)	C(7)–N(2)–C(6)	117.0(3)
O(11)–Cu(1)–N(1)#1	89.35(7)	N(2)–C(7)–C(8)	124.4(3)
N(1)–Cu(1)–N(1)#1	169.74(11)	C(9)–C(8)–C(7)	117.4(3)
O(11)#1–Cu(1)–O(1)	90.16(5)	C(8)–C(9)–C(10)	119.9(3)
O(11)–Cu(1)–O(1)	90.16(5)	C(6)–C(10)–C(9)	119.3(3)
N(1)–Cu(1)–O(1)	95.13(5)	C(11)–O(11)–Cu(1)	121.52(16)
N(1)#1–Cu(1)–O(1)	95.13(5)	O(12)–C(11)–O(11)	124.9(2)
C(1)–N(1)–C(5)	116.9(2)	O(12)–C(11)–C(12)	119.2(3)
C(1)–N(1)–Cu(1)	121.34(16)	O(11)–C(11)–C(12)	115.9(2)
C(5)–N(1)–Cu(1)	121.73(15)	C(13)–C(12)–C(11)	116.3(3)
N(1)–C(1)–C(2)	123.0(2)	Cu(1)–O(11)–C(11)–O(12)	−15.8(4)
C(1)–C(2)–C(3)	120.4(2)	O(11)–C(11)–C(12)–C(13)	−45.0(4)
C(2)–C(3)–C(4)	116.2(2)	O(12)–C(11)–C(12)–C(13)	134.7(4)
C(2)–C(3)–C(6)	120.9(2)	C(2)–C(3)–C(6)–N(2)	−8.1(3)
C(4)–C(3)–C(6)	122.9(2)	C(4)–C(3)–C(6)–C(10)	−7.9(4)
C(5)–C(4)–C(3)	120.2(2)	C(4)–C(3)–C(6)–N(2)	170.9(2)
N(1)–C(5)–C(4)	123.3(2)	C(2)–C(3)–C(6)–C(10)	173.1(2)

Symmetry transformations used to generate equivalent atoms #1: −x, y, −z + 1/2.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the complex. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|	x/a	y/b	z/c	$U_{(eq)}$
Cu(1)	0	3336(1)	2500	38(1)
N(1)	698(1)	3648(3)	2146(1)	40(1)
C(1)	806(1)	2061(4)	1719(1)	47(1)
C(2)	1284(1)	2183(4)	1482(1)	46(1)
C(3)	1680(1)	4023(4)	1679(1)	39(1)
C(4)	1555(1)	5695(4)	2108(1)	46(1)
C(5)	1071(1)	5448(4)	2328(1)	47(1)
C(6)	2210(1)	4137(4)	1446(1)	42(1)
N(2)	2316(1)	2249(4)	1122(1)	64(1)
C(7)	2798(2)	2285(6)	922(2)	78(1)
C(8)	3192(1)	4090(7)	1044(2)	73(1)
C(9)	3071(1)	5990(6)	1367(2)	74(1)
C(10)	2573(1)	6035(5)	1568(2)	61(1)
O(11)	547(1)	3346(3)	3497(1)	51(1)
O(12)	380(1)	6973(3)	3709(1)	78(1)
C(11)	578(1)	5053(5)	3910(1)	47(1)
C(12)	885(2)	4607(6)	4708(1)	73(1)
C(13)	721(3)	2525(8)	4983(2)	135(2)
O(1)	0	−476(4)	2500	58(1)
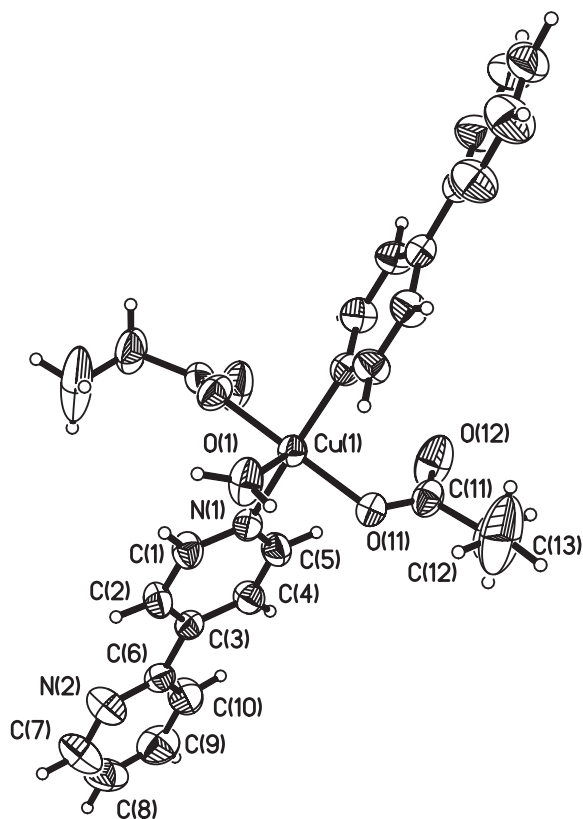
Figure 1.   The molecular structure of the complex with the atom numbering, plotted with 50% probability of displacement ellipsoids.

compond is a non-electrolyte in these solvents. The value in DMF $(17.2 \, \Omega^{-1} \, cm^2 \, mol^{-1})$ shows behaviour intermediate between those of non and 1:1 electrolytes [17].

A perspective view of the structure together with the atom numbering scheme is shown in figure 1; displacement ellipsoids are plotted with 50% probability. The asymmetric unit includes one half of the molecule. Cu(1) and O(1) atoms lie on a two-fold axis (special positions *e* of space group *C*2/*c* at 0, *y*, 1/4 [18]). The copper atom adopts slightly distorted square pyramidal coordination (figure 2). The base of copper polyhedron is *trans*-distorted and the maximum deviation 0.1064(14) Å from the least squares plane calculated through all of its atom occurs for N(1). Cu(1) is shifted 0.0746(11) Å from this plane in the same direction as oxygen atom O(11) (deviates by 0.0691(13) Å). In this way the reverse umbrella shape is created.

In the literature only two mixed ligand five-coordinated metal complexes containing two 2,4′-bipyridine ligands are described, and in both the central atom is copper. These are aquabis(2′,4-bipyridine)di(*o*-sulfobenzimidato)copper(II) [19] and aquadi(acetato-*O*)-bis(4,2′-bipyridine)copper(II), cocrystallising with diaquadi(acetato-*O*) bis(4,2′-bipyridine)copper(II) [9].

Bond valences for the present complex were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ [20,21], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single
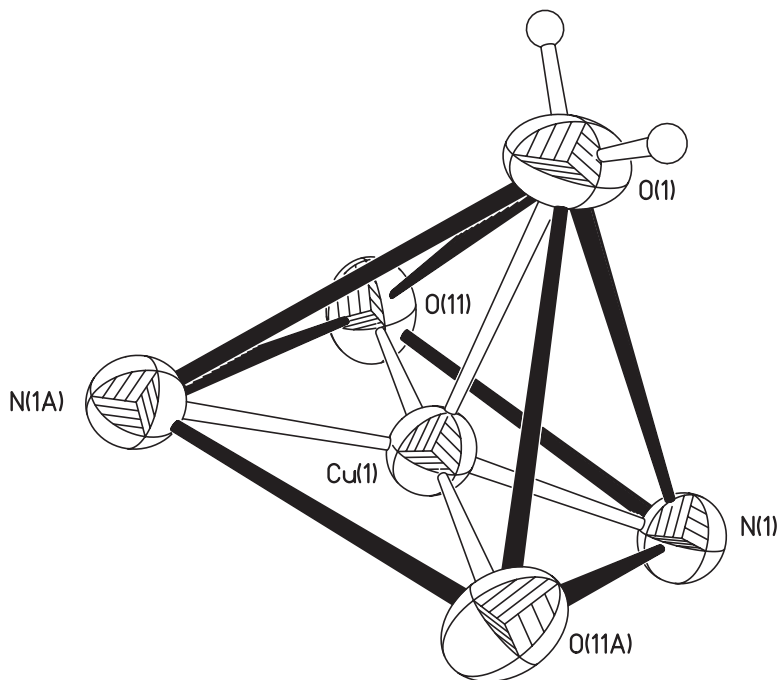
Figure 2.   The copper coordination polyhedron.

bond length between i and j atoms) [22]. R_{Cu-O} and R_{Cu-N} were taken as 1.679 [23] and 1.713 [22], respectively. The computed bond valences are $\nu_{Cu(1)-O(11)} = 0.486$, $\nu_{Cu(1)-O(1)} = 0.236$, $\nu_{Cu(1)-N(1)} = 0.432$ valence units and thus the computed valence of the Cu(1) atom is 2.07 v.u. The Cu–O$_{(propionate)}$ bonds are slightly stronger than Cu–N bonds, and Cu–O$_{(water)}$ bond is distinctly weaker.

The planar (within the experimental error) pyridine rings are inclined at 8.85(18)° to each other and the propionate substituents are distorted from planarity. C(13) deviates by 0.911(8) Å from the O(11)/O(12)/C(11)/C(12) plane (for conformation details see torsion angles in table 2).

Molecules of the complex are linked by medium strength hydrogen bonds [24] O(1)– H(10)···O(12# x, $y-1$, z) and its symmetry equivalent to form an infinite hydrogen-bonded chain along the y axis (figure 3). The possibility of D–H···π hydrogen bonds was rejected on the basis of long H···π distances (all lengths are larger than 3.6 Å).

Upon coordination with Cu(II) the IR spectrum of free 2,4′-bipy (unsymmetrical isomer of bipy) changes only in the region of the vibration modes of the 4-substituted pyridine (4-sub) [25]. A bathochromic shift of the band corresponding to a stretching ring vibration of 4-sub pyridine νC–C,C–N,C–C$_{inter-ring}$ (1595.0 cm^{-1} for the free ligand and 1614.3 cm^{-1} for the complex) was observed. At the same time, the position of νC–C,C–N,C–C$_{inter-ring}$ for the 2-substituted pyridine (1585.4 cm^{-1}) does not change in the spectra of the complex. The band at 1407.9 cm^{-1} in 2,4′-bipy (attributed to C–H$_{bend}$ + ring stretching vibration of the 4-substituted pyridine) appears in the complex at 1419.5 cm^{-1}. The characteristic ring "breathing" frequencies for the
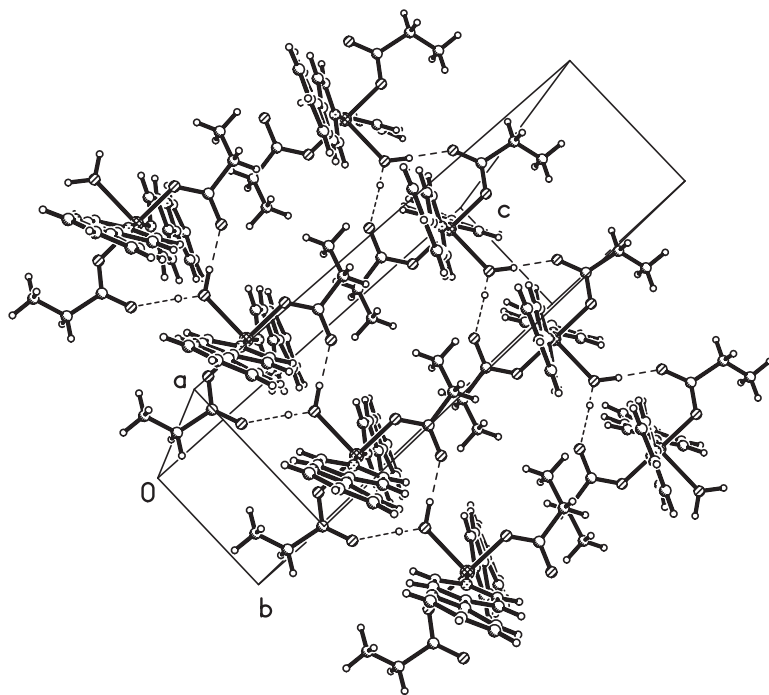
Figure 3. Fragment of the crystal packing showing the infinite hydrogen bonded chain along the y axis. Hydrogen bonds are indicated by dashed lines.

4-sub pyridine (band as a shoulder at $980\,cm^{-1}$ in free 2,4′-bipy) is observed in the IR spectrum of the complex as a strong, broad band at $1016.4\,cm^{-1}$. This band is partially obscured by the wagging vibration of the CH_3 group of propionate [26]. The observed changes are ascribed to the fact that 2,4′-bpy is coordinated to Cu(II) *via* the least hindered 4′N atom of 2,4′-bpy. The absorption band arising from symmetric $\nu_s(OCO)$ stretching vibrations occurs at $1400\,cm^{-1}$, whereas asymmetric $\nu_{as}(OCO)$ as a result of overlapping with a band of 2,4′-bpy appears as a distinct shoulder at $1560\,cm^{-1}$. The value of separation between $\nu_{as}(OCO)$ and $\nu_s(OCO)$, $160\,cm^{-1}$, is considerably higher than for sodium propionate ($\Delta\nu = 142.7\,cm^{-1}$). Thus, on the basis of literature data [26,27] we assume that the carboxylato groups in the investigated compound are monodentate. The presence of water in the complex is shown by a strong and broad band in the region 3150–$3400\,cm^{-1}$ and a weak peak in the water bending region ($1653\,cm^{-1}$). H_2O wagging vibrations and Cu–O stretching modes for coordinated water are masked by 2,4′-bipy. All the above points are entirely consistent with the X-ray structure. The electronic spectrum of the copper(II) complex consists of a broad ligand field band at $\sim 15\,580\,cm^{-1}$ and allows us to conclude that all three transitions, $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow 2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, lie within one broad envelope. The position as well as the shape of this band indicate a square pyramidal structure [28,29].

The thermal decomposition of the complex was established from thermoanalytical curves (TG, DTG, DTA) and chemical analysis, supported by powder X-ray diffraction. The complex is thermally stable up to $70°C$ and then loses water. Dehydration process takes place in the temperature range 70–$120°C$ (mass loss found 3.2%,

calc. 3.34%) and with an endothermic effect at 100°C. The anhydrous complex decomposes to CuO via undefined intermediate products in the temperature range 120–770°C. The TG curve for the anhydrous complex exhibits multiple, overlapping mass loss steps which are a result of decomposition of organic ligands. The X-ray diffraction pattern of the sinter obtained during heating of the complex at 340°C indicates the presence of Cu traces. Total mass loss in these steps is 82%. DTA shows two exothermic peaks (260°C weak, 550–700°C very strong) and an endothermic effect (200°C). A constant mass for pure CuO (found 15%, calc. 14.73%) is achieved at 770°C. On the base of literature data [5], anhydrous copper(II) propionate is more thermally stable than the anhydrous complex with 2,4′-bpy.

Acknowledgments

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