Electronic Properties and Crystal Structure of Aqua(1,10-phenanthroline)-(oxalato-O^1O^2) copper(II) monohydrate

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Abstract

The compound aqua(1,10-phenanthroline)-(oxalato-O^1O^2) copper(II)monohydrate was synthesized and characterized by spectroscopy, thermal analysis, EPR and structural measurements. The crystal and molecular structure, refined to the final R = 4.28% (R_w = 4.52%) value, shows a monomeric nature. Copper coordination is 4 + 1 in a slight distorted square pyramidal geometry, with a water oxygen atom in the apical position, at 2.237(4) Å from the metal atom. At 4.44 Å from copper lies a lattice water molecule, linked to the former by a hydrogen bond.

Introduction

As a part of our study on the preparation and characterization of polynuclear compounds with bridging polyatomic molecules [1], we decided to investigate a suitable monomeric derivative in order to get information on its physical and chemical properties.

A ternary complex of the copper(II) ion with the 1,10-phenanthroline (*o*-phen) ligand and the oxalate (ox) ion has been reported to involve anhydrous *o*-phen-ox–Cu(II) complex [2].

The present paper reports the structure determination of $[Cu(o\text{-phen})C_2O_4 \cdot H_2O]H_2O$ and its electronic and vibrational properties.

Experimental

Preparation

The complex was prepared by mixing $Cu(NO_3)_2 \cdot 3H_2O$, 1,10-phenanthroline and $Na_2C_2O_4$ in the ratio 2:2:1 in hot water. The compound obtained was recrystallized from an acetonitrile/methanol/water (1:4:3) mixture; blue crystals were collected. *Anal.* Found: C, 45.7; H, 3.2; N, 7.7. $C_{14}H_{12}CuN_2O_6$ requires: C, 45.7; H, 3.3; N, 7.6%.

Physical Measurements

The electronic spectrum of the solid compound was recorded as mull transmission spectra with a Shimadzu MPS 50L spectrometer. The infrared spectra were recorded with a Perkin–Elmer 180 spectrophotometer in KBr pellets and in nujol mull on polythene support in 4000–250 cm^{-1} and 400–100 cm^{-1} spectral ranges respectively.

The EPR spectra were recorded at X-band frequencies on a Varian E-9 spectrometer at room and liquid nitrogen temperatures.

Magnetic susceptibility was measured at room temperature by the absolute Gouy method.

Thermal Analysis

The DTA measurement was carried out on a Dupont apparatus; TGA and DTG on a Mettler TA 3000 system.

For both a scan rate of 10 °C min^{-1} was used.

Analysis

Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba Elemental Analyser Instrument Mod. 1106.

X-ray Data Collection

Intensity data were collected on a 12 × 12 × 10 mm crystal by ω–2θ scanning, using Mo-Kα, graphite monochromated, radiation (λ = 0.71069 Å) on a Philips PW 1100 automatic diffractometer. The unit cell parameters were obtained through least squares refinement of the setting angles of 20 carefully centered reflections. 2369 reflections were collected (3 standards every 250 reflections), in the 2.5–22° 2θ range with a scan width of 1.20° and scan speed of 4° min^{-1}. 2052 reflections were considered as observed; 1925 were unique, in the $\pm h$, $+k$, $+l$ region, having $I \geqslant 3\sigma(I)$.

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Crystal Data

$C_{14}H_{12}N_2O_6Cu$, $M_r = 367.78$, monoclinic, space group $P2_1/c$, $a = 17.407(3)$, $b = 9.706(3)$, $c = 8.468(3)$, $\beta = 103.83(3)$, $V = 1389.2$ Å^3, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $F(000) = 708$.

Structure Solution and Refinement

The positions of all non-hydrogen atoms were obtained by the usual Patterson and Fourier methods; the contributions of the scattering amplitudes of the H(1)–H(8) hydrogen atoms, fixed in their calculated positions (C–H = 1.080 Å) and not refined, were included in the last cycles of the refinement while H(9) and H(10) were located from a difference Fourier map.

This model converged at $R = 0.043$ and $R_w = 0.045$ $W = 1.54/(\sigma^2(F_o) + 0.0078F_o^2)$.

Scattering factors and anomalous dispersion corrections for neutral atoms were employed [3]; all the calculations were performed on a CDC Cyber 7600 computer, using the SHELX-76 program package [4] and the ORTEP plotting program [5] for drawing. Final fractional coordinates for non-hydrogen atoms are listed in Table I; hydrogen atom parameters and their bond distances and angles, and tables of observed and calculated structure factors, are all available as supplementary material.

TABLE I. Atomic Coordinates with e.s.d.s in Parentheses.

Atom	x	y	z
Cu	0.1542(0)	0.4803(1)	0.1447(1)
O(1)	0.1982(2)	0.3546(3)	0.0113(4)
O(2)	0.2275(2)	0.6149(4)	0.0933(4)
O(3)	0.3237(2)	0.6234(4)	–0.0366(5)
O(4)	0.2835(2)	0.3577(4)	–0.1460(5)
O(5)	0.2322(2)	0.4088(4)	0.3801(5)
O(6)	0.3236(2)	0.5780(4)	0.6128(6)
N(1)	0.0915(2)	0.6206(4)	0.2338(5)
N(2)	0.0623(2)	0.3580(4)	0.1549(5)
C(1)	0.1087(3)	0.7513(5)	0.2729(6)
C(2)	0.0592(3)	0.8344(6)	0.3401(6)
C(3)	–0.0092(3)	0.7813(5)	0.3675(6)
C(4)	–0.0286(3)	0.6425(5)	0.3289(6)
C(5)	–0.0969(3)	0.5742(5)	0.3582(6)
C(6)	–0.1116(3)	0.4399(5)	0.3191(6)
C(7)	–0.0593(3)	0.3606(5)	0.2466(6)
C(8)	0.0081(3)	0.4251(5)	0.2190(5)
C(9)	0.0239(3)	0.5663(5)	0.2614(5)
C(10)	–0.0715(3)	0.2218(5)	0.2019(6)
C(11)	–0.0166(3)	0.1554(6)	0.1373(6)
C(12)	0.0497(3)	0.2268(5)	0.1142(6)
C(13)	0.2703(3)	0.5625(5)	0.0051(6)
C(14)	0.2501(3)	0.4123(5)	–0.0514(6)

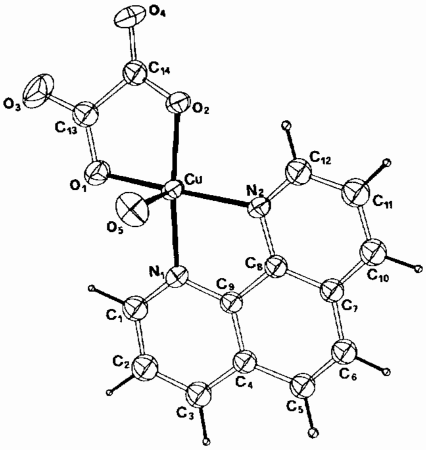

Fig. 1. Perspective view of the molecule.

Results and Discussion

Description of the Structure

A drawing of the structure, showing the labelling scheme, is given in Fig. 1.

Selected bond distances and angles are listed in Table II.

Crystals of the complex aqua(1,10-phenanthroline)-(oxalato-O^{1}O^2)copper(II) monohydrate consist of a packing of monomeric Cu(o-phen)(C_2O_4)(H_2O) molecules and interposed lattice water molecules. The shortest Cu··Cu distance at 5.917(4) Å implies no direct metal–metal interaction [6]. Moreover, the distance between the opposite-to-bonded to copper oxalato oxygen atoms O(3) and O(4) and the nearest copper atom is 4.749(4) Å, excluding any bridging effect by oxalato units. As a further confirmation, O(3) and O(4) are closer to the respective oxalato carbon atoms C(13) and C(14) [C(13)–O(3) = 1.223(6), C(14)–O(4) = 1.217(6) Å] than are the O(1) and O(2) atoms involved in copper coordination [C(13)–O(1) = 1.279(6), C(14)–O(2) = 1.281(6) Å]. The C(13)–O(3) and C(14)–O(4) distances are also shorter than those [1.258 Å, mean] existing in the free ligand [7].

From consideration of the intermolecular geometry, it can be seen that the only 'short' contact is due to a distance H(9)··O(3)′ = 2.616(6) Å, with O(5)··O(3)′ = 3.316(5) Å and O(5)–H(9)··O(3)′ = 141.93(3)° (′ = ½ – x, –½ + y, ½ – z), having no particular significance [7–9].

The copper atom is in a five coordinate, square pyramidal environment: the 1,10-phen and oxalate ligands are symmetrically coordinated in the basal plane. The oxygen atom [O(5)] of the coordinated water molecule lies above the plane, at the apex of the slight distorted pyramid at 2.237(4) Å from copper, yielding a tetragonality parameter T = 0.882 [9, 10].

TABLE II. Bond Distances (Å) and Bond Angles (deg) with e.s.d.s in Parentheses.

Cu–N(1)	2.001(4)	C(13)–C(14)	1.549(7)
Cu–N(2)	2.010(4)	C(13)–O(1)	1.279(6)
Cu–O(1)	1.941(3)	C(13)–O(3)	1.223(6)
Cu–O(2)	1.946(3)	C(14)–O(2)	1.281(6)
Cu–O(5)	2.237(4)	C(14)–O(4)	1.217(6)
Cu…O(6)	4.441(4)		
N(1)–C(1)	1.327(6)	N(2)–C(12)	1.324(6)
N(1)–C(9)	1.361(6)	N(2)–C(8)	1.361(6)
C(1)–C(2)	1.398(7)	C(11)–C(12)	1.400(7)
C(2)–C(3)	1.367(7)	C(10)–C(11)	1.370(7)
C(3)–C(4)	1.408(7)	C(7)–C(10)	1.402(7)
C(4)–C(5)	1.435(7)	C(6)–C(7)	1.436(7)
C(4)–C(9)	1.398(6)	C(7)–C(8)	1.398(6)
C(8)–C(9)	1.427(7)		
C(5)–C(6)	1.354(7)		
N(1)–Cu–N(2)	82.8(2)	Cu–O(2)–C(13)	111.6(3)
N(1)–Cu–O(2)	94.2(1)	Cu–O(1)–C(14)	112.5(3)
N(1)–Cu–O(1)	166.8(2)	O(1)–C(14)–O(4)	125.3(5)
N(2)–Cu–O(1)	94.7(1)	O(1)–C(14)–C(13)	114.4(4)
N(2)–Cu–O(2)	167.6(2)	O(4)–C(14)–C(13)	120.3(5)
O(1)–Cu–O(2)	85.4(1)	O(2)–C(13)–O(3)	124.5(5)
O(5)–Cu–O(1)	94.8(1)	O(2)–C(13)–C(14)	115.7(4)
O(5)–Cu–O(2)	96.7(2)	O(3)–C(13)–C(14)	119.8(5)
O(5)–Cu–N(1)	98.3(2)		
O(5)–Cu–N(2)	95.6(2)		
Cu–N(1)–C(1)	129.3(3)	Cu–N(2)–C(12)	129.9(3)
Cu–N(1)–C(9)	111.9(3)	Cu–N(2)–C(8)	111.7(3)
N(1)–C(9)–C(4)	122.8(4)	N(2)–C(8)–C(7)	122.8(4)
N(1)–C(9)–C(8)	116.8(4)	N(2)–C(8)–C(9)	116.8(4)
C(1)–N(1)–C(9)	118.7(4)	C(12)–N(2)–C(8)	118.4(4)
N(1)–C(1)–C(2)	122.0(5)	N(2)–C(12)–C(11)	122.1(5)
C(1)–C(2)–C(3)	119.9(5)	C(12)–C(11)–C(10)	119.9(5)
C(2)–C(3)–C(4)	119.4(5)	C(11)–C(10)–C(7)	119.1(5)
C(3)–C(4)–C(5)	124.3(4)	C(10)–C(7)–C(6)	124.0(5)
C(3)–C(4)–C(9)	117.2(4)	C(8)–C(7)–C(10)	117.6(4)
C(5)–C(4)–C(9)	118.4(4)	C(8)–C(7)–C(6)	118.4(4)
C(4)–C(5)–C(6)	121.2(5)	C(7)–C(6)–C(5)	121.2(5)
C(4)–C(9)–C(8)	120.4(4)	C(7)–C(8)–C(9)	120.4(4)

The bite angles at the copper atom are normal: that of 1,10 phen ligand is 82.78°, and that of the oxalate ligand is 86.44°. The high value for both bite angles and tetragonality factor are in agreement with the observed coplanarity of atoms in the base of the pyramid [N(1)–N(2)–O(1)–O(2), Table III]. The copper atom is only slightly (0.21 Å) displaced from the basal plane toward the water-oxygen atom, with a very slight tetrahedral distortion: N(1)–Cu–O(1) = 166.8(2)°; N(2)–Cu–O(2) = 167.6(2)° [11–13].

The uncoordinated water molecule at O(6) is linked to the coordinated one at the fifth coordination site by means of a hydrogen bond involving the H(10) atom (O(5)··O(6) = 2.759 Å, H(10)··O(6) = 1.910 Å, O(5)–H(10)··O(6) = 175.42°), while H(9) is not in proper position for hydrogen bonding (H(9)··O(6) = 3.215 Å, O(5)–H(9)··O(6) = 50.47°).

The phenanthroline molecule is planar within a root-mean-square deviation of 0.013(3) Å from the mean plane through all its atoms (Table III); bond lengths and angles are in good agreement with the mean values for other *o*-phen complexes [14] and with the weighted-mean values reported for molecular 1,10-phenanthroline [13]; its symmetry is the usual C_{2v}. The major discrepancies are found in the proximity of the nitrogen atoms, due to the bonding with copper; thus longer N(1)–C(1), N(2)–C(12) and shorter C(8)–C(9) have been found, with consequent elongation of the opposite site C(5)–C(6) = 1.354(7) Å instead of 1.33 Å. Nevertheless the rearrangement of bond distances and angles (N(1)–C(1)–C(2) = 122.0(5)°, N(2)–C(12)–C(11) = 122.1(5)°) compared to 124.4° for molecular *o*-phen [13] does not influence the symmetry of the ligand molecule, which shows a very good agreement between equivalent bonds and angles of 'left' and 'right' halves.

TABLE III. Selected Mean-plane Data.

		r.m.s.d. (Å)
Plane 1:	O(1), O(2), N(1), N(2)	0.0330
	[O(1) –0.0164, O(2) 0.0167, N(1) –0.0166, N(2) 0.0164]	
Plane 2:	N(1), C(1), C(2), C(3), C(4), C(9)	0.0043
	[max. C(3) –0.0045]	
Plane 3:	N(2), C(12), C(11), C(10), C(7), C(8)	0.0064
	[max. C(7) 0.0064]	
Plane 4:	C(8), C(9), C(4), C(5), C(6), C(7)	0.0083
	[max. C(4) –0.0091]	
Plane 5:	N(1), C(1)–C(12), N(2) = *o*-phen	0.0133
	[max. (+) = C(6) 0.0203, max. (–) = C(8) –0.0137]	
Plnae 6:	O(1), O(2), C(13), C(14), O(3), O(4) = oxalate	0.0572
	[O(1) 0.0540, O(2) –0.0474, C(13) –0.0052, C(14) –0.0074, O(3) 0.0507, O(4) –0.0448]	

Dihedral angles (deg) between planes (2)–(3) and (3)–(4) = 179.20°. Copper from plane (1): 0.2086 Å.

TABLE IV. Electronic, EPR, Infrared and Magnetic Results for Aqua(1,10-phenanthroline)-(oxalato-O^1O^2)copper(II) monohydrate.

d–d band max. (cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$g_{av.}$	μ (BM)	ν(CO) (cm^{-1})	ν(CuO) (cm^{-1})	ν(CuN) (cm^{-1})	$\nu Cu(OH_2)$ (cm^{-1})
15400	2.242	2.067	2.125	1.85	1642s	560m	326s	291m
11100						543m		

Electronic and Magnetic Properties

On the basis of the criteria to distinguish different structures, especially the regular trigonal-bipyramidal distorted structure [15], we found two well-resolved peaks at 15.4 and 11.1 kK. This suggests that the spectroscopic criteria of stereochemistry [16] should fit even the present case. The two bands are tentatively assigned as $d_{xy,xz,yz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ respectively. This choice may be supported by the fact that our complex has square-pyramidal stereochemistry of type B [17], as $\rho = 0.21$ Å and the tetragonality $T \sim 0.9$. Furthermore as $R_L < R_S + 0.3$ Å the $d_{z^2} \rightarrow d_{x^2-y^2}$ band is well resolved [18].

The ESR spectra of the powdered complex do not exhibit any hyperfine structure; the $g_{\parallel}$ value being higher than the $g_{\perp}$ is indicative of a $d_{x^2-y^2}$ (or d_{xy}) ground state in the molecule. The average g-value is calculated according to the relation, $g_{av} = 1/3g_{\parallel} + 2/3g_{\perp}$, and gives a value of 2.125, which is in agreement with an orbitally non-degenerate ground state. The $g_{\parallel}$ value is in agreement with that for CuO_2N_2 chromophores with strong planar bonding and weaker axial bonding.

The room-temperature magnetic moment, 1.85 BM, is slightly above the spin-only value but within the range normally found for magnetically dilute copper(II) complexes: no evidence of spin–spin coupling was detected, as expected for a Cu–Cu distance of 5.91 Å.

Infrared Spectra

The infrared spectra of the ternary complex exhibit absorption typical of coordinated *o*-phen [19], thus the absorptions at 1630, 1520, 1433, 862 and 722 cm^{-1} are in the range expected and are comparable to other similar complexes.

The $\nu_{as}(CO)$ principal band (Table IV), which falls at 1640 cm^{-1} in the bridging oxalate ligand [20], is found in the present complex at 1663 cm^{-1}, a value observed for a chelating oxalate ligand.

A continuous absorption at 3460–3200 cm^{-1} with a relatively sharp maximum at 3460 cm^{-1} is attributable to the simultaneous presence of aqua ligand [21] and lattice water [22].

In the far infrared region new bands due to Cu–O and Cu–N vibrations are clearly detectable. The band at 291 cm^{-1} may be assigned to $\nu(Cu(OH_2))$.

A DTA experiment shows that the two water molecules are somehow different, even if not with a substantial evidence. The two peaks are separated by 23 °C (lattice water at 90 °C and coordinated water at 113 °C), while the corresponding TGA weight loss ends at 107 °C.

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