

Crystal structure of tetrakis (μ -betaine-O,O') dichloro-dicopper(II) dichloride tetrahydrated

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Received December 3, 2000

[Cu₂(bet)₄Cl₂]Cl₂·4H₂O (bet = betaine: IUPAC name: trimethylammonioacetate) is monoclinic, space group $P2_1/c$, $a = 11.0510(10)$ Å, $b = 14.7140(4)$ Å, $c = 11.1620(15)$ Å, $\beta = 107.40(2)^\circ$. The dinuclear copper(II) cation [Cu₂(bet)₄Cl₂]²⁺ is counterbalanced by two naked Cl⁻ ions. The copper(II) ions have a square bipyramidal environment with oxygen atoms from the acetato groups in the basal planes and a chlorine and a copper atom occupying the apical positions. The metal atoms are μ_2 -bridged by four acetato groups and the molecular symmetry is close to C_{2h} . The two symmetry-independent chelating betaine molecules are present in their zwitterionic, neutral form.

KEY WORDS: Betaine compounds; dinuclear copper(II) complexes; X-ray structure.

Introduction

Recently, a great deal of attention has been paid to crystal engineering of low-dimensional magnetic structures, where a magnetic metal ion carrying an unpaired spin is bridged by diamagnetic ligands.¹ Such ligands provide a superexchange pathway which determines the strength and type of magnetic coupling, J , between the metal ions. The sign and value of the exchange constant varies with bond length and bond angle and other factors like ligand orientation. Initiatory steps are being given in order to reliably calculate the exchange constant from first principles,² and a systematic study involving different types

of ligands is desirable. Aiming at synthesizing a low-dimensional Cu(II) magnetic system we have used the ligand betaine (trimethylglycine), a well-known chelating agent of several transition metals and lanthanides.³ An additional interesting feature of betaine compounds is that betaine salts and adducts often exhibit interesting physical properties such as ferroelectric or antiferroelectric ordering at low temperature.⁴ A ferroelastic behaviour inducing phase transitions to both commensurate and incommensurate superstructures and an anomalous temperature dependence of dielectric and elastic properties has been reported for a few betaine compounds.⁵ It has been found that a stable [Cu(bet)₄]²⁺ core can be used as "metallo ligand" to bind other hard metal ions such as Ca^{II} and Li^I to form heterometallic complexes,⁶ thus providing a new synthetic route for heterometallic complexes in metal carboxylate chemistry.

Betaine has been used in Medicine for several purposes including the treatment of patients

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with homocystinuria⁷ and might be considered as a good chelating agent for promoting the excretion of copper in patients with Wilson's disease and hypersensitivity to D-penicillamine,⁸ as a suitable alternative to this drug.

We report here the synthesis and crystal structure of a new copper(II) dinuclear compound bridged by the carboxylate groups of betaine ligands. Copper(II) dinuclear compounds have been extensively studied,⁹ in the context of their magnetic properties. If the two metal ions interact through the bridge, then the local spins $S_A = S_B = 1/2$ are not good quantum numbers. The good spin quantum numbers are then $S = 0$ (singlet) and $S = 1$ (triplet), the singlet state corresponding to an "antiferromagnetic" coupling of the two spins usually lying lower in energy than the triplet. However, the 'exchange' gap, J , between singlet and triplet states can usually be overcome at temperatures below room temperature, resulting in a maximum of the magnetic susceptibility. The first compound for which the magnetic properties have been examined in detail was diaquatetra- μ -acetato-dicopper(II) where the copper atoms are separated by 2.64 Å in a square bipyramidal environment.¹⁰ The magnetic susceptibility shows a maximum around 270 K, due to an antiferromagnetic coupling between the two ions, corresponding to an exchange J value of -296 cm^{-1} .

Emori *et al.* have prepared and characterized by means of magnetic susceptibility and IR-spectroscopy a series of carboxylate compounds, finding that the mixed carboxylates with betaine have the Cu(II) acetate-type dinuclear structure. These authors tried to estimate the value of the exchange coupling through betaine bridges for the 'hypothetical' dinuclear betaine compound which we report on this work. They estimated $J = -262 \text{ cm}^{-1}$ and $\mu_{\text{eff}} = 1.44\mu_B$, for the exchange coupling and effective moments, respectively.¹¹

Experimental

Copper chloride hydrated was added to an aqueous solution of betaine in a 1:2 molar

proportion. After a few months single crystals with different shades of green grew spontaneously from the solution. Two different compounds were identified by single crystal X-ray diffraction, the title compound and bis(betainato-O)-dichloro-copper(II) dichloride.¹²

Intensity data were collected at room temperature on a CAD-4 automated 4-circle diffractometer using graphite monochromatized Mo $K\alpha$ radiation. The cell parameters were determined from a least-squares refinement of 25 strong and well-centered reflections in the θ range 10.42–14.02°. The structure was solved by direct methods using SHELXS-97.¹³ Structure refinement was performed with SHELXL-97¹⁴ and PLATON¹⁵ was used for generating the structure plots and further analysis. All hydrogen atoms were placed

Table 1. Summary of Crystal Data, Data Collection, and Structure Refinement

Compound	Cu ₂ (BET) ₄ Cl ₄ ·4H ₂ O
CCDC deposit no.	CCDC-1003/6019
Color/shape	Green/plate
Crystal dimensions (mm)	0.41 × 0.20 × 0.10
Formula weight (g/mol ¹)	809.54
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.0510(10) \text{ \AA}$ $b = 14.7140(4) \text{ \AA}$ $c = 11.1620(15) \text{ \AA}$ $\beta = 107.40(2)^\circ$
Cell volume (Å ³)	473.07(6)
Z	2
Density (calculated, g/cm ³)	1.552
$\mu_{\text{Mo } K\alpha}$, mm ⁻¹	1.6
Diffractometer/scan mode	Enraf-Nonius CAD4/ ω -2 θ
θ range for data collection	$3.4^\circ < \theta < 25.1^\circ$
Range of h, k, l	$-7 \leq h \leq 13, -17 \leq k \leq 0,$ $-13 \leq l \leq 7$
Decay of standards	<6%
Reflections measured	3182
Independent/observed reflections [$I > 2\sigma(I)$]	3071/2622
Structure solution	SHELXS-97
Structure refinement	SHELXL-97
No. refined parameters	194
Goodness of fit on F^2	1.00
Final R indices	$R_{\text{gt}}(F) = 0.0303, wR_{\text{ref}}(F^2) = 0.0878$
Largest peak and hole (e/Å ³)	-0.50, 0.74

at calculated idealized positions and refined as riding with an isotropic displacement factor equal to $1.2U_{\text{eq}}$ of the parent atoms. The compound contains two disordered water molecules, each molecule is disordered over two sites. The refinement constrained the occupancy of the disordered sites to add to unity. Hydrogen atoms of disordered water molecules were not located. Crystal data, a summary of data collection conditions, and refinement indicators are reported in Table 1.

Results and discussion

Atomic positions of the non-hydrogen atoms and equivalent isotropic thermal parameters are given in Table 2. Selected bond lengths and angles are summarized in Table 3.

The Cu–Cu dimer is tetra bridged by four betaine molecules and two chlorine atoms in axial

positions, as shown in Fig. 1. The environment of the copper ions is square bipyramidal with four carboxy oxygen atoms in the basal planes and a chlorine ion and the other copper atom in apical positions.

The basal planes of the coordination polyhedra of the metal ions are approximately parallel. The coordination complex has exact C_i symmetry, with a crystallographic centre of inversion at the midpoint of the Cu–Cu bond. An approximate binary axis perpendicular to the Cu–Cu bond and passing through the center of inversion relates the two symmetry-independent betaine molecules, which implies the presence of a mirror plane perpendicular to the binary axis. Therefore the overall approximate symmetry of the molecule is C_{2h} , the rms deviation from the ideal geometry being 0.0973 Å. The compound is isostructural with a similar Rh(II) complex reported by Zhou *et al.*,¹⁶ apart from the solvent molecules.

Table 2. Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a	Occupancy
Cu1	0.44349(3)	0.02362(2)	0.59068(3)	0.0224(1)	1
Cl1	0.32251(8)	0.07286(6)	0.72700(8)	0.0398(3)	1
O1	0.6153(2)	0.01441(17)	0.7111(2)	0.0374(7)	1
O2	0.7051(2)	−0.02029(17)	0.5621(2)	0.0393(7)	1
O3	0.4902(2)	0.14535(14)	0.5463(2)	0.0385(7)	1
O4	0.5741(2)	0.10801(14)	0.3943(2)	0.0370(7)	1
N1	0.9515(2)	0.0049(2)	0.7357(3)	0.0357(9)	1
N2	0.5835(2)	0.32716(16)	0.5452(2)	0.0263(7)	1
C1	0.7077(3)	−0.0035(2)	0.6726(3)	0.0288(9)	1
C2	0.8333(3)	−0.0037(2)	0.7757(3)	0.0338(9)	1
C3	0.9732(4)	−0.0767(3)	0.6646(4)	0.0615(16)	1
C4	1.0601(3)	0.0125(3)	0.8547(4)	0.0512(13)	1
C5	0.9477(4)	0.0899(3)	0.6608(4)	0.0524(14)	1
C6	0.5416(3)	0.16311(19)	0.4638(3)	0.0267(8)	1
C7	0.5704(3)	0.26099(19)	0.4396(3)	0.0273(9)	1
C8	0.6846(3)	0.2966(2)	0.6611(3)	0.0377(10)	1
C9	0.4609(3)	0.3426(2)	0.5742(3)	0.0362(10)	1
C10	0.6240(3)	0.4152(2)	0.5015(3)	0.0345(10)	1
Cl2	0.89856(9)	0.21305(7)	0.95253(10)	0.0517(3)	1
O5 ^b	0.7455(7)	−0.2723(6)	1.2042(7)	0.140(3)	0.717(9)
O6 ^b	0.828(2)	−0.1881(17)	0.967(2)	0.1400	0.582(10)
O7 ^b	0.8143(10)	−0.2500(8)	0.9921(10)	0.137(4)	0.283(9)
O8 ^b	0.8126(13)	−0.2181(10)	0.8705(16)	0.1370	0.418(10)

^a $U_{\text{eq}} = 1/3$ of the trace of the orthogonalized *U* Tensor.

^bDisordered positions.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Bond length			
Cu1—Cl1	2.4175(10)	Cu1—O1	1.976(2)
Cu1—O3	1.968(2)	Cu1—Cu1 ^a	2.7664(6)
Cu1—O2 ^a	1.983(2)	Cu1—O4 ^a	1.959(2)
O1—C1	1.249(4)	O2—C1	1.250(4)
O3—C6	1.246(4)	O4—C6	1.247(4)
Bond angle			
Cl1—Cu1—O1	101.08(7)	Cl1—Cu1—O3	96.99(7)
Cu1 ^a —Cu1—Cl1	172.54(3)	Cl1—Cu1—O2 ^a	94.42(7)
Cl1—Cu1—O4 ^a	98.90(7)	O1—Cu1—O3	87.86(10)
Cu1 ^a —Cu1—O1	85.89(7)	O1—Cu1—O2 ^a	164.48(10)
O1—Cu1—O4 ^a	88.49(10)	Cu1 ^a —Cu1—O3	80.48(7)
O2 ^a —Cu1—O3	91.04(10)	O3—Cu1—O4 ^a	164.09(10)
Cu1 ^a —Cu1—O2 ^a	78.66(7)	Cu1 ^a —Cu1—O4 ^a	83.82(7)
O2 ^a —Cu1—O4 ^a	88.36(10)	O1—C1—O2	127.0(3)

^a1 - x, -y, 1 - z.

The Cu—Cu separation is equal to 2.7665(7) Å. The Cu₂Cl₂ group is not completely linear, Cl1—Cu—Cuⁱ angle is 172.54(3)°, the Cu—Cl1 distance is 2.4175(8) Å (i: 1 - x, -y, 1 - z). A similar geometry is spotted in related compounds like tetrakis(μ₂-β-alanine)dichloro-di-copper(II) dichloride monohydrate,¹⁷ tetrakis(μ₂-γ-ammoniobutyrate-O,O')-dichloro-di-copper(II) dichloride trihydrate,¹⁸ and bis(betainato-O)-dichloro-copper(II) dichloride.¹²

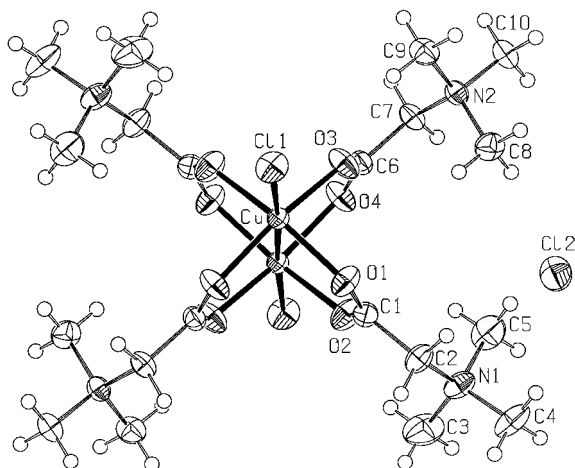


Fig. 1. ORTEP plot of the title compound showing the displacement ellipsoids (drawn at the 50% level) and the labelling scheme. Disordered water molecules were omitted.

The neutral betaine molecules are present in the dipolar, zwitterionic form. Inspection of the C—O distances in the carboxyl groups [1.248(4) Å, 1.248(4) Å; 1.245(4) Å, 1.248(4) Å] shows that these are deprotonated. The geometry of the betaine molecules compares well with other structural studies of betaine adducts.^{19–21} Skeletons C1—C2—N1—C4 and C6—C7—N2—C10 are planar and the remaining methyl groups lie approximately symmetrically above and below this planes (as seen from the torsion angles C1—C2—N1—C3 -67.3(4)°, C1—C2—N1—C5 57.2(4)°, C6—C7—N2—C8 56.9(3)°, C6—C7—N2—C9 -67.1(3)°). The angles C1—C2—N1 and C6—C7—N1 are slightly larger than the ideal tetrahedral value by 7.50(2)° [7.30(2)°]. The carboxylic groups are twisted [18.7(4)° and 23.4(4)°] around the C1—C2 and C6—C7 bonds, respectively. The

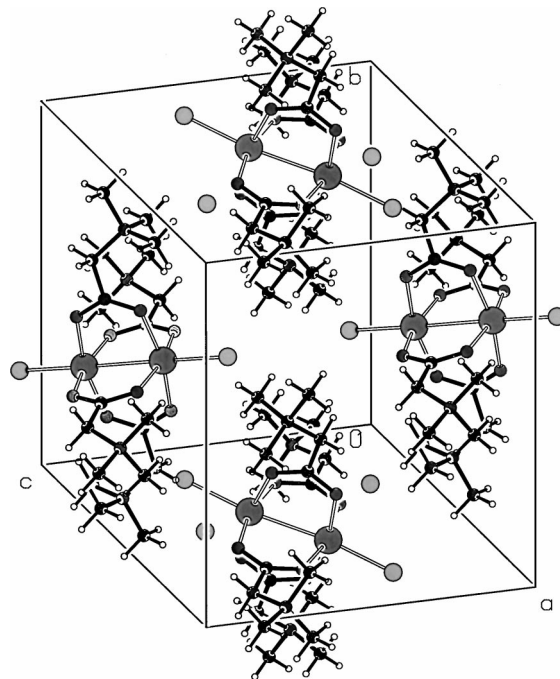


Fig. 2. View of the unit cell contents. Copper atoms are represented as large grey spheres, while chlorine atoms are medium grey spheres. Smaller spheres represent the betaine moieties. For clarity, disordered water molecules were omitted.

carboxy angles O1–C1–O2 and O3–C6–O4 $127.0(3)^\circ$ [$127.1(3)^\circ$], are slightly larger than the average value found in similar acetato complexes but well within the values found in other coordination compounds of betaine.

No classic hydrogen bonds linking the anions and cations together could be identified, although the disordered water molecules are likely to be involved in hydrogen bonding and probably make a significant contribution to the cohesion energy, as found in the similar Rh(II) complex. In addition, a few C–H...X bonds are present, two of them linking the betaines to the isolated anion (C2–H2A...Cl2 with distance $3.706(3)$ Å and angle 157.72° and C7–H7A...Cl2ⁱⁱ with distance $3.606(4)$ Å and angle 156.48° , ii: $x, 1/2 - y, -1/2 + z$). See Fig. 2 for crystal packing. Inspection of the structure with PLATON showed that there are no residual voids accessible to solvent molecules.

Acknowledgment

This work was supported by Fundação para a Ciência e a Tecnologia (FCT).

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