

Structure of Tetrakis(μ -acetato- $\kappa O:\kappa O'$)-bis(2-cyano- κN -guanidine)dicopper(II)

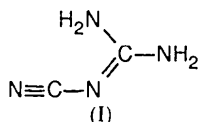
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Abstract. $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_2\text{H}_4\text{N}_4)_2]$, $M_r = 531.19$, monoclinic, $P2_1/n$ (non-standard setting of $P2_1/c$), $a = 8.416$ (2), $b = 15.423$ (5), $c = 8.679$ (3) Å, $\beta = 110.08$ (5)°, $V = 1058.06$ Å³, $Z = 2$, $D_m = 1.65$, $D_x = 1.67$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 21.46$ cm⁻¹, $F(000) = 540$, $T = 295$ K, $R = 0.039$ for 152 least-squares parameters and 1725 unique reflections with $I > 3\sigma(I)$. The centrosymmetric molecular structure of $[\text{Cu}(\text{OAc})_2(\text{cnge})]_2$ (OAc = acetate; cnge = 2-cyanoguanidine) comprises a tetrakis(acetato)-bridged dinuclear copper(II) core with axially located cnge moieties. An intramolecular hydrogen bond dictates a bent coordination mode for the weakly bound cnge molecule.

Introduction. In all previous structural characterizations of copper(II)–cnge [cnge = 2-cyanoguanidine (I)] complexes, the two cnge ligands were found to be located *trans* to each other in the equatorial positions of a tetragonally elongated octahedral copper(II) coordination sphere $\{[\text{Cu}(\text{cnge})_2\text{Cl}_2(\text{H}_2\text{O})_2]$ (Chiesi, Coghi, Mangia, Nardelli & Pelizzi, 1971) and $[\text{Cu}(\text{cnge})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Begley, Hubberstey & Moore, 1985)}. Even in the presence of the tridentate chelating ligand 1-(2-aminoethyl)biguanide (aebg), cnge remains similarly located $\{[\text{Cu}(\text{cnge})(\text{aebg})]\text{SO}_4 \cdot \text{H}_2\text{O}$ (Coghi, Mangia, Nardelli, Pelizzi & Sozzi, 1968)}. The dinuclear structure of copper(II) acetates, $[\text{Cu}(\text{OAc})_2L]_2$, promised the possibility of cnge being located in an axial position of the copper(II) coordination sphere, thus providing a better understanding of the coordination properties of cnge. The synthesis and structural characterization of $[\text{Cu}(\text{OAc})_2(\text{cnge})]_2$ is reported in this paper.



Experimental. The title compound was prepared by the reaction of 2-cyanoguanidine (1.68 g, 0.02 mol) with copper(II) acetate monohydrate (3.99 g, 0.02 mol) in aqueous solution (100 cm³). Evaporation of solvent at 278 K over a period of 5 d gave

dark green crystals. Yield 3.7 g, 70%. A suitable crystal (0.3 × 0.2 × 0.2 mm) was chosen and mounted in a Lindemann tube. D_m was determined by flotation in hexane/bromoform. Oscillation and Weissenberg photographs revealed the space group $[P2_1/n$; non-standard setting of $P2_1/c$ (No.14)] and preliminary cell parameters. X-ray diffraction data were collected on a Hilger & Watts Y290 four-circle diffractometer using $\omega/2\theta$ scans. 12 reflections having $11 < \theta < 14^\circ$ were used to determine accurate cell parameters. Absorption corrections were not applied. Data were collected with $-9 < h < 9$, $0 < k < 18$, $0 < l < 10$. No intensity loss for three control reflections. Max. $\sin\theta/\lambda = 0.5946$ Å⁻¹. Of the 3309 unique reflections measured, 1725 had net counts exceeding $3\sigma(I)$ and were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods, with a weighting scheme based on a four-term Chebyshev polynomial with coefficients 136.8907, 195.3351, 71.9150 and 4.8661, using the CRYSTALS suite of programs (Watkin, Carruthers & Betteridge, 1985). H atoms of the cnge moiety were found in a difference map and refined isotropically; those of the acetate moieties were placed geometrically with 50% occupancy of the two possible staggered conformations; 152 least-squares parameters; refinement on F magnitudes gave $R = 0.039$, $wR = 0.045$. Max. (Δ/σ) in last cycle = 0.68; largest peak in final difference Fourier map had a height of 0.71 e Å⁻³ (most intense peaks in the vicinity of the heavy atoms); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The molecular structure and atomic numbering scheme for $[\text{Cu}(\text{OAc})_2(\text{cnge})]_2$ are shown in Fig. 1 and the crystal packing is displayed in Fig. 2. Atomic coordinates are listed in Table 1,† interatomic distances and angles are given in Table 2.

† Lists of structure factors, anisotropic thermal parameters for H and non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55435 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0493]

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The centrosymmetric dimeric molecular unit comprises a tetrakis(acetato)-bridged dinuclear copper(II) core with 2-cyanoguanidine in the axial positions (Fig. 1). The dimers are held in the lattice by an intermolecular hydrogen-bonding network involving the H atoms of the cnge molecule (Fig. 2; Table 3). The geometry of the [Cu₂(OAc)₄] core is similar to that in [Cu(OAc)₂(H₂O)]₂ and related compounds (de Meester, Fletcher & Skapski, 1973; Brown & Chidambaram, 1973), the effective magnetic moment of [Cu(OAc)₂(cnge)]₂ ($\mu_{\text{eff}} = 1.39$ BM) being typical of these dimeric species (Kato & Muto, 1988). However, the N—C≡N group of the cnge molecule is not collinear with the Cu...Cu vector, the Cu...N≡C angle being 135.9(3)°. In all other structurally characterized copper(II)-cnge complexes the N—C≡N group is effectively collinear with the coordination axis (Coghi *et al.*, 1968; Chiesi *et al.*, 1971; Begley *et al.*, 1985). The distortion of the coordination geometry is attributed to the formation

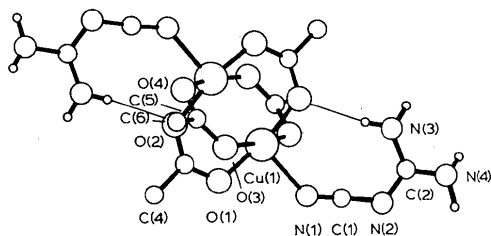


Fig. 1. Molecular structure and atomic numbering scheme for [Cu(OAc)₂(cnge)]₂ showing the intramolecular hydrogen bonding.

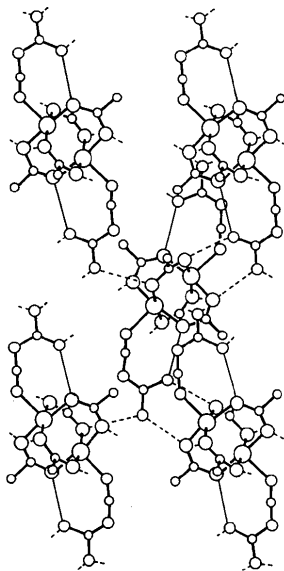


Fig. 2. Crystal packing for [Cu(OAc)₂(cnge)]₂ showing the intermolecular hydrogen bonding.

Table 1. Final positional parameters ($\times 10^3$) and equivalent isotropic temperature parameters ($\times 10^3$) for [Cu(OAc)₂(cnge)]₂

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq} (Å ²)
Cu(1)	462.69 (2)	54.10 (2)	98.97 (4)	28.2
C(1)	344.7 (4)	216.8 (2)	231.4 (3)	35.9
C(2)	263.9 (4)	340.9 (2)	89.2 (4)	38.4
N(1)	389.6 (4)	146.2 (2)	245.9 (3)	40.0
N(2)	292.4 (5)	296.4 (2)	227.2 (4)	51.0
N(3)	284.0 (5)	308.5 (2)	-43.5 (5)	46.6
N(4)	217.5 (4)	423.3 (2)	89.9 (4)	54.5
O(1)	584.9 (3)	-27.6 (1)	275.2 (3)	41.4
O(2)	359.8 (3)	121.2 (1)	-106.2 (3)	41.7
O(3)	260.0 (3)	-18.4 (2)	46.1 (3)	42.2
O(4)	684.4 (3)	106.6 (1)	131.2 (3)	41.1
C(3)	648.7 (4)	-96.9 (2)	245.2 (4)	35.7
C(4)	743.1 (6)	-152.0 (3)	390.1 (5)	61.4
C(5)	219.1 (4)	-77.1 (2)	-59.4 (4)	35.3
C(6)	44.9 (4)	-114.4 (3)	-104.9 (5)	50.0

Table 2. Interatomic distances (Å) and angles (°) in [Cu(OAc)₂(cnge)]₂

Cu(1)—Cu(1) ⁱ	2.621 (1)	O(3)—C(5)	1.249 (4)
Cu(1)—N(1)	2.136 (3)	O(4)—C(5)	1.266 (4)
Cu(1)—O(1)	1.976 (2)	C(5)—C(6)	1.496 (4)
Cu(1)—O(2)	1.983 (2)	N(1)—C(1)	1.146 (4)
Cu(1)—O(3)	1.958 (2)	C(1)—N(2)	1.300 (4)
Cu(1)—O(4)	1.964 (2)	N(2)—C(2)	1.328 (4)
O(1)—C(3)	1.264 (4)	C(2)—N(3)	1.318 (4)
O(2)—C(3)	1.242 (4)	C(2)—N(4)	1.331 (5)
C(3)—C(4)	1.499 (5)		
N(1)—Cu(1)—O(1)	98.2 (1)	N(2)—C(2)—N(3)	123.7 (4)
N(1)—Cu(1)—O(2)	93.6 (1)	N(2)—C(2)—N(4)	116.9 (4)
N(1)—Cu(1)—O(3)	96.5 (1)	N(3)—C(2)—N(4)	119.4 (4)
N(1)—Cu(1)—O(4)	95.5 (1)	Cu(1)—O(1)—C(3)	121.7 (2)
O(1)—Cu(1)—O(2)	168.1 (1)	Cu(1)—O(2)—C(3)	125.3 (2)
O(1)—Cu(1)—O(3)	89.9 (1)	O(1)—C(3)—O(2) ⁱ	124.6 (3)
O(1)—Cu(1)—O(4)	86.3 (1)	O(1)—C(3)—C(4)	116.6 (3)
O(2)—Cu(1)—O(3)	90.6 (1)	O(2)—C(3)—C(4)	118.8 (3)
O(2)—Cu(1)—O(4)	90.8 (1)	Cu(1)—O(3)—C(5)	125.8 (2)
O(3)—Cu(1)—O(4)	167.8 (1)	Cu(1)—O(4)—C(5)	121.4 (2)
Cu(1)—N(1)—C(1)	135.9 (3)	O(3)—C(5)—O(4) ⁱ	124.0 (3)
N(1)—C(1)—N(2)	175.1 (4)	O(3)—C(5)—C(6)	118.1 (3)
C(1)—N(2)—C(2)	117.9 (3)	O(4)—C(5)—C(6)	118.0 (3)

Symmetry code: (i) 1 - x, -y, -z.

Table 3. Hydrogen-bonding distances (Å) and angles (°) for [Cu(OAc)₂(cnge)]₂

N—H...O	N...O	N—H	H...O	N—H...O
N(3)—H(1)...O(2) ⁱ	3.04	0.85	2.20	171.4
N(3)—H(2)...O(4) ⁱⁱ	2.96	0.84	2.12	173.2
N(4)—H(3)...O(1) ⁱⁱⁱ	3.04	0.77	2.27	172.7
N(4)—H(4)...O(3) ^{iv}	3.23	1.01	2.23	168.0

Symmetry code: (i) x, y, z; (ii) -0.5 + x, 0.5 - y, 0.5 + z; (iii) -0.5 + x, 0.5 - y, -0.5 + z; (iv) 0.5 - x, 0.5 + y, 0.5 - z.

of an intramolecular hydrogen bond [N(3)—H(1)...O(2); Fig. 1, Table 3] and is facilitated by the weak binding of the cnge molecule compared with that in other copper(II)-cnge complexes as seen by the considerably extended Cu(1)—N(1) distance (Table 4). Weak axial binding is typical of d^9 systems with singly occupied $d_{x^2-y^2}$ and fully occupied d_{z^2}

Table 4. Coordination bond lengths (Å) and angles (°) for copper(II)-cnge complexes

	Free cnge ^a	Acetate ^b	Nitrate ^c	Chloride ^d	Sulfate ^e
Cu(1)—N(1)	—	2.136	1.92	1.92	1.96
N(1)—C(1)	1.174	1.146	1.16	1.16	1.17
C(1)—N(2)	1.307	1.300	1.29	1.29	1.28
N(2)—C(2)	1.343	1.328	1.33	1.33	1.36
C(2)—N(3)	1.344	1.318	1.34	1.34	1.33
C(2)—N(4)	1.335	1.331	1.31	1.32	1.33
$\nu_{as}(\text{NCN})$	2209 2165	2209 2168	2240 2200	2250 2200	— —

References: (a) Hirschfeld & Hope (1980); (b) [Cu(OAc)₂(cnge)]₂, this work; (c) [Cu(cnge)₂(H₂O)₂](NO₃)₂·2H₂O (Begley, Hubberstey & Moore, 1985); (d) [Cu(cnge)₂(H₂O)₂Cl₂] (Chiesi, Coghi, Mangia, Nardelli & Pelizzi, 1971); (e) [Cu(cnge)(aebg)]SO₄·H₂O [aebg = 1-(2-aminoethyl)biguanide] (Coghi, Mangia, Nardelli, Pelizzi & Sozzi, 1968).

orbitals. IR spectroscopy confirms the weakness of the coordination; the $\nu_{as}(\text{NCN})$ doublet, which normally shifts from 2209/2165 cm⁻¹ for free cnge to higher frequency on coordination to copper(II), is virtually unaltered for [Cu(OAc)₂(cnge)]₂ at 2209/2168 cm⁻¹ (Table 4). The molecular geometry of the cnge molecule in [Cu(OAc)₂(cnge)]₂ does not differ sufficiently from those of the cnge molecules in the

other complexes (Table 4) to provide supporting evidence for a different type of interaction. Nonetheless, the bent coordination angle suggests that the interaction might involve *p* orbitals on the nitrile N atom with both σ and π symmetry; the *d*_{z² orbital of the Cu atom exactly bisects these two orbitals.}

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Structure of Bis(2,2'-bipyrimidine-*N,N'*)dichlorocobalt(II), [Co(bpm)₂Cl₂]

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Abstract. [CoCl₂(C₈H₆N₄)₂], *M_r* = 446.2, triclinic, *P* $\bar{1}$, *a* = 8.848 (2), *b* = 9.375 (1), *c* = 11.906 (2) Å, α = 74.10 (1), β = 74.36 (1), γ = 83.43 (1)°, *V* = 913.8 (3) Å³, *Z* = 2, *D_x* = 1.622 g cm⁻³, $\lambda(\text{Mo K}\alpha)$ = 0.71069 Å, μ = 12.5 cm⁻¹, *F*(000) = 450, *T* = 298 K, final *R* = 0.034 and *wR* = 0.037 for 3017 reflections with *I* > 3 σ (*I*). The compound consists of neutral [Co(bpm)₂Cl₂] units (bpm = 2,2'-bipyrimidine). Two bidentate bpm ligands and two Cl anions occupying *cis* positions achieve a distorted octahedral environment around the metal ion. The bipyrimidine acts as

a bidentate ligand. This compound represents the first structurally characterized example of a bipyrimidine-cobalt(II) mononuclear complex.

Introduction. Compounds of 2,2'-bipyrimidine (bpm) with transition metals have received great attention in the last decade. These complexes were studied for diverse chemical applications such as (a) synthetic models for the active site of cytochrome oxidase (Petty, Welch, Wilson, Bottomley & Kadish, 1980), (b) photocatalyzed processes (Haim, 1983; Petersen,