

Sinditskii, V. P., Sokol, V. I., Vogelzang, A. E., Dutov, M. D., Serushkin, V. V., Porai-Koshits, M. A. & Svetlov, B. S. (1987). *Zh. Neorg. Khim.* **32**, 1950–1955.
 Syntex (1973). *XTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California, USA.
 Vreugdenhil, W., Haasnoot, J. G. & Reedijk, J. (1990). *Inorg. Chim. Acta*, **167**, 109–113.

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Aqua[1,3-propanediyl-diiminobis(1,3-dimethyl-5-nitrosouracilato)- $\kappa^4 N^5, N^6, N^{15}, N^{16}$]copper(II) Monohydrate

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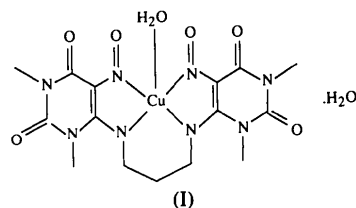
Abstract

The versatile $C_{15}H_{20}N_8O_6$ ligand is coordinated through four of its N atoms to the Cu^{II} atom in a double-deprotonated tetradentate fashion to give the title complex, aqua[1,3-propanediyl-diimino- $\kappa^2 N$ -bis(1,3-dimethyl-5-nitroso-2,4(1*H*,3*H*)-pyrimidinedionato- $\kappa^2 N^5, N^6(2-)$]copper(II) monohydrate, $[Cu(C_{15}H_{18}N_8O_6)(H_2O)] \cdot H_2O$. A water molecule occupies the axial position of the distorted square-pyramidal coordination environment of the Cu atom.

Comment

In a previous report we showed that α, ω -bis(1,3-dimethyl-5-nitrosouracil-6-ylamino)propane (H_2L), a dioxime pyrimidine ligand, reacts with copper(II) in basic medium giving the mononuclear complex $[Cu(L)(H_2O)] \cdot 3H_2O$ (Colacio, Dominguez-Vera, Escuer, Kivekäs & Romerosa, 1994). In this compound, the Cu^{II} atom occupies the N_4 inner site of the ligand and a water

molecule coordinates at the axial position. The three lattice water molecules and the $[Cu(L)(H_2O)]$ complex unit are involved in an extended network of hydrogen bonds, which is responsible for the weak antiferromagnetic interaction observed for the compound. In this paper, we describe the preparation and present the X-ray results for the monohydrated complex, $[Cu(L)(H_2O)] \cdot H_2O$, (I).



The H_2L ligand is coordinated through four of its N atoms to the Cu^{II} atom in a double-deprotonated tetradentate fashion (L^{2-}), the deprotonated N atoms being N(6) and N(16). The complex unit of the present compound is essentially similar to that of $[Cu(L)(H_2O)] \cdot 3H_2O$ (Colacio, Dominguez-Vera, Escuer, Kivekäs & Romerosa, 1994), the Cu atom occupying the inner site of the tetradentate L^{2-} ligand. The complex unit is approximately coplanar and the six-membered ring [Cu, N(6), C(7), C(8), C(17), N(16)] has a boat conformation. The C—O distances are typical for C=O bonds. Moreover, the distances and angles in the CNO groups are approximately similar in both compounds and the values agree quite well with those reported for oximate complexes (Korvenranta, Saarinen & Näsäkkälä, 1982) and also with those observed for 6-amino-3-methyl-5-nitrosouracil complexes (Romero, Moreno, Ruiz, Sanchez & Nieto, 1986).

The coordination of the Cu^{II} atoms in the title compound and in $[Cu(L)(H_2O)] \cdot 3H_2O$ is quite similar, the polyhedra being distorted square-based pyramids. However, there are also some significant differences between the two coordination spheres. The basal plane of the coordination sphere is more planar in the title compound than in $[Cu(L)(H_2O)] \cdot 3H_2O$, the greatest deviation of an

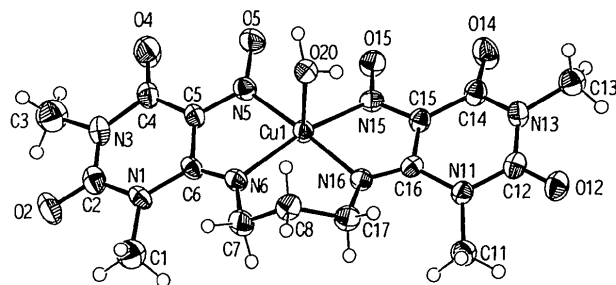


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as spheres of arbitrary radii.

N atom from the basal N₄ plane being 0.083 (3) Å compared with 0.138 (3) Å in [Cu(L)(H₂O)]·3H₂O. In the title compound, the axial Cu(1)—O(20) distance is about 0.062 (3) Å shorter than in [Cu(L)(H₂O)]·3H₂O and the metal is shifted more from the basal N₄ plane towards the axial ligand [0.224 (1) versus 0.152 (1) Å], indicating a stronger Cu—O bond in the title compound.

The hydrogen-bond networks are different in the two compounds compared above. The number of hydrogen bonds is smaller in the title compound owing to fewer molecules of water of crystallization.

Experimental

The ligand C₁₅H₂₀N₈O₆ (H₂L) was prepared as described by Colacio, Dominguez-Vera, Escuer, Kivekäs & Romerosa (1994). [Cu(ClO₄)₂].6H₂O (4 mmol) was added to a stirred suspension of H₂L (1 mmol) in 50 ml ethanol. After 10 min, all the ligand had dissolved and a green powder of the complex [Cu(μ-L)Cu(ClO₄)₃].CH₃CH₂OH.2H₂O precipitated, which was filtered off, washed with ethanol and air dried. Recrystallization from an acetonitrile/water (25:1 v/v) solution produced a small amount of [Cu(L)(H₂O)]·H₂O crystals.

Crystal data

[Cu(C ₁₅ H ₁₈ N ₈ O ₆)(H ₂ O)]· H ₂ O	Mo Kα radiation
<i>M_r</i> = 505.94	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2 ₁ / <i>c</i>	θ = 8.4–13.2°
<i>a</i> = 10.809 (1) Å	μ = 1.21 mm ⁻¹
<i>b</i> = 8.4044 (9) Å	<i>T</i> = 296 K
<i>c</i> = 21.119 (3) Å	Prism
β = 96.63 (1)°	0.32 × 0.30 × 0.25 mm
<i>V</i> = 1905.7 (4) Å ³	Blue
<i>Z</i> = 4	
<i>D_x</i> = 1.763 Mg m ⁻³	

Data collection

Nicolet P3F diffractometer	<i>R</i> _{int} = 0.017
ω scans	θ _{max} = 26.5°
Absorption correction:	<i>h</i> = 0 → 14
empirical via ψ scans	<i>k</i> = 0 → 11
<i>T</i> _{min} = 0.894, <i>T</i> _{max} = 1.000	<i>l</i> = -27 → 27
4470 measured reflections	3 standard reflections
3959 independent reflections	monitored every 150 reflections
3121 observed reflections	intensity decay: 1.0%
[<i>F</i> > 4σ(<i>F</i>)]	

Refinement

Refinement on <i>F</i>	Weighting scheme based on measured e.s.d.'s
<i>R</i> = 0.040	(Δ/σ) _{max} = 0.57
<i>wR</i> = 0.036	Δρ _{max} = 0.5 e Å ⁻³
<i>S</i> = 2.064	Δρ _{min} = -0.6 e Å ⁻³
3121 reflections	Atomic scattering factors from <i>Xtal3.0</i> (Hall & Stewart, 1990)
321 parameters	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu1	0.97034 (3)	0.72694 (4)	0.42757 (2)	0.0279 (1)
N1	1.1802 (2)	0.6967 (3)	0.2745 (1)	0.0332 (9)
C1	1.1336 (4)	0.5811 (4)	0.2245 (2)	0.0474 (9)
O2	1.3495 (2)	0.7257 (3)	0.2208 (1)	0.0512 (9)
C2	1.2974 (3)	0.7585 (4)	0.2673 (1)	0.037 (1)
N3	1.3546 (2)	0.8572 (3)	0.3138 (1)	0.0369 (9)
C3	1.4813 (4)	0.9113 (5)	0.3072 (2)	0.057 (1)
O4	1.3610 (2)	0.9939 (3)	0.4060 (1)	0.054 (1)
C4	1.3027 (3)	0.9043 (4)	0.3684 (1)	0.035 (1)
O5	1.1572 (2)	0.9570 (3)	0.4672 (1)	0.0428 (8)
N5	1.1200 (2)	0.8593 (3)	0.4255 (1)	0.0318 (9)
C5	1.1834 (3)	0.8332 (4)	0.3750 (1)	0.029 (1)
N6	1.0101 (2)	0.6774 (3)	0.3390 (1)	0.0302 (8)
C6	1.1184 (3)	0.7278 (4)	0.3276 (1)	0.0283 (9)
C7	0.9156 (3)	0.5945 (5)	0.2950 (2)	0.038 (1)
C8	0.7858 (3)	0.6199 (4)	0.3147 (2)	0.036 (1)
N11	0.7052 (2)	0.4533 (3)	0.5034 (1)	0.0299 (8)
C11	0.6632 (3)	0.3115 (4)	0.4655 (1)	0.0368 (8)
O12	0.5584 (2)	0.3999 (2)	0.5687 (1)	0.0433 (8)
C12	0.6500 (3)	0.4747 (4)	0.5589 (1)	0.032 (1)
N13	0.7052 (2)	0.5818 (3)	0.6030 (1)	0.0339 (9)
C13	0.6403 (3)	0.6178 (4)	0.6583 (2)	0.0420 (9)
O14	0.8744 (2)	0.7174 (3)	0.6476 (1)	0.0495 (9)
C14	0.8234 (3)	0.6492 (4)	0.6012 (1)	0.034 (1)
O15	1.0452 (2)	0.7795 (3)	0.56553 (9)	0.0374 (7)
N15	0.9707 (2)	0.7119 (3)	0.5236 (1)	0.0291 (8)
C15	0.8714 (3)	0.6341 (4)	0.5398 (1)	0.028 (1)
N16	0.8308 (2)	0.5756 (3)	0.4303 (1)	0.0273 (8)
C16	0.7994 (3)	0.5530 (3)	0.4866 (1)	0.0262 (9)
C17	0.7568 (4)	0.5223 (5)	0.3714 (2)	0.038 (1)
O20	0.8365 (3)	0.9271 (3)	0.4097 (1)	0.0360 (9)
O21	0.6356 (3)	0.8477 (4)	0.4742 (2)	0.061 (1)

Table 2. Selected geometric parameters (Å, °)

Cu1—N5	1.968 (3)	O5—N5	1.236 (3)
Cu1—N15	2.031 (2)	O15—N15	1.261 (3)
Cu1—N6	2.011 (2)	N5—C5	1.351 (4)
Cu1—N16	1.979 (3)	N15—C15	1.334 (4)
Cu1—O20	2.222 (3)	N6—C6	1.293 (4)
O2—C2	1.218 (4)	N16—C16	1.287 (4)
O4—C4	1.216 (4)		
N5—Cu1—N6	80.3 (1)	Cu1—N5—O5	124.1 (2)
N5—Cu1—N15	98.7 (1)	Cu1—N15—O15	126.9 (2)
N5—Cu1—N16	174.4 (1)	Cu1—N5—C5	114.8 (2)
N5—Cu1—O20	95.1 (1)	Cu1—N15—C15	112.1 (2)
N6—Cu1—N15	160.0 (1)	O5—N5—C5	121.1 (3)
N6—Cu1—N16	98.0 (1)	O15—N15—C15	120.5 (2)
N6—Cu1—O20	101.8 (1)	Cu1—N6—C7	118.5 (2)
N15—Cu1—N16	81.1 (1)	Cu1—N16—C17	120.9 (2)
N15—Cu1—O20	98.2 (1)	C7—C8—C17	115.0 (3)
N16—Cu1—O20	90.5 (1)		

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O(20)—H(20A)···O(21)	0.76 (4)	2.775 (4)	180 (4)
O(20)—H(20B)···O(15 ⁱ)	0.95 (4)	2.799 (3)	159 (3)
O(21)—H(21A)···O(4 ⁱ)	0.84 (4)	2.856 (4)	179 (4)
O(21)—H(21B)···O(12 ⁱⁱ)	0.83 (4)	3.017 (4)	151 (4)

Symmetry codes: (i) 2 - *x*, 2 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*.

Non-H atoms were refined with anisotropic displacement parameters and H atoms with isotropic displacement parameters, except for those of the methyl groups, which were refined as rigid groups. The structure was solved with *SHELXS86* (Sheldrick, 1985) and refined using *Xtal3.0* (Hall & Stewart, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AB1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Colacio, E., Dominguez-Vera, J. M., Escuer, A., Kivekäs, R. & Romerosa, A. (1994). *Inorg. Chem.* **33**, 3914–3924.
- Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal3.0 Reference Manual*. Univs. of Western Australia, Australia, and Maryland, USA.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Korvenranta, J., Saarinen, H. & Näsäkkälä, M. (1982). *Inorg. Chem.* **21**, 4296–4300.
- Romero, M. A., Moreno, M. N., Ruiz, J., Sanchez, M. P. & Nieto, F. (1986). *Inorg. Chem.* **25**, 1498–1501.
- Sheldrick, G. M. (1985). *SHELX86. Program for Crystal Structure Determination*. Univ. of Göttingen, Germany.

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Copper Disordered Hexakis(phenylethynyl)pentaargentate(I) Cluster

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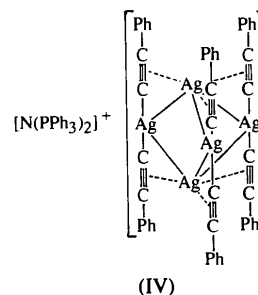
Abstract

The X-ray single-crystal structure determination of an anionic cluster, $[\text{Ag}_{4.46}\text{Cu}_{0.54}(\text{C}_8\text{H}_5)_6]^-$, with bis(triphenylphosphine)iminium counterions, $[\text{N}(\text{C}_{18}\text{H}_{15}\text{P})_2]^+$, prepared from the reaction of $[\text{Cu}(\text{C}\equiv\text{CPh})_2]^-$ and $[\{\text{Ag}(\text{C}\equiv\text{CPh})\}_n]^-$ in a 1:4 mole ratio, revealed a trigonal bipyramidal arrangement of Ag_5 with positional disorder, with copper substituting silver in some equatorial positions making the ratio of metal atoms 8.3 Ag:1 Cu. Each equatorial metal atom is σ bonded to the alkynyl ligands in an almost linear fashion. Ag atoms in apical positions are asymmetrically π bonded, with varying degrees of strength, to three alkyne ligands each.

Comment

We have recently reported the syntheses and structures of the pentanuclear clusters $[\text{Au}_3\text{Cu}_2(\text{C}\equiv\text{CPh})_6]^-$, (I) (Abu-Salah, Al-Ohaly & Knobler, 1985), and $[\text{Au}_3\text{Ag}_2(\text{C}\equiv\text{CPh})_6]^-$, (II) (Mazhar-Ul-Haque, Horne & Abu-Salah, 1992). The structures of both clus-

ters comprise trigonal bipyramids of metal atoms, with Au atoms occupying equatorial positions and Cu or Ag atoms in apical positions. We have also reported the syntheses and characterization of the homonuclear $[\text{Ag}_5(\text{C}\equiv\text{CPh})_6]^-$ and the heteronuclear $[\text{Ag}_4\text{Cu}(\text{C}\equiv\text{CPh})_6]^-$ anionic clusters (Abu-Salah, Al-Ohaly & Mutter, 1990). We assigned the Cu atom in the latter cluster an equatorial position with the four Ag atoms in two environments, namely two equatorial and two apical. X-ray single-crystal structure determination of the same silver–copper cluster compound, (IV), showed that copper is not present in the 4:1 ratio, but in a lower one of 8.3:1, which has also been shown by recent elemental analyses.



The crystal structure of the pentanuclear anionic cluster compound is shown in Figs. 1 and 2. The metal atoms have a trigonal bipyramidal arrangement. The equatorial positions were found to be disordered between Ag and Cu atoms in the ratio 4.6:1. Thus, the total Ag:Cu ratio in the crystal is 8.3:1. This ratio is in full agreement with the chemical analysis. Since the Ag atoms are predominant and the presence of the Cu atom, which has shorter $\text{Cu}\cdots\text{C}$ bond length than $\text{Ag}\cdots\text{C}$, does not have an obvious effect on the displacement parameters of the C atoms bonded to the metal atoms, the anionic cluster will be described as $[\text{Ag}_5(\text{C}\equiv\text{CPh})_6]^-$.

The present anionic cluster, (IV), is generally similar to that found in (I) and (II), except it has higher symmetry. The Ag(1) atom lies on the twofold axis, which passes through the midpoints of $\text{Ag}(2)\cdots\text{Ag}(2a)$ and $\text{Ag}(3)\cdots\text{Ag}(3a)$. The non-bonding metal–metal distances are $\text{Ag}(1)\cdots\text{Ag}(2)$ 3.945 (1), $\text{Ag}(2)\cdots\text{Ag}(2a)$ 3.893 (1) Å and axial $\text{Ag}(3)\cdots\text{Ag}(3a)$ 3.783 (1) Å. The latter distance is equal to the axial $\text{Ag}\cdots\text{Ag}$ distance in (II). On the other hand, the distances of Ag(3) to the equatorial atoms, Ag(1), Ag(2) and Ag(2a) are 3.024 (1), 2.903 (1) and 2.934 (1) Å, respectively, indicating substantial metal–metal bonding.

These bond lengths are less than or equal to the $\text{Ag}\cdots\text{Ag}$ bond of 3.033 Å found in polymeric $[\text{Ag}_2(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2]$, (III) (Corfield & Shearer, 1966). Each Ag atom at an equatorial position is end-on σ -bonded to two ethynyl atoms in a nearly linear fashion; the $\text{C}(81)\text{—Ag}(1)\text{—C}(81a)$ and $\text{C}(82)\text{—}$