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A Dinuclear Copper(II) Complex Bridged by a *trans*-Oxamidate Ligand

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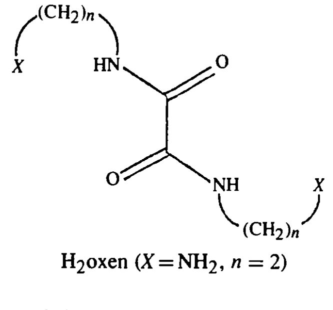
Abstract

The title complex, μ-*N*,*N*′-bis(2-aminoethyl)oxamidato-*N*,*O*′:*N*′,*O*-bis[(thiocyanato-*N*)copper(II)], $[Cu_2(NCS)_2(C_6H_{12}N_4O_2)]$, forms a centrosymmetric binuclear molecule with oxen^{2-} [*N*,*N*′-bis(2-aminoethyl)oxamide dianion] acting as a bis-chelating terdentate ligand. The structure consists of molecular Cu^{II}–Cu^{II} units in which the Cu^{2+} ions are bridged by an oxamidato group in a *trans* conformation, and are located in an approximately square-planar environment.

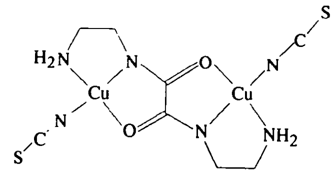
Comment

The *N*,*N*′-disubstituted oxamides, such as H_2oxen, constitute one of the most thoroughly investigated families of bridging ligands (Ojima & Nonoyama, 1988).



H_2oxen ($X = NH_2$, $n = 2$)

The versatility of these ligands is based on (i) the bidentate character of their mononuclear complexes, which can be used as chelating units towards a second metal ion to form polymetallic species (Journaux, Sletten & Kahn, 1985, 1986), (ii) the wide variety of substituted derivatives which can be obtained, yielding different numbers of chelate rings with different donor atoms (Ojima & Nonoyama, 1988), and (iii) their facile *cis*–*trans* conformational change affording symmetric and asymmetric bridges (Lloret *et al.*, 1992). Most of the copper(II) complexes have symmetrical *cis* oxamidato bridges; there are very few reports of crystal structures of copper(II) complexes with oxamidato bridges exhibiting the *trans* conformation (Bencini, Di Vaira, Fabretti, Gatteschi & Zanchini, 1984). The present paper describes the crystal structure of a dinuclear copper(II) complex of *N*,*N*′-bis(2-aminoethyl)oxamide, (I), with the *trans* conformation.



(I)

This complex forms a centrosymmetric binuclear molecule with oxen^{2-} acting as a bis-chelating terdentate ligand. The Cu^{II} ions are bridged by a *trans*-oxamidato group with an inversion centre at the midpoint of the C(1)—C(1*a*) bond, as illustrated in Fig. 1, which also shows the atom-labelling scheme. The packing of the crystal is depicted in Fig. 2.

Each Cu^{II} atom is in an approximately square-planar environment with three atoms [O, N(1) and N(2)] from the oxen^{2-} ligand and one atom [N(3)] from a thiocyanate. The largest deviation from the least-square plane through N(1), N(2), N(3) and O is 0.1405 Å at the O-atom site, and the Cu atom lies only 0.0543 Å out of this plane. The Cu—N(1) bond distance [1.928 (2) Å], which is shorter than Cu—O and Cu—N(2) [2.035 (1) and 2.038 (2) Å, respectively], is in agreement with those found in other oxamidato-bridged copper(II) complexes (Lloret *et al.*, 1992; Okawa, Matsumoto, Koikama, Takede & Kida, 1990). The significant shortening of the Cu—N(1) bond length agrees with the strong basicity of the deprotonated amide N atom.

The deprotonated oxen^{2-} ligand adopts the *trans* conformation forming a five-membered chelate ring with each metal ion. The three atoms Cu, C(2) and C(1*a*) around N(1) lie in a plane with bond angles about N(1) of 116.4 (1), 116.6 (1) and 126.5 (2)° for Cu—N(1)—C(2), Cu—N(1)—C(1*a*) and C(2)—N(1)—C(1*a*), respectively. These data, together with the bond lengths and planarity of the oxamidato bridge, reveal that N(1) and its symmetry-related atom N(1*a*) are sp^2 hybridized and that the π electrons of C(1)—O and C(1*a*)—O(*a*) are delocalized to form a conjugated system. The bridging group [atoms O, N(1*a*), C(1), C(1*a*), O(*a*), N(1)] is planar within experimental error, the Cu atom being displaced by 0.1844 Å from this plane.

Each thiocyanate ligand is approximately linear [N(3)—C(4)—S = 178.7 (2)°], whereas its linkage to Cu is slightly bent [Cu—N(3)—C(4) 168.4 (2)°]. The Cu···Cu separation through the oxen^{2-} bridge is 5.284 Å.

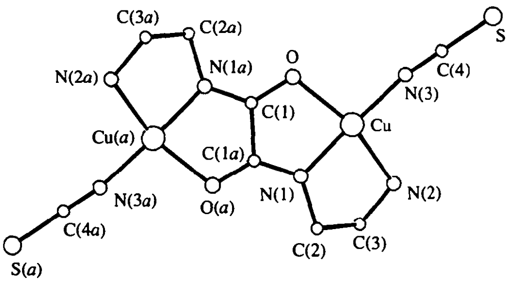


Fig. 1. Molecular structure of the title complex showing the atom-labelling scheme.

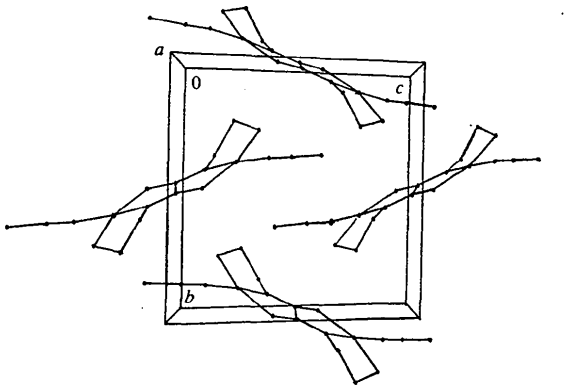


Fig. 2. Crystal packing of the title complex.

Experimental

The H_2oxen ligand and its mononuclear complex, Cu(oxen).$2H_2O$, were obtained according to the literature method (Ojima & Yamada, 1968). The dinuclear complex was prepared as follows. To a heated aqueous solution of Cu(oxen).$2H_2O$ (1 mmol, 40 ml) was added an aqueous solution of copper perchlorate (1 mmol, 5 ml) with stirring. Then, an aqueous solution of sodium thiocyanate (2 mmol, 5 ml) was poured dropwise into the above blue solution, affording a blue–green precipitate that was filtered, washed with water, and dried in a desiccator containing silica gel. Yield: 92%. Analysis: found, C 23.10, H 2.89, N 20.22, Cu 30.35%; calculated for $C_8H_{12}N_6O_2S_2Cu_2$, C 22.98, H 2.98, N 20.06, Cu 30.59%. Well shaped single crystals of this complex were obtained by the slow-diffusion method using an 'H' tube.

Crystal data

$[Cu_2(NCS)_2(C_6H_{12}N_4O_2)]$
$M_r = 415.5$
Monoclinic
$P2_1/c$
$a = 7.046$ (2) Å
$b = 9.919$ (3) Å
$c = 10.392$ (3) Å
$\beta = 109.80$ (2)°
$V = 683.4$ (3) Å^3
$Z = 2$
$D_x = 2.02$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 4.25$–11.9°
$\mu = 3.424$ mm^{-1}
$T = 295$ (2) K
Prismatic
0.44 × 0.32 × 0.30 mm
Blue–green

Data collection

*R*3*m*/*E* diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scans
$T_{min} = 0.819$, $T_{max} = 0.995$
2606 measured reflections
2263 independent reflections
1754 observed reflections
$[I \geq 3\sigma(I)]$

$R_{int} = 0.0092$
$\theta_{max} = 30°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: <1.9%

Refinement

Refinement on *F*
$R = 0.0288$
$wR = 0.0316$
$S = 1.157$
1754 reflections
116 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + (0.003)F^2] \times [1-\exp\{-5(\sin\theta/\lambda)^2\}]$
$(\Delta/\sigma)_{max} = 0.14$

$\Delta\rho_{max} = 0.657$ e Å^{-3}
$\Delta\rho_{min} = -0.471$ e Å^{-3}
Extinction correction: *SHELX76* (Sheldrick, 1976)
Extinction coefficient: 0.0063 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
Cu	0.5490 (1)	0.1040 (1)	0.7432 (1)	0.027 (1)
S	0.2738 (1)	0.1434 (1)	1.0957 (1)	0.037 (1)
N(1)	0.7029 (3)	0.0720 (2)	0.6241 (2)	0.024 (1)
N(2)	0.7857 (3)	0.2281 (2)	0.8378 (2)	0.030 (1)
N(3)	0.4085 (3)	0.1271 (2)	0.8726 (2)	0.032 (1)
O	0.3324 (2)	0.0017 (2)	0.5947 (2)	0.026 (1)
C(1)	0.3929 (3)	−0.0194 (2)	0.4935 (2)	0.021 (1)
C(2)	0.9076 (3)	0.1248 (2)	0.6693 (2)	0.025 (1)
C(3)	0.8983 (3)	0.2553 (2)	0.7431 (2)	0.028 (1)
C(4)	0.3547 (3)	0.1328 (2)	0.9653 (2)	0.025 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu—N(1)	1.928 (2)	N(2)—C(3)	1.483 (4)
Cu—O	2.035 (1)	C(1)—N(1*a*)	1.290 (2)
N(1)—C(1*a*)	1.290 (2)	Cu—N(3)	1.935 (3)
O—C(1)	1.279 (3)	N(1)—C(2)	1.455 (3)
C(2)—C(3)	1.517 (3)	N(3)—C(4)	1.150 (3)
Cu—N(2)	2.038 (2)	C(1)—C(1*a*)	1.518 (4)
S—C(4)	1.642 (3)		
N(1)—Cu—N(2)	82.1 (1)	N(1)—Cu—N(3)	175.6 (1)
N(2)—Cu—N(3)	96.9 (1)	N(1)—Cu—O	82.6 (1)
N(2)—Cu—O	161.4 (1)	N(3)—Cu—O	99.0 (1)
Cu—N(1)—C(2)	116.4 (1)	Cu—N(1)—C(1*a*)	116.6 (1)
C(2)—N(1)—C(1*a*)	126.5 (2)	Cu—N(2)—C(3)	108.9 (1)
Cu—N(3)—C(4)	168.4 (2)	Cu—O—C(1)	109.4 (1)

O—C(1)—N(1*a*)	129.2 (2)	O—C(1)—C(1*a*)	118.9 (2)
N(1)—C(2)—C(3)	105.2 (2)	N(2)—C(3)—C(2)	107.7 (2)
S—C(4)—N(3)	178.7 (2)		

All crystallographic computations were performed using the *SHELX*76 program package (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichloro[(1*H*-benzimidazol-2-ylmethyl)(ethyl)ammonium-*N*^{3}]cobalt(II)

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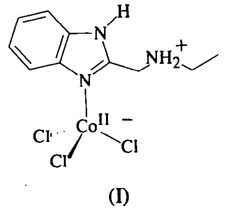
Abstract

The title compound, $[CoCl_3(C_{10}H_{14}N_3)]$, has slightly distorted tetrahedral geometry with monodentate coordination of the protonated ligand. The three Co—Cl distances are 2.2665 (7), 2.2615 (9) and 2.2712 (10) Å. The Co—N distance is 2.029 (2) Å. Antiparallel pairwise packing of molecules allows effective hydrogen bonding of the chloro ligands with both the benzimidazole N [3.439 (2) and 3.699 (2) Å] and ammonium N [3.220 (2) and 3.240 (2) Å] atoms. The respective Cl···H separations are 2.76, 2.90, 2.29 and 2.47 Å.

Comment

As a part of our study of the formation of dinuclear unsymmetrical cobalt(II) complexes, we are investigating the coordination chemistry of cobalt(II) with benzimidazole-containing ligands, which are biologically relevant surrogates for histidine. This type of modeling is of some relevance to bioinorganic chemists, because Co^{II} is used as a spectroscopic or NMR probe for structural changes in reconstituted metalloproteins (Elgren, Ming & Que, 1994; Bertini, Turano & Vila, 1993), as well as being present in the active site of cobalt-dependent methionine aminopeptidase, a non-cobalamin metalloprotein with a dinuclear cobalt species (Roderick & Matthews, 1993). We observed the selective cleavage of the C—N bond linking the 1*H*-benzimidazol-2-ylmethyl and 2-(aminomethyl) moieties by the reaction of Co^{II} perchlorate with a potentially dinucleating unsymmetrical ligand, 6-[bis(1*H*-benzimidazol-2-ylmethyl)aminomethyl]-2-[*N*-(1*H*-benzimidazol-2-ylmethyl)-*N*-(phenylmethyl)aminomethyl]-4-methylphenol (Kamaras, 1994). Site-selective and quantitative C—N bond cleavage in a cobalt(III) polyamine has been observed and a radical reaction mechanism proposed (Calafat & Marzilli, 1993). In order to elucidate whether cleavage of the C—N bond is facilitated by a dinuclear cobalt(II) species or is a typical reaction of cobalt(II) perchlorate with *N*-(1*H*-benzimidazol-2-ylmethyl)alkylamines, we reacted cobalt(II) perchlorate with *N*-(1*H*-benzimidazol-2-ylmethyl)ethylamine. No cleavage was observed and crystals of the title compound, (I), were obtained instead.



(I)

The Co^{II} atom has distorted tetrahedral coordination with three chloride ligands and a 1*H*-benzimidazole ligand. The crystal structure together with the labeling scheme is shown in Fig. 1. The uncoordinated secondary amino group is protonated and compensates the negative charge of the Co^{II}Cl$_3^-$ moiety. The Co atom is displaced from the benzimidazole ligand mean plane (unweighted mean deviation 0.008 Å) by 0.119 (1) Å. The crystal packing (Fig. 2) shows an antiparallel orientation of molecules, allowing effective hydrogen bonding and van der Waals interactions.

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