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[6-(2-Pyridylmethyl)-2,6,10-triazaundecane-1,11-diylbis(2-phenolato)(1−)]copper(II) Tetrafluoroborate Methanol Acetonitrile Solvate (1/1/0.3/0.7)

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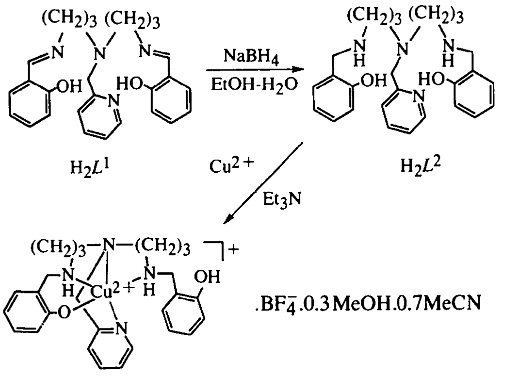
Abstract

In the title compound, $[Cu(C_{26}H_{33}N_4O_2)]BF_4.0.3CH_3OH.0.7CH_3CN$, the ligand is monodeprotonated and pentadentate with an N_4O donor set. The geometry at the Cu^{II} atom is approximately trigonal bipyramidal.

Comment

As part of a program (Adams, Bailey, Fenton & He, 1994; Adams, Bailey, Rodriguez de Barbarin, Fenton & He, 1995) to study the reactivity of copper(II) complexes derived from tripodal and closely related ligands, we have recently shown that linear trinuclear copper(II) complexes can be prepared from acyclic hexadentate (N_4O_2) Schiff base ligands such as H_2L^1, derived from 1,4,7-triazaheptane (3,3′-iminobispropylamine) (Bailey *et al.*, 1995). Reduction of the Schiff base ligand (He, 1995) provides a new saturated ligand (H_2L^2) and, in contrast to the earlier work, no trinuclear complexes have been isolated in reactions with copper(II) salts. This paper presents the crystal structure of a mononuclear copper(II) complex, (I), derived from H_2L^2.



(I)

The copper(II) complex was prepared by addition of 1.5 equivalents of $[Cu(BF_4)_2].H_2O$ to a methanolic solution containing the proligand H_2L^2 and two equivalents of triethylamine (see scheme above). Yellow–green microcrystals of the complex were obtained by adding ethyl acetate to the solution and leaving it to stand at room temperature overnight; recrystallization of these microcrystals from acetonitrile–ethyl acetate gave brown–green single crystals which were suitable for X-ray crystallography.

The structure of the complex cation present in $[Cu(HL^2)]BF_4.0.3MeOH.0.7MeCN$ is shown in Fig. 1. The asymmetric unit contains a mononuclear $[Cu(HL^2)]^+$ cation, a BF_4^- anion and some disordered solvent. Neither the solvent nor the tetrafluoroborate anion interact with the cation. The cation consists of the monodeprotonated ligand coordinated to a single copper ion *via* all three amine N-donor atoms, the pyridine N atom and an O atom from one phenolate group. The second phenol group is neither deprotonated nor coordinated to the metal. The geometry at the copper ion is approximately trigonal bipyramidal with the copper almost in the trigonal plane defined by two secondary amine and one pyridyl N atoms (copper deviates 0.159 Å out of this trigonal plane in the direction of the N2 atom). The tertiary amine N atom and one phenolic O atom occupy the two apical positions in the trigonal bipyramid. The most significant deviation from this geometry is the long bond to the bridgehead amine N2 atom which probably arises due to ligand steric constraints imposed by the ligand.

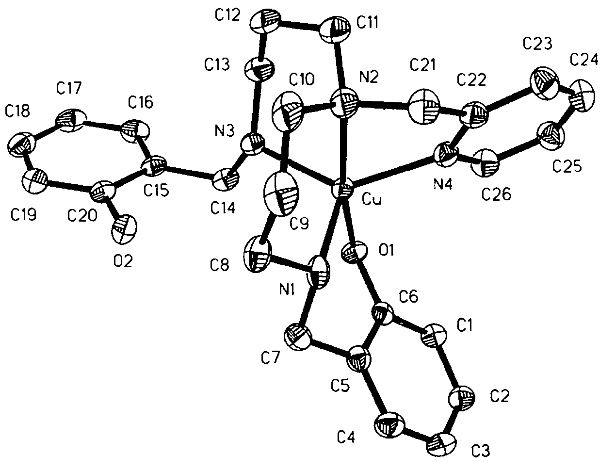


Fig. 1. The coordination environment of the mononuclear cation of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The H atom of the second phenolate group (O2) was located from a difference map and lies in the plane of the phenyl ring. This phenol group forms a hydrogen bond to the phenolate of the second cation [O2···O1(x, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 2.624 (4) Å] resulting in a hydrogen-bonded chain running along the **z** direction. The tertiary amine N3 atom is also within hydrogen-bonding distance of the O2 atom, but the interaction is rather long [O2···N3 2.980 (5) Å]. The 'solvent' is disordered about a centre of symmetry. The N1*S*—C2*S*—C3*S* region is approximately linear and corresponds to the bond lengths expected for acetonitrile. The model consists of 70% acetonitrile and 30% methanol.

This crystal structure demonstrates clearly that the reduced acyclic hexadentate amine phenol H_2L^2 interacts with copper(II) in a completely different manner to the Schiff base precursor H_2L^1. In complexation reactions with copper(II), the acyclic hexadentate Schiff base can fold to form a trinuclear linear complex by sharing three Cu atoms with another ligand molecule. All of the Cu^{II} atoms are four-coordinate but are situated in two different coordination spheres and geometries. The terminal Cu atoms are bonded to an N_3O donor combination which gives a strongly distorted tetrahedral environment, whereas the central Cu atom is in a square-planar environment provided by an N_2O_2 donor set (Bailey *et al.*, 1995). The reduced amine phenol ligands favour the formation of five-coordinate mononuclear complexes which leave one of the phenolic OH groups intact and uncoordinated; this coordination pattern may be accounted for by the flexibility of the reduced ligands. The original imine ligands would have to lose one of the imine C═N bonds in order to generate similar five-coordinate mononuclear complexes.

Experimental

$[Cu(HL^2)]BF_4.0.3MeOH.0.7MeCN$ was prepared by adding a solution of $[Cu(BF_4)_2].H_2O$ (1.5 mmol, 0.36 g) in methanol (5 ml) to a methanolic solution (50 ml) containing proligand H_2L^2 (1 mmol, 0.44 g; He, 1995) and triethylamine (2 mmol, 0.21 g). After stirring at reflux temperature for 1 h, the dark green solution was evaporated to dryness. MeOH (5 ml) and then ethyl acetate (25 ml) were added to dissolve the residue. The mixture was allowed to stand at room temperature overnight whereupon crystals deposited. Recrystallization from acetonitrile–ethyl acetate gave orange–brown single crystals which readily lost solvent on exposure to the atmosphere (yield 0.35 g, 60%). The elemental analysis data shows the result for a dry sample of $[Cu(HL^2)]BF_4$; found (required for $C_{26}H_{33}BCuF_4N_4O_2$) (%): C 53.30 (53.50), H 5.60 (5.70), N 9.45 (9.60). Selected IR bands [KBr disc, ν (cm^{-1})]: 3261 (OH), 3060, 2925 and 2876 (NH), 1608 [C═N (py)], 1083 (BF_4^-).

Crystal data

$[Cu(C_{26}H_{33}N_4O_2)]BF_4.$-
$0.3CH_4O.0.7C_2H_3N$
$M_r = 622.26$
Monoclinic
$P2_1/c$
$a = 10.7300\,(10)$ Å
$b = 27.197\,(4)$ Å
$c = 10.127\,(2)$ Å
$\beta = 99.440\,(10)°$
$V = 2915.3\,(8)$ Å^3
$Z = 4$
$D_x = 1.418$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 5.0$–$12.5°$
$\mu = 0.810$ mm^{-1}
$T = 123\,(2)$ K
Block
0.82 × 0.23 × 0.20 mm
Orange–brown

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction:
ψ scans (*SHELXTL/PC*; Sheldrick, 1990*b*)
$T_{min} = 0.756$, $T_{max} = 0.850$
5625 measured reflections
5115 independent reflections

3809 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0390$
$\theta_{max} = 25°$
$h = -12 \rightarrow 12$
$k = -32 \rightarrow 1$
$l = 0 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0524$
$wR(F^2) = 0.1024$
$S = 1.216$
5088 reflections
375 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2 + 8P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	2.036 (3)	Cu—N3	2.075 (3)
Cu—N1	2.082 (4)	Cu—N4	2.058 (4)
Cu—N2	2.246 (4)		
O1—Cu—N4	93.46 (13)	N3—Cu—N1	110.28 (14)
O1—Cu—N3	95.44 (12)	O1—Cu—N2	171.60 (13)
N4—Cu—N3	130.81 (14)	N4—Cu—N2	78.49 (14)
O1—Cu—N1	94.38 (13)	N3—Cu—N2	88.17 (14)
N4—Cu—N1	117.11 (14)	N1—Cu—N2	91.46 (15)

All the non-H atoms, except the 30% occupancy O1*S* atom, were refined with anisotropic atomic displacement parameters. H atoms were inserted at calculated positions except for that on the phenol O2 atom, which was located from a difference map and not further refined.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The authors thank the University of Sheffield for a scholarship to QH.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BM1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adams, H., Bailey, N. A., Fenton, D. E. & He, Q.-Y. (1994). *Inorg. Chim. Acta*, **215**, 1–3.

Adams, H., Bailey, N. A., Rodriguez de Barbarin, C. O., Fenton, D. E. & He, Q.-Y. (1995). *J. Chem. Soc. Dalton Trans.* pp. 2323–2331.

Bailey, N. A., Fenton, D. E., He, Q.-Y., Terry, N., Haase, W. & Werner, R. (1995). *Inorg. Chim. Acta*, **235**, 273–279.

He, Q.-Y. (1995). PhD thesis, University of Sheffield, England.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Disorder in Bis(tetraethylammonium) Bis(μ-sulfido)bis[(1,2,3,4-tetrathiabutane-1,4-diyl-*S*,*S*)thiotungstate(V)]

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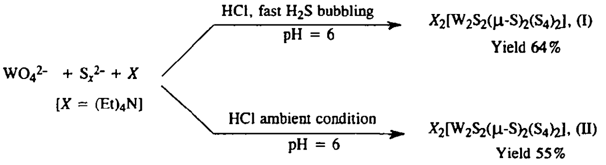
Abstract

Disorder in the terminal η^2-S$_4$ ligands of the [W$_2$S$_2$(μ-S)$_2$(η^2-S$_4$)$_2$]$^{2-}$ anions of the title dinuclear tungsten–sulfur complex, di-μ-sulfido-1:2κ^4S-disulfido-1κS,2κS-bis(tetrasulfanediyl)-1κ^2S^1,S^4;2$\kappa^2S^{1'}$,$S^{4'}$-ditungsten(V), (Et$_4$N)$_2$[W$_2$S$_2$(μ-S)$_2$(η^2-S$_4$)$_2$], results in two anionic orientations (*A* and *B*). In both orientations, the metal center is bonded to five S atoms, with a distorted square-pyramidal coordination polyhedron. The dihedral angle between orientations *A* and *B*, defined as that between the basal planes through two bridging and two η^2-S atoms of the anion, is 9.5 (3)°. The five-membered chelate rings of the anions in orientations *A* and *B* display envelope geometry, with atoms S9 and S3 at the flaps.

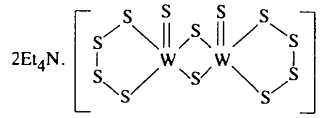
Comment

Polysulfide ions (S_x^{2-}, x = 2–9) have attracted attention because of their reducing as well as polydentate ligand behavior towards metal ions (Muller, Jaegermann & Enemark, 1982; Draganjac & Rauchfuss, 1985; Shibahara, 1993). Reaction of metal complexes with S_x^{2-} ions is a convenient method for directly introducing the ligand, leading to a variety of mono- or polymetal–polysulfur complexes (Muller & Diemann, 1987; Bhattacharya *et al.*, 1991; Chakraborty, Bhattacharya, Pierpont & Bhattacharya, 1992; Yamasaki & Shibahara, 1993). As part of our systematic study of tungstate–polysulfide systems, the title compound, (Et$_4$N)$_2$[W$_2$S$_2$(μ-S)$_2$(η^2-S$_4$)$_2$], was obtained in two forms [(I) and (II)] by acidification (6 *M* HCl) of an alkaline solution containing S_x^{2-}, WO_4^{2-} and Et$_4$N$^+$ following the reaction scheme below.



(I)

The synthesis, electrochemistry, reaction mechanism and crystal structure of (I) have been described previously (Chakraborty *et al.*, 1996). We report here the synthesis and crystal structure of (Et$_4$N)$_2$[W$_2$S$_2$(μ-S)$_2$(η^2-S$_4$)$_2$], (II). The structure of (II) consists of dinuclear units of disordered complex [W$_2$S$_{12}$]$^{2-}$ anions and disordered tetraethylammonium (Et$_4$N)$^+$ cations. The anions are located at crystallographic twofold sites with half of the dimer comprising the asymmetric unit. The *syn*-[W$_2$S$_2$(μ-S)$_2$]$^{2+}$ core in the anion of (II), unlike that of (I), is coordinated by two bidentate η^2-S$_4$ ligands disordered over two well defined unequally occupied orientations, *A* and *B*, with occupancy factors of 0.61 (1) and 0.39 (1), respectively. Orientation *A* comprises atoms S7–S10 and orientation *B*, atoms S3–S6.



(II)

A comparative study of the skeletal geometry of the anion with several related tungsten–sulfur complexes is reported in Table 3. The single crystallographically independent W atom in [W$_2$S$_{12}$]$^{2-}$ is bonded to five S atoms in a distorted square-pyramidal arrangement. The distortion of the coordination sphere is reflected in the wide range of angles formed by the S atoms at the metal center; S$_{\rm apical}$—W—S$_{\rm basal}$ 101.3 (3)–119.7 (3)°, *cis*-S$_{\rm basal}$—W—S$_{\rm basal}$ 66.4 (4)–100.7 (1)° and *trans*-S$_{\rm basal}$—W—S$_{\rm basal}$ 131.7(3)–152.2 (2)°. The apical site occupied by the S1 atom is 2.746 (5) (for orientation *A*) and 2.925 (5) Å (for *B*) away from the basal planes through S2, S2$^{\rm i}$, S7, S10 and S2, S2$^{\rm i}$, S3, S6, respectively, with the metal W1 atom deviating by 0.642 (3) (for orientation *A*) and 0.835 (3) Å (for *B*) in the same direction as the S1 atom. The dihedral angle between the basal planes is 9.5 (3)°. The bridging S atoms (S$_b$) are symmetrically bonded to W atoms and the W—S$_b$ [2.308 (8) and 2.332 (9) Å] and W═S [2.106 (4) Å] bond lengths are comparable to the corresponding distances in similar systems (Table 3).

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