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Bis(ethylenediamine)copper(II) bis(*O*,*O*′-diethyl dithiophosphate)

Hoong-Kun Fun,[a]* Qingli Hao,[b] Jiang Wu,[b] Xujie Yang,[b] Lude Lu,[b] Xin Wang,[b] Suchada Chantrapromma,[a]† Ibrahim Abdul Razak[a] and Anwar Usman[a]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China
Correspondence e-mail: hkfun@usm.my

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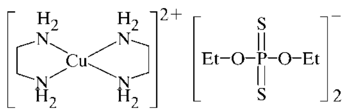
In the structure of the title compound, $[Cu^{II}(en)_2][(EtO)_2P(S)S]_2$ (en is ethylenediamine) or $[Cu(C_2H_8N_2)_2](C_4H_{10}O_2PS_2)_2$, the Cu atom lies on a center of inversion and is coordinated in a slightly distorted square coordination geometry by four N atoms from two ethylenediamine molecules. The diethyl dithiophosphate moieties, $(EtO)_2P(S)S^-$, act as counter-anions.

Comment

Compounds of bivalent copper exhibit different coordination arrangements, some being apparently four-coordinate, whereas others are generally five- and occasionally six-coordinate. The ligand-field strength of the donors is an important factor; weaker ligands may lead to an increased coordination number (Baker *et al.*, 1970). Usually, the donor capacity of the ligands decreases in the following order en > phen > dmp, where en is ethylenediamine, phen is phenanthroline and dmp is 2,9-dimethyl-1,10-phenanthroline (Kudrev, 1994).



(I)

Dialkyl dithiophosphates have extensive applications, such as antioxidants and antiwear additives in the rubber industry and in lubrication engineering (Kovtun *et al.*, 1992; Harrison & Kikabhai, 1987), as well as flotation agents for mineral ores and solvent extraction reagents for metals (Haiduc *et al.*, 1995; Rickelton & Boyle, 1990).

The reactions of copper(II) with the $(RO)_2P(S)S^-$ ion and nitrogen-base ligands have been investigated (Lawton *et al.*, 1972; Yordanov *et al.*, 1993; Drew *et al.*, 1987). These copper(II) complexes can cause DNA damage in the presence of H_2O_2. It was reported that $Cu^{II}(en)_2$ and hydrogen peroxide at physiological conditions could cause the DNA strand to break (Ozawa *et al.*, 1993). Additionally, $Cu^{II}(en)_2$ complexes may be used as good catalysts for all oxidizers, and the catalytic activities for all oxidizers decreased in the order Cu > Ni > Cd >> Zn (Sinditskii *et al.*, 1994).

In order to investigate the properties of the $(EtO)_2P(S)S^-$ ion complexed with $Cu^{II}(en)_2$, the title complex, (I), was synthesized and an X-ray structure analysis undertaken.

The asymmetric unit of (I) (Fig. 1) consists of one half of the complex molecule, and the unit cell contains two complexes. One half of the complex is related to the other by an inversion center at the Cu atom. The Cu atom is coordinated by four N atoms in a slightly distorted square coordination geometry. The Cu—N bond lengths are 2.016 (2) and 2.019 (2) Å, and the N—Cu—N bond angles are 84.6 (1) and 95.3 (1)°. The Cu—N values are normal for primary amines (Allen *et al.*, 1987). The bond lengths and angles of the title complex (Table 1) are comparable with those in a previous report of the same complex (Pervukhina & Podbereskaya, 1985), but the structure was solved in the wrong space group, $P2_1$. However, intensity statistics, as well as systematic extinctions, clearly indicate the space group to be $P2_1/c$. The Cu—N bond lengths are in good agreement with those observed in $Cu(en)[N(NO_2)CH_3]_2$ [Cu—N = 2.019 (3) Å; Palopoli *et al.*, 1988], while the N—Cu—N angles are slightly outside the bite-angle range for ethylenediamine in Cu^{II} complexes, typically 85–86° (Palopoli *et al.*, 1988).

The Cu^{II}–ethylenediamine complex molecule is not planar and adopts a twisted conformation. Atoms N1, N4, C2 and C3 deviate by 0.160 (2), −0.126 (2), −0.286 (3) and 0.267 (4) Å, respectively, from the mean plane of the Cu^{II}–ethylenediamine moiety, while the dihedral angle between the Cu1/N1/C2 and Cu1/N4/C3 planes is 19.5 (2)°.

In the $(EtO)_2P(S)S^-$ anion, the P atom is coordinated tetrahedrally by two S atoms and two O atoms. The bond

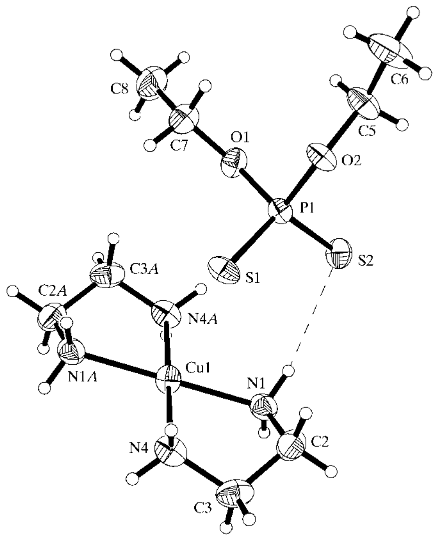


Figure 1
The structure of the title complex showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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† Permanent address: Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

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lengths around the P atom correspond to a P=S double bond and the P—O bond of an alkoxy O atom. The angles around the P atom are in the range 102.84 (11)–119.03 (5)°, implying a distorted tetrahedral coordination geometry for the P atom. The two ethoxy groups attached to the P atoms are nearly planar and make a dihedral angle of 86.3 (2)°.

The crystal structure of the title complex is built from alternating molecular layers of Cu^{II}–ethylenediamine and $(EtO)_2P(S)S^-$ stacked along the *c* axis. Atoms S1 and S2 are involved in intermolecular interactions with the amine (Table 2). These interactions link the molecular layers into a three-dimensional arrangement.

Experimental

The preparation of the title complex was divided into two steps. First, $Cu[(EtO)_2PS_2]_2$ was prepared, following the method of Drew *et al.* (1987), as a brown solid and 5 mmol was dissolved in ethanol (20 ml). Secondly, for the preparation of $[Cu^{II}(en)_2][(EtO)_2P(S)S]_2$, en (10 mmol) was added with stirring to an ethanol solution of $Cu[(EtO)_2PS_2]_2$. A deep-blue solution formed immediately. As the EtOH evaporated slowly, purple single crystals of $[Cu^{II}(en)_2][(EtO)_2P(S)S]_2$ suitable for X-ray analysis were obtained.

Crystal data

$[Cu(C_2H_8N_2)_2](C_4H_{10}O_2PS_2)_2$
$M_r = 554.22$
Monoclinic, $P2_1/c$
$a = 14.6683$ (3) Å
$b = 6.9409$ (1) Å
$c = 13.5889$ (1) Å
$\beta = 111.157$ (1)°
$V = 1290.25$ (3) Å^3
$Z = 2$
$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5321 reflections
$\theta = 1.5$–28.3°
$\mu = 1.32$ mm^{-1}
$T = 293$ (2) K
Slab, purple
0.36 × 0.14 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.649$, $T_{max} = 0.858$
8941 measured reflections
3144 independent reflections
2125 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$
$\theta_{max} = 28.3°$
$h = -19 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.106$
$S = 0.92$
3144 reflections
126 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -1.14$ e Å^{-3}

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their parent C and N atoms in the refinement.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Table 1
Selected geometric parameters (Å, °).

Cu1—N4	2.016 (2)	O2—C5	1.442 (3)
Cu1—N1	2.019 (2)	N1—C2	1.478 (4)
P1—O1	1.606 (2)	N4—C3	1.477 (4)
P1—O2	1.6098 (19)	C2—C3	1.500 (5)
P1—S1	1.9652 (10)	C7—C8	1.498 (5)
P1—S2	1.9664 (10)	C5—C6	1.467 (5)
O1—C7	1.449 (4)		
$N4^i$—Cu1—N1	95.33 (10)	O2—P1—S2	112.24 (8)
N4—Cu1—N1	84.67 (10)	S1—P1—S2	119.03 (5)
O1—P1—O2	102.84 (11)	C7—O1—P1	119.28 (19)
O1—P1—S1	111.76 (8)	C5—O2—P1	120.08 (19)
O2—P1—S1	104.72 (8)	C2—N1—Cu1	107.85 (18)
O1—P1—S2	105.20 (8)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···$S2^i$	0.90	2.76	3.599 (2)	155
N1—H1B···S2	0.90	2.61	3.486 (3)	165
N4—H4A···$S1^{ii}$	0.90	2.54	3.368 (2)	153

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, -y, -z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1146). Services for accessing these data are described at the back of the journal.

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