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Bis[bis(*N*,*N*-diethyl-1,1-diselenocarbamato)copper(II)], $[Cu(Se_2CNEt_2)_2]_2$

Mutai Bao, Jiabao Weng, Weiping Su, Rong Cao and Maochun Hong*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: hmc@ms.fjirsm.ac.cn

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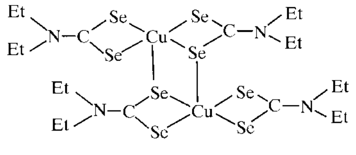
The title centrosymmetric Cu^{II} binuclear complex, bis(μ-*N*,*N*-diethyl-1,1-diselenocarbamato-*Se*,*Se*′:*Se*)bis[(*N*,*N*-diethyl-1,1-diselenocarbamato-*Se*,*Se*′)copper(II)], $[Cu(Se_2CNEt_2)_2]_2$ or $[Cu_2(C_5H_{10}NSe_2)_4]$, is built from two symmetry-related $[Cu\{Se_2CN(Et)_2\}_2]$ units by pairs of Cu—Se bonds. The coordination geometry at the unique Cu atom is distorted square pyramidal, with Cu—Se distances in the range 2.4091 (11)—2.9095 (10) Å.

Comment

In sharp contrast to many studies on the chemistry of metal complexes with 1,1-dithiolate ligands, the chemistry of metal complexes with 1,1-diselenolate ligands has received scant attention. Although the 2,2-dicyanoethylene-1,1-diselenolate and *N*,*N*-diethyl-1,1-diselenocarbamate ligands were prepared many years ago (Jensen & Henriksen, 1970; Barnard & Woodbridge, 1961), to our surprise, there are very few papers referring to such diselenolate ligands, among which the investigation was focused on the spectroscopic properties (Jensen & Krishnan, 1970), and very few crystal structures, such as bis(tetra-*n*-butylammonium) bis(2,2-dicyanoethylene-1,1-diselenolato)selenium(II) (Hummel *et al.*, 1992) and selenium bis(1-pyrrolidinecarbodiselenoate) (Esperas *et al.*, 1975), have been determined.

Current research interest is directed towards the understanding of the activation and cleavage of C—S and C—Se bonds in transition metal complexes featuring thiolate ligands (Hong *et al.*, 1997, 1998; Cao *et al.*, 1994). In an attempt to observe how the C—Se bonds were activated by transition metal active centers, we prepared a series of complex containing *N*,*N*-diethyl-1,1-diselenocarbamate ligands. Herein we report a centrosymmetric binuclear Cu^{II} complex, $[Cu(Se_2CNEt_2)_2]_2$, (I), which was prepared from the reaction of $CuSO_4$ and $Se[(Se_2CNEt_2)_2]_2$ in THF. Each bivalent Cu atom in the complex is coordinated by two *N*,*N*-diethyl-1,1-diselenocarbamate ligands in a distorted square-planar geometry forming a $[Cu(Se_2CNEt_2)_2]$ unit. Two such units are linked by Cu—Se bonds to form the binuclear complex. Thus, the coordination geometry of each Cu atom is distorted square pyramidal involving $CuSe_5$. *N*,*N*-Diethyl-1,1-diselenocarbamate acts as a chelating ligand to coordinate the Cu atom with an Se—Cu—Se angle of 79.04 (5)°. Two kinds of Cu—Se bonds are present in the complex: the shorter are in the range 2.4091 (11)–2.4455 (8) Å (average 2.428 Å) and the longer is 2.9095 (10) Å. The shorter average is compatible with distances found in the related compounds bis(tetra-*n*-butyl) bis(1,1-dicyanoethene-2,2-diselenolato-*Se*,*Se*′)nitridotechnetium(V) (Abram *et al.*, 1991) and bis(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile)nickel(IV) (Kaiser *et al.*, 1980)



(I)

Experimental

The title compound was obtained from the reaction of $CuSO_4$ and and $Se[\{Se_2CN(Et)_2\}_2]_2$ (molar ratio 1:1) in THF. To a solution of $Se[\{Se_2CN(Et)_2\}_2]_2$ (0.69 g, 1 mmol) in THF (20 ml) was added solid $CuSO_4$ (0.15 g, 1 mmol). The reaction solution turned brown–red gradually. After stirring for 2 h, the brown–red solution was filtered. The filtrate was kept in an icebox for one week to yield brown–red prisms of the title complex. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from THF/hexane at room temperature.

Crystal data

$[Cu_2(C_5H_{10}NSe_2)_4]$
$M_r = 1095.32$
Monoclinic, $P2_1/n$
$a = 9.825$ (2) Å
$b = 10.904$ (2) Å
$c = 16.051$ (3) Å
$\beta = 101.44$ (3)°
$V = 1685.4$ (6) Å^3
$Z = 2$

$D_x = 2.158$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 397 reflections
$\theta = 12.6$–$19.8°$
$\mu = 9.917$ mm^{-1}
$T = 293$ (2) K
Prism, brown–red
0.29 × 0.24 × 0.22 mm

Data collection

SMART CCD diffractometer
ω scans
Absorption correction: empirical empirical from equivalent reflections (*XEMP* in *SHELXTL*; Sheldrick, 1994)
$T_{min} = 0.168$, $T_{max} = 0.269$
7952 measured reflections

2929 independent reflections
2474 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.02°$
$h = -10 \rightarrow 11$
$k = -7 \rightarrow 12$
$l = -19 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.082$
2929 reflections
155 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.5791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.10$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0090 (4)

Table 1
Selected geometric parameters (Å, °).

Se1—C11	1.866 (5)	Se3—C21	1.865 (5)
Se1—Cu	2.4091 (11)	Se3—Cu	2.4127 (11)
Se2—C11	1.867 (5)	Se4—C21	1.856 (5)
Se2—Cu	2.4455 (8)	Se4—Cu	2.4397 (8)
Se2—Cu^{i}	2.9095 (10)	Cu—Se2^{i}	2.9095 (10)
C11—Se1—Cu	85.45 (14)	Se1—Cu—Se2	78.84 (3)
C11—Se2—Cu	84.37 (14)	Se3—Cu—Se2	99.51 (3)
C11—Se2—Cu^{i}	99.31 (14)	Se4—Cu—Se2	172.43 (3)
Cu—Se2—Cu^{i}	85.96 (3)	Se1—Cu—Se2^{i}	100.93 (3)
C21—Se3—Cu	84.43 (15)	Se3—Cu—Se2^{i}	99.85 (3)
C21—Se4—Cu	83.84 (14)	Se4—Cu—Se2^{i}	93.53 (3)
Se1—Cu—Se3	159.22 (4)	Se2—Cu—Se2^{i}	94.04 (3)
Se1—Cu—Se4	99.65 (3)	Se1—C11—Se2	111.3 (2)
Se3—Cu—Se4	79.23 (3)	Se4—C21—Se3	112.5 (2)

Symmetry code: (i) $-x, 2-y, -z$.

Data collection: *SMART CCD Software* (Siemens, 1994); cell refinement: *SMART CCD Software*; data reduction: *SMART CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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