$a = 26.9834\,(6)$ Å
$b = 16.8216\,(4)$ Å
$c = 28.1000\,(4)$ Å
$\beta = 90.164\,(1)°$
$V = 12754.6\,(5)$ Å^3
$Z = 4$
$D_x = 1.857$ Mg m^{-3}
D_m not measured

$\mu = 2.248$ mm^{-1}
$T = 173\,(2)$ K
Block
0.28 × 0.20 × 0.12 mm
Colorless

Data collection

Siemens SMART Platform CCD diffractometer
Multi-scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.445$, $T_{\max} = 0.763$
31 322 measured reflections
11 061 independent reflections

7586 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 25°$
$h = -32 \rightarrow 32$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.102$
$S = 1.076$
11 061 reflections
729 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.947$ e Å^{-3}
$\Delta\rho_{\min} = -1.051$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1994*b*). Data reduction: *SHELXTL-Plus* (Siemens, 1994*a*). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1056). Services for accessing these data are described at the back of the journal.

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Aquadiisothiocyanato(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′)copper(II)

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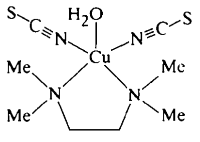
Abstract

The crystal structure of $[\mathrm{Cu(NCS)_2}(N,N,N',N'\text{-tmen})(\mathrm{H_2O})]$ (N,N,N',N'-tmen is N,N,N',N'-tetramethylethylenediamine, $C_6H_{16}N_2$) consists of discrete non-centrosymmetric molecules connected by a network of O—H···S hydrogen bonds. The coordination polyhedron around the Cu$^{\rm II}$ atom is square pyramidal, with the Cu atom about 0.22 Å above the plane of the four N atoms. The Cu—N basal-plane bond length has a mean value of 1.9999 Å. The fifth (apical) position is occupied by the O atom of the water molecule [Cu—O 2.342 (3) Å]. The N,N,N',N'-tetramethylethylenediamine chelate ring displays an unsymmetrical '*gauche*' configuration.

Comment

Replacement of the ethylenediamine (en) in $[\mathrm{Cu(en)_2(SCN)_2}]$ (Brown & Lingafelter, 1964) by *N*-methylethylenediamine (*N*-meen) to give $[\mathrm{Cu}(N\text{-meen})_2\mathrm{(SCN)_2}]$ (Pajunen & Hämäläinen, 1972) and by N,N'-dimethylethylenediamine (N,N'-deen) to give $[\mathrm{Cu}(N,N'\text{-deen})_2\mathrm{(NCS)_2}]$ (Korvenranta & Pajunen, 1970), leads to a different orientation of the thiocyanate groups in the coordination polyhedron of the Cu$^{\rm II}$ atom. The different orientation of the thiocyanate groups in these three structures is not due to electronic effects, but instead to reticular or environmental requirements.

We have determined the crystal structure of $[\mathrm{Cu}(N,N,N',N'\text{-tmen})\mathrm{(NCS)_2(H_2O)}]$, (I), where N,N,N',N'-tmen is N,N,N',N'-tetramethylethylenediamine, which



(I)

is, in our opinion, a further example of the influence of steric effects on the arrangement of the thiocyanate group. The steric hindrance of four *N*-methyl groups restricts the free volume around the Cu^{II} atom; the Cu—N(NCS) contact is thus preferred to Cu—S(SCN), together with the presence of only one diamine ligand around the central Cu^{II} atom. The crystal structure of the title compound consists of relatively isolated non-centrosymmetric molecules; the shortest intermolecular contacts [O1—H1···S1^{i} 2.60 (5) and O2—H2···S2^{i} 2.70 (5) Å; symmetry code: (i) $1-x$, $y-\frac{1}{2}$, $1-z$] indicate the presence of weak hydrogen bonds. The coordination polyhedron around the Cu^{II} atom is a tetragonal pyramid with the basal plane occupied by the chelating amine [Cu1—N1 2.026 (3) and Cu—N2 2.042 (3) Å] and two thiocyanate N atoms [Cu—N3 1.963 (3) and Cu—N4 1.964 (3) Å; Table 1]. The apical position is occupied by the O atom of the water molecule at a distance of 2.342 (3) Å. The Cu^{II} atom is 0.2202 (2) Å from the N1–N4 mean plane, on the same side as the O atom. The nearly linear thiocyanate groups [N—C—S 178.8 (3) and 179.6 (3)°] are coordinated by the N atom in the equatorial plane. The Cu—N—C(thiocyanate) angles [161.4 (3) and 161.7 (3)°] agree with the values observed in isothiocyanate complexes: 163.3° in [Cu(tren)(NCS)](SCN) [tren is tris(2-aminoethyl)amine; Jain & Lingafelter, 1967] and 160° in $[Cu(py)_2(NCS)_2]$ (py is pyridine; Porai-Koshits & Tishchenko, 1959). The structure of $[Cu(N,N,N',N'\text{-tmen})(NCS)_2(H_2O)]$ is an uncommon example of thiocyanate bonding in the equatorial plane through the N atoms. The *N*,*N*,*N*′,*N*′-tetramethylethylenediamine chelate ring displays an unsymmetrical '*gauche*' configuration, with the C2 atom 0.217 (5) Å from the N1/Cu1/N2 plane and the other C atom (C1) at a greater distance of −0.477 (5) Å.

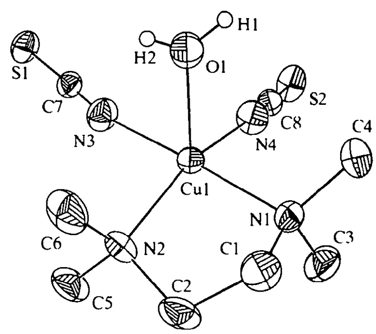


Fig. 1. View of the title molecule showing the labelling of the atoms. Displacement ellipsoids are shown at 50% probability levels.

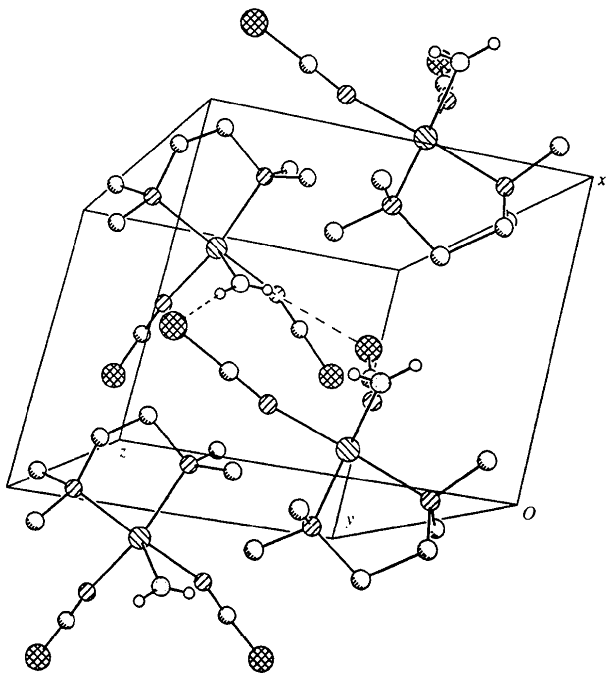


Fig. 2. The packing of the $[Cu(N,N,N',N'\text{-tmen})(NCS)_2(H_2O)]$ molecules in the unit cell.

Experimental

Dark-green crystals of the title compound were prepared by dissolving potassium thiocyanate (0.1 mol) in water (100 ml) and adding a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.2 mol) and $Cu(NO_3)_2$ (0.1 mol) in water (50 ml). Crystals of the title complex were collected by filtration and were recrystallized from ethanol.

Crystal data

$[Cu(NCS)_2(C_6H_{16}N_2)(H_2O)]$
$M_r = 313.92$
Monoclinic
$P2_1$
$a = 7.095\ (2)$ Å
$b = 11.761\ (4)$ Å
$c = 8.419\ (3)$ Å
$\beta = 98.40\ (2)°$
$V = 695.1\ (4)$ Å^3
$Z = 2$
$D_x = 1.500$ Mg m^{-3}
$D_m = 1.51\ (1)$ Mg m^{-3}
D_m measured by flotation in bromoform/hexane

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 11.4$–$26.8°$
$\mu = 1.858$ mm^{-1}
$T = 293\ (2)$ K
Block
0.15 × 0.10 × 0.10 mm
Dark green

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.594$, $T_{max} = 0.830$

1786 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30.06°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = -11 \rightarrow 11$

2132 measured reflections
2132 independent reflections
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.024$
$wR(F^2) = 0.059$
$S = 0.901$
2132 reflections
217 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.043$
$\Delta\rho_{\max} = 0.504$ e Å^{-3}
$\Delta\rho_{\min} = -0.269$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0047 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.100 (13)

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

Cu1—N4	1.964 (3)	S2—C8	1.605 (3)
Cu1—N3	1.963 (3)	N1—C1	1.468 (5)
Cu1—N1	2.026 (3)	N2—C2	1.484 (5)
Cu1—N2	2.042 (3)	N3—C7	1.141 (4)
Cu1—O1	2.342 (3)	N4—C8	1.154 (4)
S1—C7	1.622 (3)	C1—C2	1.502 (6)
N4—Cu1—N3	89.48 (13)	N3—Cu1—O1	88.53 (13)
N4—Cu1—N1	90.60 (12)	N1—Cu1—O1	94.72 (12)
N3—Cu1—N1	176.65 (13)	N2—Cu1—O1	99.35 (12)
N1—Cu1—N2	86.61 (11)	N3—C7—S1	178.8 (3)
N4—Cu1—O1	102.99 (14)	N4—C8—S2	179.6 (3)

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1023). Services for accessing these data are described at the back of the journal.

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Diaquabis(pyridazin-1-ium-3,6-dicarboxylato-N^2,O^3)copper(II) dihydrate

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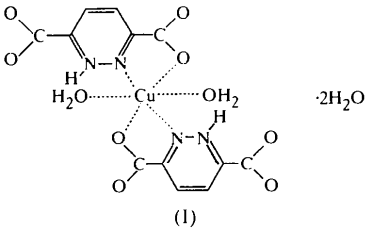
Abstract

The crystal structure of the title compound, $[Cu(C_6H_3N_2O_4)_2(H_2O)_2]\cdot 2H_2O$, shows it to exist as a monometalic and centrosymmetric complex with octahedral coordination of copper to each of two pyridazinium-3,6-dicarboxylate groups lying in the equatorial plane *via* one N and one O atom, and to two water molecules in *trans*-diaxial positions. Two additional water molecules are included in the cell. A network of hydrogen bonding links the carboxyl groups and the water molecules of the cell.

Comment

Interest in complexes of copper with small heterocyclic molecules stems from their use as organic precursors for bismuth-based metal oxides (Conflant *et al.*, 1992).

The title compound, diaquabis(pyridazin-1-ium-3,6-dicarboxylato)copper(II) dihydrate, (I), crystallizes as a monometalic cluster with a pseudo-octahedral copper(II) ion bound in the equatorial plane to each of two bidentate pyridazinium-3,6-dicarboxylate molecules *via* an N atom of the pyridazine ring and one O atom of the carboxylate group *ortho* to it [Cu—N 1.970 (2) and Cu—O 1.960 (2) Å]. Two distant and *trans*-diaxial water molecules complete the coordination sphere [Cu—O 2.506 (3) Å].



(I)

Monomeric clusters lie on parallel planes and are linked by a network of hydrogen bonding. The copper-bonded water molecules (O88) are found on the planes adjacent to those of the Cu atom (bound to the water