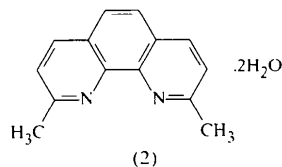


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of slight deviations from the crystallographic mirror symmetry.

### Comment

2,9-Dimethyl-1,10-phenanthroline (neocuproine) is a versatile ligand frequently used in the synthesis of metal–organic complexes (Baggio *et al.*, 1996, 1997). A hemihydrate form of the free molecule, (1), has already been described (Britton *et al.*, 1991) as crystallizing in tetragonal *I4<sub>1</sub>/a*. We report here the crystal and molecular structure of a second monoclinic dihydrated crystal form, (2), of free neocuproine.



The molecule is planar, with expected values for interatomic distances and angles, and molecular geometry in agreement, within experimental error, with that of (1).

The most substantial difference is in the packing. Molecule (1) can be considered to be formed by pairs of neocuproine molecules bridged by single water molecules, which lie on twofold axes. These units, in turn, interact weakly through long C—H...OH<sub>2</sub> contacts (H...O 2.56 Å) to form two sets of orthogonal linear chains parallel to the *a* and *b* axes. In (2), water

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## 2,9-Dimethyl-1,10-phenanthroline Dihydrate

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### Abstract

A novel dihydrated form of 2,9-dimethyl-1,10-phenanthroline (neocuproine), C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>·2H<sub>2</sub>O, is described. The molecule is very similar to that already reported in the literature, the main differences being in the packing. The positioning of the H atoms had a great influence in the convergence of the refinement process. This was performed in *C2/m*, though there were some suggestions

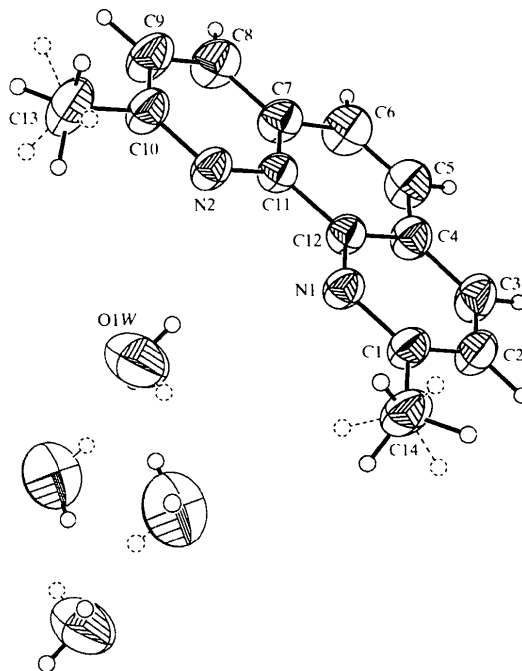


Fig. 1. The molecular diagram of (2) showing the numbering of atoms. Note the cluster of four hydration water molecules with disordered H atoms which build up around the twofold symmetry axis. Displacement ellipsoids are drawn at the 40% probability level.

molecules occur in clusters of four; the O atoms are related by crystallographic  $2/m$  symmetry, and make, approximately, a square of side 2.8 Å. One H atom of each water molecule is directed outwards from the cluster towards a neocuproine N atom, and is well defined, although the N—H...O distance is rather long for a hydrogen bond. The other four H atoms in the cluster are each disordered over two positions. Thus, there are two possible orientations for each water molecule and for the sequence of hydrogen bonds around the square cluster. These clusters, in turn, act as bridges between neocuproine molecules, forming parallel chains along the  $b$  axis.

## Experimental

Specimens of the title compound appeared during the crystallization of a zinc thiosulfate complex containing neocuproine as a ligand. Among an overwhelming majority of crystals of the main product (Baggio *et al.*, 1997), a few sparsely interspersed single crystals of a new monoclinic phase of the free ligand were thus fortuitously obtained.

### Crystal data

$C_{14}H_{12}N_2 \cdot 2H_2O$

$M_r = 244.29$

Monoclinic

$C2/m$

$a = 18.155 (5) \text{ \AA}$

$b = 6.871 (2) \text{ \AA}$

$c = 11.077 (3) \text{ \AA}$

$\beta = 110.96 (2)^\circ$

$V = 1290.3 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.257 \text{ Mg m}^{-3}$

$D_m$  not measured

### Data collection

Rigaku AFC-7S diffractometer

$\omega/2\theta$  scans

Absorption correction: none

1457 measured reflections

1249 independent reflections

860 reflections with

$I > 2\sigma(I)$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7.5\text{--}12.5^\circ$

$\mu = 0.085 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block

$0.22 \times 0.18 \times 0.16 \text{ mm}$

Colourless

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25.05^\circ$

$h = -21 \rightarrow 20$

$k = 0 \rightarrow 8$

$l = -1 \rightarrow 13$

2 standard reflections

every 98 reflections

intensity decay: <2%

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.139$

$S = 1.01$

1249 reflections

132 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.073P)^2$

$+ 0.418P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.01$

$\Delta\rho_{\text{max}} = 0.159 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.137 \text{ e \AA}^{-3}$

Extinction correction:

*SHELXL97* (Sheldrick, 1997)

Extinction coefficient:

0.016 (3)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
C1	0.68775 (15)	0	-0.0306 (2)	0.0562 (7)
C2	0.76112 (17)	0	-0.0469 (2)	0.0662 (8)
C3	0.82901 (16)	0	0.0579 (3)	0.0692 (8)
C4	0.82522 (14)	0	0.1819 (2)	0.0583 (7)
C5	0.89387 (15)	0	0.2972 (3)	0.0741 (9)
C6	0.88705 (15)	0	0.4139 (3)	0.0784 (9)
C7	0.81182 (14)	0	0.4285 (2)	0.0619 (7)
C8	0.80241 (17)	0	0.5483 (2)	0.0756 (8)
C9	0.72884 (18)	0	0.5530 (2)	0.0762 (9)
C10	0.66256 (15)	0	0.4380 (2)	0.0621 (7)
C11	0.74294 (13)	0	0.3170 (2)	0.0498 (6)
C12	0.74952 (12)	0	0.1907 (2)	0.0484 (6)
C13	0.58063 (17)	0	0.4405 (3)	0.0849 (11)
C14	0.61233 (17)	0	-0.1451 (2)	0.0709 (9)
N1	0.68206 (11)	0	0.08515 (16)	0.0503 (5)
N2	0.66933 (11)	0	0.32307 (16)	0.0545 (6)
O1W	0.55243 (14)	0.7033 (4)	0.1309 (3)	0.1118 (8)

Table 2. Selected bond and hydrogen-bond distances ( $\text{\AA}$ )

C1—N1	1.323 (3)	C8—C9	1.355 (4)
C1—C2	1.407 (4)	C9—C10	1.405 (4)
C1—C14	1.497 (3)	C10—N2	1.322 (3)
C2—C3	1.358 (4)	C10—C13	1.497 (4)
C3—C4	1.400 (3)	C11—N2	1.362 (3)
C4—C12	1.413 (3)	C11—C12	1.445 (3)
C4—C5	1.430 (4)	C12—N1	1.358 (3)
C5—C6	1.343 (4)	O1W...O1W <sup>i</sup>	2.794 (4)
C6—C7	1.431 (4)	O1W...O1W <sup>ii</sup>	2.843 (4)
C7—C8	1.397 (3)	O1W...N1 <sup>iii</sup>	3.287 (3)
C7—C11	1.409 (3)	O1W...N2 <sup>iiii</sup>	3.156 (3)

Symmetry codes: (i)  $x, 1 - y, z$ ; (ii)  $1 - x, y, -z$ ; (iii)  $x, 1 + y, z$ .

The crystal structure was solved with some difficulty in space group  $C2$ ; however, the model obtained displayed  $C2/m$  symmetry, with the neocuproine molecule lying on a mirror plane, and so the centrosymmetric space group was finally chosen for refinement. H atoms on the methyl groups were treated as disordered across the mirror plane. All neocuproine H atoms were treated as riding, with  $U_{\text{iso}}$  refined, and this gave sensible values in the range 0.06–0.15. The H atoms of one of the water molecules appeared to be disordered over two sites (not mirror symmetry related); positions and  $U_{\text{iso}}$  were refined for these H atoms, with restraints applied to the O—H and H...H distances. Several atoms of the neocuproine molecule were found to have slightly large  $U^{22}$  values. It is quite possible that in the true structure there are some deviations of these atoms from the plane at  $y = 0$ , and that either there is disorder or the true crystal symmetry is lower than  $C2/m$ . However, the present data are unable to resolve these possibilities.

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFD Diffractometer Control Software*. Data reduction: *MSCI/AFD Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP in SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCR electronic archives (Reference: HA1227). Services for accessing these data are described at the back of the journal.

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### 5-*R*-3*H*-1,2-Dithiole-3-thione (*R* = Ethylthio and Methylthio)

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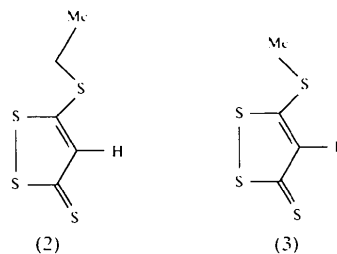
#### Abstract

The title compounds, 5-ethylthio-3*H*-1,2-dithiole-3-thione [C<sub>5</sub>H<sub>6</sub>S<sub>4</sub>, (2)] and 5-methylthio-3*H*-1,2-dithiole-3-thione, [C<sub>4</sub>H<sub>4</sub>S<sub>4</sub>, (3)] crystallize in space groups *C2/c* and *P2<sub>1</sub>/n*, respectively. The molecules are planar, with heterocyclic characteristics similar to those shown by other members of the 3*H*-1,2-dithiole-3-thione family. The striking difference between the corresponding melting points [340–341 K for (2) and 438–440 K for (3)] does not seem to arise from the rather similar main intermolecular interactions but rather from apparently much weaker ones.

#### Comment

In spite of the fact that drugs containing the 3*H*-1,2-dithiole-3-thione unit have been found to show important chemotherapeutic properties, few structural studies have been carried out. A brief summary can be found in a report by Baggio *et al.* (1997, and references

therein), where the structure of 4-benzyl-5-ethylthio-3*H*-1,2-dithiole-3-thione [hereafter (1)] is reported. This was the first structure to be determined as part of a planned long-term project concerning the crystal structure determination of new 3*H*-1,2-dithiole-3-thione derivatives obtained through a novel synthetic route for 5-alkylthio derivatives (Aimar & de Rossi, 1996). In this second report, we present the crystal structures of 5-ethylthio-3*H*-1,2-dithiole-3-thione, (2), and 5-methylthio-3*H*-1,2-dithiole-3-thione, (3); these two apparently very similar structures present, however, quite different properties in the solid state, *viz.*, melting points differing by *ca* 100 K [340–341 K for (2) and 438–440 K for (3)].



Both structures are monoclinic; compound (2) crystallizes in space group *C2/c*, while (3) crystallizes in *P2<sub>1</sub>/n*. Molecular diagrams for the two compounds showing the common numbering scheme are presented in Fig. 1. The great similarity of the two 3*H*-1,2-dithiole-3-thione moieties is apparent both by inspection of Fig. 1 and by analysis of their interatomic bond distances and angles; the structural characteristics thoroughly discussed by Baggio *et al.* (1997) for compound (1) (*i.e.* absolute planarity of the cycle, angle at S2 larger than that at S1, *etc.*) are also found here. It is perhaps worth pointing out that the difference arising between the corresponding *U*<sub>eq</sub> values [*e.g.* 0.047 Å<sup>2</sup> for (2) and 0.039 Å<sup>2</sup> for (3)] is in clear accord with (2) being ‘softer’ at room temperature.

The ethylthio group in (2), as well as the homologous methylthio group in (3), lie in the planes of their respective heterocycles, as shown by the relevant torsion angles [C4—C5—S7—C8 −179.6(1)° in (2) and 177.7(2)° in (3); C5—S7—C8—C9 −174.7(2)° in (2)], making the two molecules basically planar.

As usual in this type of compound, packing appears to be governed by S···S interactions, the closest intermolecular approaches being reported in Table 5. The shortest S···S distances present in (2) [3.385(1) Å] and (3) [3.384(1) Å] are comparable with the shortest distances found in related structures [*e.g.* 3.374(1) and 3.363(1) Å in phenyl-3*H*-1,2-dithiole-3-thione (Wei, 1986)] and contribute to the formation of zigzag chains, which evolve in a severely twisted fashion along the unique monoclinic axis; these chains, in turn, are interconnected through weaker interactions (see below).

This solid-state packing with rather short S···S intermolecular distances appears to be a characteristic