Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A second monoclinic polymorph of 2,9-dimethyl-1,10-phenanthroline dihydrate

Ahmet Köroglu,[a] Ahmet Bulut,[a] Ibrahim Uçar,[a] Gary S. Nichol,[b] Ross W. Harrington[b] and William Clegg[b]*

[a]Department of Physics, Faculty of Arts and Sciences, University of Ondokuz Mayıs, Kurupelit 55139, Samsun, Turkey, and [b]School of Natural Sciences (Chemistry), Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

Received 12 October 2005
Accepted 14 October 2005
Online 19 October 2005

A second monoclinic polymorph of the title compound, neocuproine dihydrate, $C_{14}H_{12}N_2\cdot 2H_2O$, is reported. Unlike the first polymorph [Baggio, Baggio & Mombrú (1998). *Acta Cryst.* C**54**, 1900–1902], in which the phenanthroline ring system was constrained to lie in a crystallographic mirror plane, here there is no such imposed symmetry. Consequently, the molecule shows small deviations from planarity, the outer rings being twisted slightly in opposite directions from the plane of the central ring. The hydrogen-bonding motifs remain essentially the same as in the first polymorph, involving small rings of four water molecules and large rings containing four water molecules and two neocuproine molecules, but with no H-atom disorder for the water molecules in this case. There are also aromatic π–π stacking interactions.

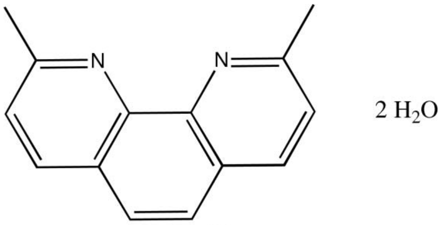
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.062
wR factor = 0.154
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal complexes of squaric acid and their structures have been reported (Uçar *et al.*, 2004, 2005; Bulut *et al.*, 2004). We have used such co-ligands as isonicotinamide and 2,9-dimethyl-1,10-phenanthrolione (neocuproine) in our research and, while synthesizing an iron complex of squaric acid and neocuproine, we obtained crystals of neocuproine dihydrate, (I), as a side product. A unit cell search of the Cambridge Structural Database (CSD, Version 5.26 plus three updates; Allen, 2002) did not find a match, and it was only by carrying out a structure-based search that we found that a structure of the same compound, also as a dihydrate, had previously been reported (Baggio *et al.*, 1998). The crystal structure of a hemihydrate has also been determined (Britton *et al.*, 1991). A unit-cell determination with our sample at 298 K gave essentially the same parameters as were determined at 150 K, with the expected slight expansion, and so we are confident that we are reporting the crystal structure of a second monoclinic polymorph of (I), and not the result of a phase transition at low temperature.



(I)

This second monoclinic polymorph of (I), shown in Fig. 1, crystallizes in space group $C2/c$ with all atoms lying in general

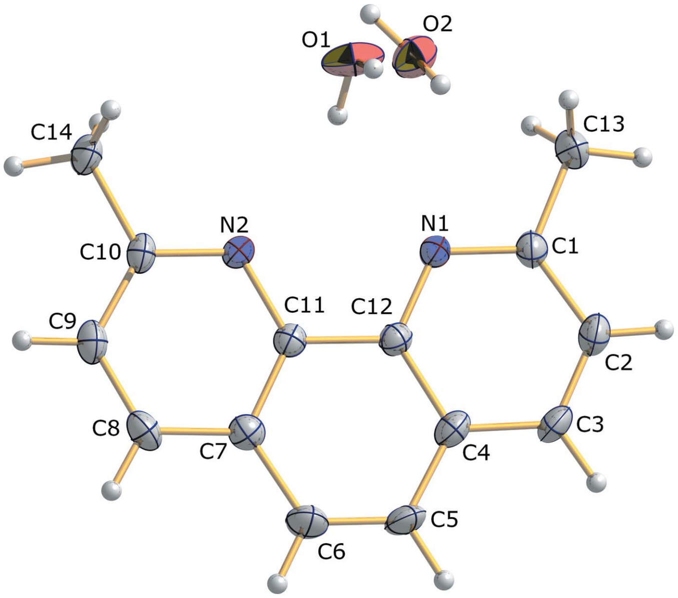


Figure 1
The asymmetric unit of compound (I), with displacement ellipsoids drawn at the 50% probability level.

positions. Britton *et al.* (1991) reported some slight tilting of the individual six-membered rings with respect to one another within the phenanthroline system in the hemihydrate. Baggio *et al.* (1998) reported that the molecule was exactly planar in the first polymorph of the dihydrate, as a consequence of crystallographic mirror symmetry. A least-squares plane fitted through all non-H atoms of the phenathroline skeleton of (I) has an r.m.s. deviation of 0.024 Å, and the dihedral angle between two mean planes fitted through the outermost rings is 2.37 (2)°, indicating a small deviation of the molecule from planarity. This distortion consists mainly of a twist of the outer rings in opposite directions out of the plane of the central ring, as indicated by the N1—C12—C11—N2 torsion angle of −2.8 (3)°, almost the same as the above dihedral angle.

The overall crystal packing of (I) is similar to that in the first monoclinic polymorph, albeit without the perfectly planar sheets achieved by imposed mirror symmetry. In the first polymorph, H-atom disorder in the water molecules means there is more than one possible orientation of each water molecule and hence some uncertainty about the hydrogen-bonding arrangement. In (I), all H atoms were easily and convincingly located in a difference map and water H atoms were freely refined. The hydrogen-bonding arrangement is shown in Fig. 2. The water molecules form hydrogen bonds around an inversion centre to generate a square $R_4^4(8)$ motif (Bernstein *et al.*, 1995). A second large $R_6^6(18)$ motif links two neocuproine molecules together *via* the water molecules.

Unlike the first polymorph, we find no evidence of weak C—H···O hydrogen bonding here. However, the separations between parallel neocuproine molecules stacked along the *b* axis are alternately 3.32 and 3.39 Å, and each molecule has approximately a half-ring overlap with the next molecule in the stack, characteristic of aromatic π–π interactions.

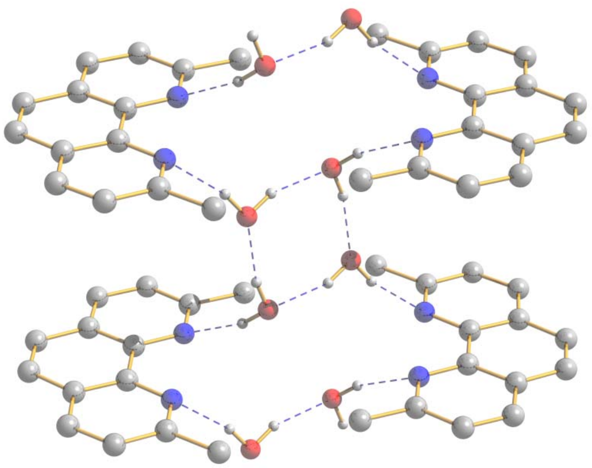


Figure 2
The hydrogen-bonding motifs in (I). Dashed lines indicate the hydrogen bonds.

Experimental

Squaric acid, H_2Sq (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and the mixture was added to a hot solution of $FeCl_2 \cdot 6H_2O$ (1.17 g, 5 mmol) dissolved in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The brown crystals that formed were filtered off, washed with water and ethanol, and dried *in vacuo*. A solution of 2,9-dimethyl-1,10-phenanthroline (0.435 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of $FeSq \cdot 2H_2O$ (0.21 g, 1 mmol) in water (50 ml). The brown solution was refluxed for about 2 h and then cooled to room temperature. A few days later, brown crystals of the desired Fe complex had formed, along with some well formed colourless crystals of (I) as a side-product.

Crystal data

$C_{14}H_{12}N_2 \cdot 2H_2O$
$M_r = 244.29$
Monoclinic, $C2/c$
$a = 22.942$ (2) Å
$b = 6.7388$ (7) Å
$c = 17.9594$ (18) Å
$\beta = 116.019$ (2)°
$V = 2495.2$ (4) Å^3
$Z = 8$
$D_x = 1.301$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6879 reflections
$\theta = 2.4$–28.8°
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.61 × 0.38 × 0.21 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Thin–slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.928$, $T_{\max} = 0.982$
8619 measured reflections
2191 independent reflections
1781 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 25.0$°
$h = -27 \rightarrow 27$
$k = -7 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.154$
$S = 1.22$
2191 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 4.5458P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

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Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1O⋯N2	0.84 (4)	2.31 (4)	3.105 (3)	157 (3)
O1—H2O⋯O2	0.87 (5)	1.95 (5)	2.805 (3)	167 (4)
O2—H3O⋯N1^{i}	0.88 (4)	2.15 (4)	3.005 (3)	164 (3)
O2—H4O⋯O1^{ii}	0.89 (3)	1.97 (3)	2.810 (3)	158 (3)

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

All H atoms were located in a difference Fourier map. Water H atoms were freely refined, giving O—H distances shown in Table 1. Other H atoms were treated as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ and C—H = 0.95 Å for aromatic, and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$ and C—H = 0.98 Å for methyl groups.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank the EPSRC for equipment and partial studentship funding.

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