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# *trans*-Bis(ethylenediamine)bis(*p*-nitrobenzoxasulfamato)copper(II)

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.004 Å
*R* factor = 0.035
*wR* factor = 0.091
Data-to-parameter ratio = 12.6

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

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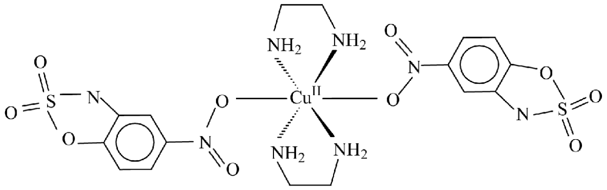
The structure of *trans*-[Cu(nbs)$_2$(en)$_2$] [nbs is the *p*-nitrobenzoxasulfamate anion ($C_6H_3N_2O_5S$)$^-$ and en is ethylenediamine, $C_2H_8N_2$] consists of neutral molecules. The $Cu^{2+}$ ion occupies an inversion centre and exhibits an elongated distorted octahedral geometry, with two monodentate nbs anions and two bidentate en ligands. Both nbs ligands are O-coordinated *via* an O atom of the nitro group. The crystal structure is stabilized by hydrogen bonds and weak aromatic $\pi$–$\pi$ stacking interactions between the benzene rings of nbs ligands, forming a three-dimensional network.

## Comment

Sulfamate derivatives have considerable commercial importance as artificial sweeteners (Spillane *et al.*, 1996; Drew *et al.*, 1998) and drugs (Howarth *et al.*, 1994; Maryanoff *et al.*, 1998; Gautun *et al.*, 1999) and have been used in the preparation of flame retarding (Lewin, 1997) and antistatic polymers (Spiridonov & Malushko, 2000). Crystal structures of acyclic sulfamates of monovalent metal ions, such as lithium (Stade *et al.*, 2001), potassium (Cox *et al.*, 1967), rubidium (Schreuer, 1999*a*), caesium (Schreuer, 1999*b*), silver (Belaj *et al.*, 1987) and thallium (Haussuhl & Haussuhl, 1995) have been described in the literature. Metal(II) complexes of acyclic sulfamates are rare and only a mixed-ligand sulfamato complex of $Cu^{II}$ has been reported by Melnyk *et al.* (2001). Recently, we have started a project on the synthesis and crystallographic characterization of metal salts and ligation properties of a cyclic sulfamate, namely the *p*-nitrobenzoxasulfamate ion (nbs), $C_6H_3N_2O_5S^-$. In the course of our research work, we reported the X-ray crystal structures of sodium (Yazicilar *et al.*, 2002) and potassium (Bekdemir *et al.*, 2002) salts of nbs, and aquabis(*p*-nitrobenzoxasulfamato)metal(II) complexes with $Co^{II}$ (Kazak *et al.*, 2004), $Cu^{II}$ (Yilmaz, Andac *et al.* 2002), $Cd^{II}$ and $Hg^{II}$ (Yilmaz, Yazicilar *et al.*, 2002). In the present paper, we report the synthesis and crystal structure of the first mixed-ligand copper(II) complex of nbs with ethylenediamine (en), *viz.* *trans*-[Cu(nbs)$_2$(en)$_2$], (I) (Fig. 1).



(I)

The structure of (I) consists of isolated molecules of [Cu(nbs)$_2$(en)$_2$]. The copper(II) ion occupies an inversion

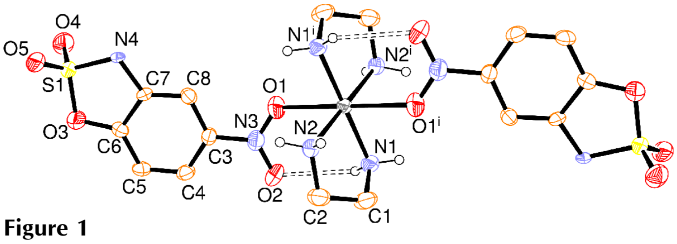


**Figure 1**
Molecular view of (I), with 40% probability displacement ellipsoids. H atoms attached to C atoms have been omitted for clarity. Hydrogen bonds are indicated by dashed lines. Symmetry code as in Table 1.

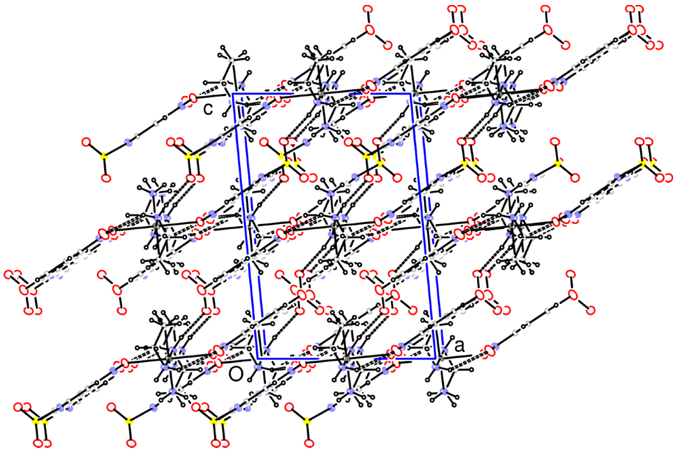


**Figure 2**
Packing diagram of (I), showing hydrogen bonds as dashed lines.

centre and is octahedrally coordinated by two en and two nbs ligands, forming a $CuN_4O_2$ coordination environment. The en ligands act as bidentate ligands, forming two five-membered chelate rings with a *trans* arrangement. In contrast to the aquacopper(II) complex of nbs (Yilmaz, Andac *et al.*, 2002), both nbs anions behave as *O*-donor monodentate ligands through an O atom of the nitro group and the negatively charged N atom is not involved in coordination. Although the interaction of the nitro group was first observed with mercury(II) in $[Hg(nbs)_2(H_2O)_3]$ (Yilmaz, Yazicilar *et al.*, 2002), the long $Hg-O_{nitro}$ bond distance [3.216 (2) Å] suggests semicoordination of the nitro O atoms to the mercury(II) ions as weak contacts. Therefore, the title complex is also the first example of the $O_{nitro}$-coordinated nbs ligand. The coordination of copper(II) clearly shows the geometrical pattern typical of the Jahn–Teller effect. The two $Cu-N_{en}$ bond distances are almost equivalent, but significantly shorter than the $Cu-O_{nbs}$ bond distances, resulting in the formation of a distorted octahedral geometry elongated along the $Cu-O_{nbs}$ bonds. Thus, the en N atoms form the equatorial plane of the coordination octahedron, while the nitro O atoms of nbs occupy the axial positions. Distortion is also evident from the *cis* angles in the coordination polyhedron (Table 1).

The nbs ligand (C3–C8/O3/S1/N4) is essentially planar, with a root-mean-square (r.m.s.) deviation of 0.030 Å, and the $NO_2$ group is also in the same plane as the nbs backbone. The en chelate ring (C1/C2/N1/N2/Cu1) is also close to planarity, with an r.m.s. deviation of 0.180 Å. The dihedral angle between the mean planes of the nbs ligand and en ring is 59.28 (11)°. The bond distances and angles within the nbs ligands are almost identical to those found in $[Cu(nbs)_2(H_2O)_3]\cdot H_2O$ (Yilmaz, Andac *et al.*, 2002). The crystal structure of the complex exhibits numerous hydrogen bonds (Table 1). The amine H atoms form intramolecular hydrogen bonds with the uncoordinated O atoms of the nitro groups, as illustrated in Fig. 1. The amine H atoms of the en ligands are also involved in intermolecular hydrogen bonding with the nitro, sulfonyl and ring O atoms of neighbouring nbs ligands. One of the amine H atoms (H1) forms bifurcated hydrogen bonds with the O atoms of the nitro and sulfonyl groups of adjacent molecules. The nbs ligands of neighbouring molecules adopt a parallel alignment and the benzene rings are approximately superimposed on each other and are connected by weak $\pi-\pi$ interactions [$Cg\cdots Cg^{vi} = 3.831$ (2) Å; symmetry code: (vi) $-x, y, \frac{1}{2}-z$], yielding sheet-like entities, which are connected by hydrogen bonds to give a three-dimensional network.

## Experimental

$Na(nbs)\cdot H_2O$ (0.51 g, 2.0 mmol) dissolved in acetone (20 ml) was mixed with an aqueous solution of $CuCl_2\cdot 2H_2O$ (0.17 g, 1.0 mmol) (5 ml). Then, en (0.12 g, 2 mmol) was added to this mixture dropwise and the resulting solution was stirred for 15 min at room temperature. X-ray quality crystals were obtained by slow evaporation over several days. The brown crystals were collected by suction filtration and dried in air.

*Crystal data*

$[Cu(C_6H_3N_2O_5S)_2(C_2H_8N_2)_2]$
$M_r = 614.08$
Monoclinic, $C2/c$
$a = 10.2967$ (11) Å
$b = 14.4563$ (9) Å
$c = 15.3929$ (14) Å
$\beta = 95.429$ (8)°
$V = 2281.0$ (4) Å$^3$
$Z = 4$
$D_x = 1.788$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 14720 reflections
$\theta = 2.4$–29.4°
$\mu = 1.21$ mm$^{-1}$
$T = 293$ (2) K
Plate, brown
0.60 × 0.30 × 0.07 mm

*Data collection*

Stoe IPDS-II diffractometer
$\omega$ scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{min} = 0.652$, $T_{max} = 0.919$
2132 measured reflections
2132 independent reflections
1472 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.5°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.091$
$S = 0.91$
2132 reflections
169 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.76$ e Å$^{-3}$
$\Delta\rho_{min} = -0.54$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.007 (3) | Cu1—O1 | 2.550 (3) |
| Cu1—N2 | 2.010 (3) | | |
| N1—Cu1—N2$^i$ | 95.54 (12) | O1—Cu1—N1 | 94.11 (12) |
| N1—Cu1—N2 | 84.46 (12) | O1—Cu1—N2 | 90.00 (11) |
| N1—Cu1—O1$^i$ | 85.89 (12) | | |

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

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*B*···O5$^{ii}$ | 0.90 | 2.18 | 3.069 (4) | 168 |
| N1—H1*A*···O4$^{iii}$ | 0.90 | 2.38 | 2.993 (4) | 125 |
| N1—H1*A*···O2 | 0.90 | 2.55 | 3.265 (5) | 136 |
| N2—H2*A*···O3$^{iv}$ | 0.90 | 2.31 | 3.178 (4) | 163 |
| N2—H2*B*···O3$^{v}$ | 0.90 | 2.24 | 3.134 (4) | 169 |

Symmetry codes: (ii) $x-1, 1-y, z-\frac{1}{2}$; (iii) $1-x, 1-y, 1-z$; (iv) $x-1, y, z$; (v) $1-x, y, \frac{3}{2}-z$.

All H atoms were placed in idealized locations (C—H = 0.93 and 0.97 Å, and N—H = 0.90 Å) and refined as riding on their carrier atoms. The constraint $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom) was applied in all cases.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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