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Bis[μ-4,5-dicyano-*N*,*N'*-bis(*p*-tolylsulfonyl)-*o*-phenylenediaminato]bis[diamminecopper(II)] dihydrate

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The title complex, $[Cu_2(C_{22}H_{16}N_4O_4S_2)_2(NH_3)_4]\cdot 2H_2O$, is a centrosymmetric dimer. The two copper ions are bridged by two 4,5-dicyano-*N*,*N'*-bis(*p*-tolylsulfonyl)-*o*-phenylenediamine ligands; the Cu$\cdots$Cu distance is 8.749 (1) Å. Each copper ion is in a distorted square-pyramidal geometry, defined by two N atoms from one ligand, two N atoms from two coordinated ammonia molecules and one CN from the other ligand apically. The hydrogen-bonding network leads to a layered structure.

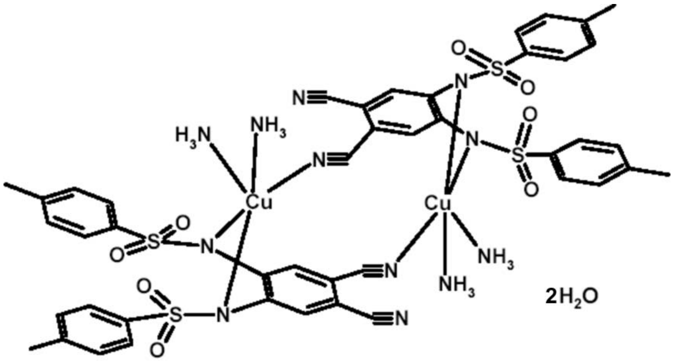
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.056
wR factor = 0.059
Data-to-parameter ratio = 10.2

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

Comment

Phthalonitriles are common precursors for the synthesis of phthalocyanines which have attracted considerable interest during recent decades owing to their potential applications in wide areas of materials science such as chemical sensors (Öztürk *et al.*, 1995), liquid crystals (Simon & Sirlin, 1989), catalysis (Sorokin & Tuel, 1999) and nonlinear optics (Torres *et al.*, 2000). A particular feature of phthalocyanines is the ability to tune their physical and electronic properties by changing the nature of the substituents or the central metallic atom (McKeown, 1998).



(I)

In a recent article, we reported the synthesis of 4,5-dicyano-*N*,*N'*-ditosyl-*o*-phenylenediamine (Yuksel *et al.*, 2005). In the course of this synthesis, compound (I) was obtained as a reaction intermediate.

The crystal structure of complex (I) is shown in Fig. 1. It is a centrosymmetric dinuclear complex in which the Cu$\cdots$Cu distance is 8.749 (1) Å. In the dimer, each copper ion is five-coordinated in a distorted square-pyramidal environment. The basal coordination positions are occupied by four N atoms, two from tosylamido units of the one ligand and two from ammonia molecules. The apical coordination position is occupied by an N atom from the nitrile unit of the other

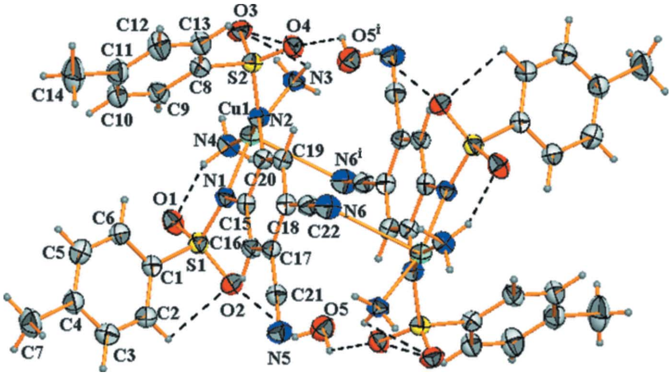


Figure 1
The structure of (I) (30% probability displacement ellipsoids). Dashed lines indicate hydrogen bonds. [Symetry code: (i) $1 - x$, $-y$, $1 - z$.]

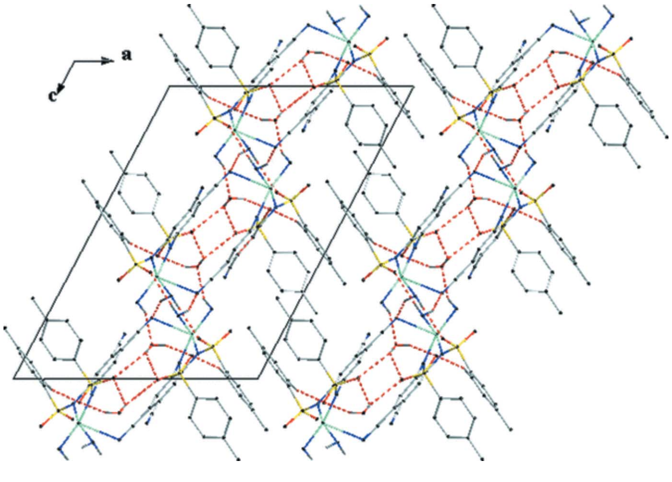


Figure 2
View of the packing of (I) along the *b* axis of the unit cell (H atoms have been omitted for clarity).

ligand. From a least-square plane calculation, the four coordinated atoms, N1, N2, N3 and N4, in the basal positions deviate from the plane by −0.244 (4), 0.252 (4), −0.228 (4) and 0.2199 (4) Å, respectively. The Cu—N bonds and angles are reported in Table 1. Those involving the basal N atoms are in agreement with those reported for similar compounds (Zukerman-Schpector *et al.*, 1991; Luo *et al.*, 2004), while the apical Cu1–N6^{i} [2.810 (5) Å] distance [symmetry code: (i) $1 - x, -y, 1 - z$] is greater than those usually reported for five-coordinated Cu atoms.

The stability of complex (I) is achieved through N—H···O, O—H···O and C—H···O inter- and intramolecular hydrogen bonds, which are detailed in Table 2. As seen in Fig. 2, the intermolecular hydrogen bonding leads to the formation of layers in the (*bc*) plane.

Experimental

A mixture of 4,5-dibromo-*N*,*N*′-ditosyl-*o*-phenylenediamine (25.41 g, 44.24 mmol), CuCN (12.32 g, 137.56 mmol) and 120 ml anhydrous DMF was heated to 413 K for 20 h under an argon atmosphere. Upon cooling, a dark-brown mixture appeared, which was then mixed with aqueous NH_4OH (25%, 300 ml) under an air flow for 14 h. The resulting brown precipitate was filtered off and thoroughly washed with water. Soxlet extraction of the brown solid product gave a violet solution in ethanol. Finally, the solution was concentrated by evaporation and water (1/3 part of ethanol) was slowly added. After several days green needle crystals appeared.

Crystal data

$[Cu_2(C_{22}H_{16}N_4O_4S_2)_2(NH_3)_4]\cdot 2H_2O$
$M_r = 1160.32$
Monoclinic, $P2_1/c$
$a = 14.1946$ (8) Å
$b = 10.1475$ (7) Å
$c = 19.267$ (1) Å
$\beta = 118.117$ (3)°
$V = 2447.7$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.11$ mm^{-1}
$T = 293$ K
0.27 × 0.19 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: part of the refinement model (Δ*F*) (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.670$, $T_{\max} = 0.847$
8752 measured reflections
4827 independent reflections
3315 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.059$
$S = 1.05$
3315 reflections
325 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.998 (3)	Cu1—N4	1.931 (3)
Cu1—N2	1.944 (3)	Cu1—N6^{i}	2.810 (5)
Cu1—N3	1.981 (3)		
N1—Cu1—N2	81.07 (14)	N2—Cu1—N4	166.69 (15)
N1—Cu1—N3	164.55 (14)	N2—Cu1—N6^{i}	95.79 (14)
N1—Cu1—N4	98.94 (14)	N3—Cu1—N4	88.15 (15)
N1—Cu1—N6^{i}	88.37 (14)	N3—Cu1—N6^{i}	77.05 (14)
N2—Cu1—N3	95.17 (15)	N4—Cu1—N6^{i}	97.51 (14)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H2···O3	0.85	2.48	2.860 (5)	108
N4—H4···O1	0.83	1.93	2.648 (5)	144
O5—H7···O2	0.81	2.38	2.934 (6)	126
C2—H21···O2	0.93	2.53	2.905 (7)	105
C13—H131···O4	0.92	2.54	2.900 (7)	104
O5^{i}—H8^{i}···O4	0.81	2.41	2.962 (6)	126
N3—H1···O2^{ii}	0.85	2.18	2.993 (5)	159
N4—H5···O5^{ii}	0.83	2.07	2.630 (5)	124
N3—H3···N6^{iii}	0.84	2.22	2.970 (6)	148
O5—H8···O4^{iv}	0.81	2.54	3.178 (5)	137
O5—H7···O3^{iv}	0.81	2.54	3.239 (6)	146
C2—H21···O3^{iv}	0.93	2.53	3.422 (7)	162

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

All the hydrogen atoms were discernible in a difference Fourier map. They were initially refined with soft restraints on the bond length (C—H in the range 0.93–0.98 Å, N—H in the range 0.86–

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0.89 Å and O—H = 0.82 Å) and their isotropic displacement parameters [$U_{\rm iso}$(H) in the range 1.2–1.5 times $U_{\rm eq}$ of the parent atom], after which the positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001).; cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1996); software used to prepare material for publication: *CRYSTALS*.

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Brandenburg, K. & Putz, H. (1996). *DIAMOND*. Version 3. Crystal Impact GbR, Bonn, Germany.

Luo, J., Zhou, X. G., Gao, S., Weng, L. H., Shao, Z. H., Zhang, C. M., Li, Y. R., Zhang, J. & Cai, R. F. (2004). *Polyhedron*, **23**, 1243–1248.

McKeown, N. B. (1998). *Phtalocyanine Materials: Synthesis, Structure and Function.* Cambridge University Press.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Öztürk, Z. Z., Zhou, R., Weimar, U., Ahsen, V., Bekaroglu, Ö. & Göpel, W. (1995). *Sens. Actuators*, **26–27**, 208–216.

Simon, J. & Sirlin, C. (1989). *Pure Appl. Chem.* **61**, 1625–1629.

Sorokin, A. B. & Tuel, A. (1999). *New J. Chem.* **23**, 473–476.

Torres, T., Maya, E. M., Garcia, C., Garcia-Frutos, E. M. & Vazquez, P. (2000). *J. Org. Chem.* **65**, 2733–2739.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Yuksel, F., Gurek, A. G., Lebrun, C. & Ahsen, V. (2005). *New J. Chem.* **29**, 726–732.

Zukerman-Schpector, J., Castellano, E. E., De Simone, C. A., Oliva, G. & Mauro, A. E. (1991). *Acta Cryst.* C**47**, 957–959.

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