Acta Crystallographica Section E
Structure Reports Online

ISSN 1600-5368

Tetrakis(1*H*-benzimidazole-κN^3)(sulfato-κO)-copper(II) dimethyl sulfoxide solvate

Lesław Sieroń

Institute of General & Ecological Chemistry, Technical University of Łódź, Żeromskiego 116, 90-924 Łódź, Poland

Correspondence e-mail: lsieron@p.lodz.pl

Received 6 January 2007
Accepted 9 January 2007

Key indicators

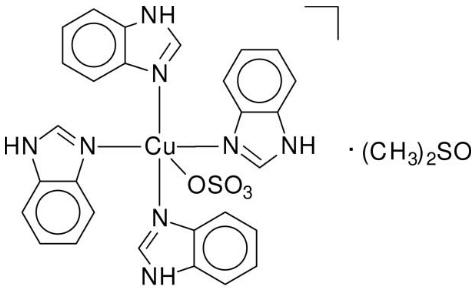
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.041
wR factor = 0.092
Data-to-parameter ratio = 12.9

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

The title copper(II) compound, $[Cu(SO_4)(C_7H_6N_2)_4]\cdot(CH_3)_2SO$, displays a square-pyramidal coordination geometry formed by four benzimidazole ligands and a sulfate anion. The molecules are linked by N—H···O and C—H···O hydrogen bonds, forming an extensive two-dimensional network in the *ab* plane.

Comment

Benzimidazole (bim) and its derivatives are important heterocyclic compounds, having a wide spectrum of pharmacological activities (Kataev *et al.*, 2002; Valdez *et al.*, 2002). This work forms part of a continuing study on Cu^{II} complexes with benzimidazole (Sieroń *et al.*, 1999, 2002), providing the second example of $Cu(bim)_4$ coordination. In the molecule of the title complex, (I) (Fig. 1), the Cu^{II} atom is coordinated by four bim molecules and one sulfate anion, displaying a square-pyramidal (4 + 1) geometry.



(I)

The arrangement in the Cu coordination environment is very similar to the one described in tetrakis(benzimidazole-*N*)(sulfato-*O*)copper(II) dimethylformamide solvate dihydrate (Fan *et al.*, 2006). The most distinct difference is in the location of the sulfate ligand [Cu—O—S is 134.5 (2)° in (I) *versus* 150.2 (2)°]. The degree of trigonality τ = 0.026 [τ is defined by Addison *et al.* (1984); for a regular square-pyramidal (SQP) structure, the trigonality parameter is 0, and for a trigonal-bipyramidal (TBP) structure, it increases to 1] indicates almost ideal SQP coordination of the Cu atom. The Cu atom deviates by 0.155 (2) Å from the basal plane towards the apical atom O2.

According to Brown (1992), the bond length to bond valence correlation represents a measure of bond strength that is independent of the atomic size. The valence-sum rule states that the sum of the bond valences formed by an atom is equal to the valence (formal oxidation state) of the atom ($V_i = \Sigma\nu_{ij}$). The bond valences were computed according to Brown (1992, 1997) and O'Keeffe & Brese (1991) as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$, where R_{ij} is the bond-valence parameter (formally it is the single-bond length between the i and j atoms) and d_{ij} is the observed bond length. $R_{\mathrm{Cu-O}}$ and $R_{\mathrm{Cu-N}}$ were taken as 1.679 and 1.713 Å (Sieroń *et al.*, 1999). The four strong Cu–N bonds have bond valences ranging from 0.43 to 0.47 and the Cu–O bond has a bond valence of 0.24. Finally, the valence of the five-coordinate Cu atom is consistent with the valence-sum rule ($V_i = \Sigma\nu_{ij}$), which gives V_{Cu} = 2.026 v.u.

The structure has extensive hydrogen bonds that link it in a two-dimensional network of N—H···O and weak C—H···O interactions parallel to the *ab* plane (Table 1).

Experimental

A solution of $CuSO_4 \cdot 5H_2O$ (1 mmol) dissolved in water (20 ml) was added to benzimidazole (4 mmol) dissolved in a hot mixture of water (20 ml) and dimethyl sulfoxide (DMSO) (4 ml). After several days, prismatic blue crystals were obtained.

Crystal data

$[Cu(SO_4)(C_7H_6N_2)_4] \cdot C_2H_6OS$
M_r = 710.31
Triclinic, $P\bar{1}$
a = 10.347 (2) Å
b = 10.744 (2) Å
c = 15.121 (3) Å
α = 98.99 (3)°
β = 109.88 (3)°
γ = 91.45 (3)°
V = 1555.8 (6) Å^3
Z = 2
D_x = 1.516 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.89 mm^{-1}
T = 293 K
Prism, blue
0.40 × 0.30 × 0.15 mm

Data collection

Siemens P3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.68, $T_{\max}$ = 0.87
5683 measured reflections
5456 independent reflections
3972 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
$\theta_{\max}$ = 25.0°
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.092
S = 1.02
5456 reflections
424 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.1051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N13—H13···O5$^{\mathrm{i}}$	0.86	1.89	2.741 (3)	170
N23—H23···O3$^{\mathrm{ii}}$	0.86	2.04	2.830 (4)	153
N33—H33···O3$^{\mathrm{iii}}$	0.86	1.96	2.813 (4)	171
N43—H43···O4$^{\mathrm{iv}}$	0.86	1.94	2.793 (4)	171
C12—H12···O1$^{\mathrm{v}}$	0.93	2.35	3.253 (4)	163
C22—H22···O2	0.93	2.40	2.941 (4)	117
C42—H42···O5	0.93	2.47	3.282 (4)	146

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+2, -y+1, -z+2$; (iii) $-x+2, -y+2, -z+2$; (iv) $-x+1, -y+2, -z+2$; (v) $x, y, z+1$.

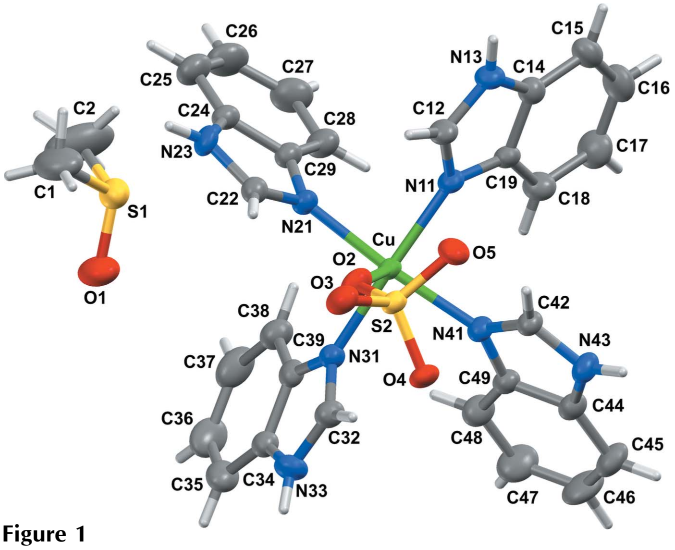


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids. For clarity, only the major orientation of the disordered DMSO molecule is shown.

The sulfur atom S1/S1′ in the DMSO molecule is disordered over two positions with site occupancies of 0.85 and 0.15. This site occupancy was determined by restraining the two sites to sum to 1.0 and using an overall isotropic displacement parameter. Once the site occupancies had been determined, they were fixed and not further refined. In the final stage of refinement, the S atoms were anisotropically refined. The geometry of the disordered DMSO was restrained to reasonable values. All H atoms were included at geometrically idealized positions and refined as riding, with C—H = 0.93 and 0.96, N—H = 0.86 Å, and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C,N})$ or $1.5U_{\mathrm{eq}}$(methyl C).

Data collection: *P3 Software* (Siemens, 1989); cell refinement: *P3 Software*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. W. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1355.
Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.
Brown, I. D. (1997). *Acta Cryst.* B**53**, 381–393.
Fan, C., Ma, C.-B., Hu, M.-Q., Chen, C.-N. & Liu, Q.-T. (2006). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **25**, 285–289. (In Chinese.)
Kataev, V. A., Spirikhin, L. V., Khaliullin, A. N. & Gailyunas, I. A. (2002). *Russ. J. Org. Chem.* **38**, 1057–1059.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.
Sheldrick, G. M. (1990). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1989). *P3 Software*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
Sieroń, L. & Bukowska-Strzyżewska, M. (1999). *Acta Cryst.* C**55**, 1230–1234.
Sieroń, L., Bukowska-Strzyżewska, M., Korabik, M. & Mroziński, J. (2002). *Polyhedron*, **21**, 2473–2479.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Valdez, J., Cedillo, R., Campos, A. H., Yepez, L., Luis, F. H., Vazquez, G. N., Tapia, A., Cortes, R., Hernandez, M. & Castillo, R. (2002). *Bioorg. Med. Chem. Lett.* **12**, 2221–2224.