Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of μ-oxalodihydroxamato-bis[(2,2′-bipyridyl)(dimethyl sulfoxide-κO)-copper(II)] bis(perchlorate)

Irina A. Odarich,[a] Anna V. Pavlishchuk,[b]* Valentina A. Kalibabchuk[a] and Matti Haukka[c]

[a]O.O. Bohomolets National Medical University, Department of General Chemistry, Pr. Pobedy, 34, Kiev, 03055 , Ukraine, [b]Taras Shevchenko National University of Kiev, Department of Chemistry, Volodymyrska str. 62, Kiev, 01601 , Ukraine, and [c]University of Joensuu, Department of Chemistry, PO Box 111, FI-80101 Joensuu, Finland. *Correspondence e-mail: annpavlis@ukr.net

Received 1 December 2015
Accepted 2 January 2016

Edited by J. Simpson, University of Otago, New Zealand

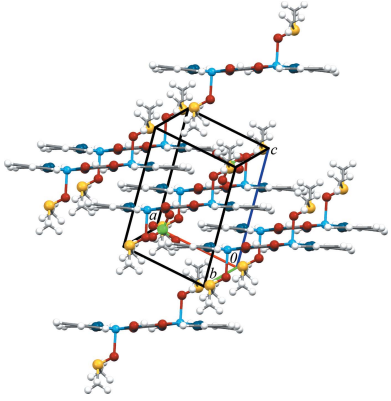
Keywords: crystal structure; Cu(II) complex; oxalodihydroxamic acid

CCDC reference: 1445115
Supporting information: this article has supporting information at journals.iucr.org/e

The centrosymmetric binuclear complex, $[Cu_2(C_2H_2N_2O_4)(C_{10}H_8N_2)_2(C_2H_6OS)_2](ClO_4)_2$, contains two copper(II) ions, connected through an N-deprotonated oxalodihydroxamic acid dianion, two terminal 2,2′-bipyridine ligands, and two apically coordinating dimethylsulfoxide molecules. Two non-coordinating perchlorate anions assure electrical neutrality. The copper(II) ions in the complex dication $[Cu_2(C_{10}H_8N_2)_2(\mu\text{-}C_2H_2N_2O_4)(C_2H_6SO)_2]^{2+}$ are in an O_2N_3 square-pyramidal donor environment, the Cu–Cu separation being 5.2949 (4) Å. Two hydroxamate groups in the deprotonated oxalodihydroxamic acid are located *trans* to one each other. In the crystal, O—H···O and C—H···O hydrogen bonds link the complex cations to the perchlorate anions. Further C—H···O hydrogen bonds combine with π–π contacts with a centroid-to-centroid separation of 3.6371 (12) Å to stack the molecules along the *a*-axis direction.

1. Chemical context

Syntheses of complexes based on functionalized hydroxamic acids are of particular interest due to their non-trivial magnetic (Pavlishchuk *et al.*, 2014) and luminescence (Jankolovits *et al.*, 2011) properties, potential applications in bioinorganic modeling (Marmion *et al.*, 2004), adsorption (Pavlishchuk *et al.*, 2010, 2011*a*;), catalysis (Mezei *et al.*, 2007) and the creation of recognition agents (Lim *et al.*, 2011). The majority of complexes obtained with hydroxamic acids and additional donor ligands belong to different families of metallacrown coordination compounds (Mezei *et al.*, 2007). Other topologies for polydentate hydroxamate-based complexes are more unusual (Gumienna-Kontecka *et al.*, 2013; Golenya *et al.*, 2014). Here we present the structure of the binuclear complex $[Cu_2(C_{10}H_8N_2)_2(\mu\text{-}C_2H_2N_2O_4)(C_2H_6SO)_2](ClO_4)_2$ (I), obtained from oxalodihydroxamic acid and bipyridine in DMSO solution.



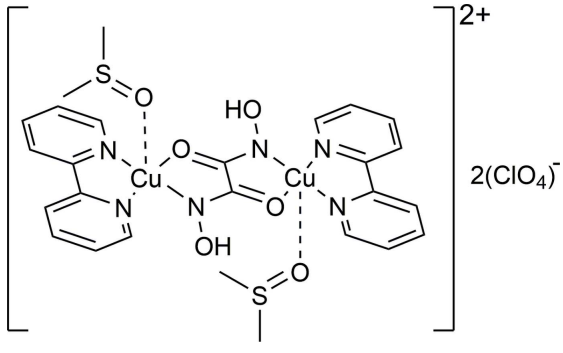


Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9848 (16)	Cu1—O2	2.2516 (16)
Cu1—N2	1.985 (2)	O1—C11	1.286 (3)
Cu1—N3^{i}	1.986 (2)	O5—N3	1.404 (3)
Cu1—N1	1.9966 (19)		
O1—Cu1—N2	90.36 (7)	O1—Cu1—O2	98.04 (6)
O1—Cu1—N3^{i}	82.73 (7)	N2—Cu1—O2	97.53 (7)
N2—Cu1—N1	81.76 (8)	N3^{i}—Cu1—O2	96.15 (7)
N3^{i}—Cu1—N1	103.13 (8)	N1—Cu1—O2	90.72 (7)

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

2. Structural commentary

The title compound (I) consists of a centrosymmetric complex di-cation $[Cu_2(C_{10}H_8N_2)_2(\mu\text{-}C_2H_2N_2O_4)(C_2H_6SO)_2]^{2+}$ with two uncoordinating perchlorate counter-anions (Fig. 1). The two copper(II) cations are connected through a doubly deprotonated oxalodihydroxamic acid, which serves as a bridging ligand between the copper ions which are coordinated by two nitrogen atoms from the 2,2′-bipyridine ligand, one carbonyl oxygen atom and the deprotonated hydroxamate nitrogen atom from one half of the oxalodihydroxamato ligand and the O atom of a DMSO molecule. The oxalodihydroxamato dianion is in a *trans*-form, while for metallacrown formation the *cis*-form is preferred. The coordination sphere of the copper(II) cation is square-pyramidal (τ = 0.21; Addison *et al.*, 1984) and the copper(II) ion deviates from the mean plane of the O1/N1/N2/N3 donor atoms by 0.1868 (2) Å. The separation between the copper (II) cations is 5.2949 (4) Å. The equatorial Cu—N and Cu—O distances are typical of those for copper(II) complexes with hydroxamate and oxime donor groups (Buvailo *et al.*, 2012; Duda *et al.*, 1997; Pavlishchuk *et al.*, 2011*b*; Safyanova *et al.*, 2015, Table 1). The elongated apical bond, Cu1—O2 (2.2516 (16) Å), compared to the Cu—O and Cu—N distances in the equatorial plane that range from 1.9848 (16) to 1.9966 (19) Å, Table 1, is most likely due to Jahn–Teller distortion.

The C—N and C—C bond lengths in the 2,2′-bipyridine ligands are also normal for 2-substituted pyridine derivatives (Krämer *et al.*, 2000; Strotmeyer *et al.*, 2003; Fritsky *et al.*, 2004). The coordinating oxalohydroxamate dianion also has C—C, C—N, N—N bond lengths that are typical of N-deprotonated hydroxamate groups (Świątek-Kozłowska *et al.*, 2000; Dobosz *et al.*, 1999).

3. Supramolecular features

In the crystal structure, O5—H5*O*···O6 together with C12—H12*A*···O9 hydrogen bonds link the cations and associated perchlorate anions. An extensive series of other C—H···O contacts, Table 2, link the complex cations to other anions. The O2 atom of the DMSO ligand acts as a bifurcated acceptor forming C4—H4···O2 and C7—H7···O2 hydrogen bonds. These hydrogen bonds combine with π–π contacts between the N2/C6–C10 ring of the bipyridine and the Cu1/O1/C11/C11^{i}/N3 ring formed by the chelating oxalodihydroxamate ligand with a centroid-to-centroid distance of 3.6371 (12) Å to stack the cations along the *a*-axis direction, Fig. 2.

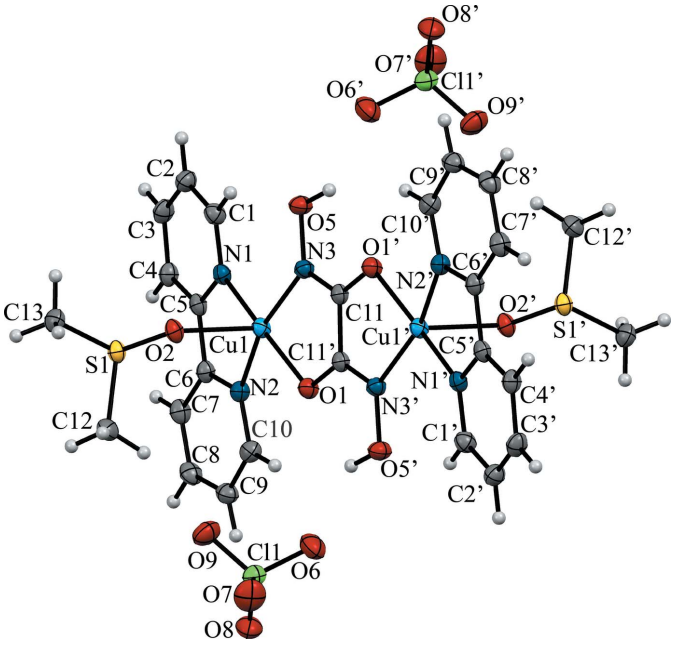


Figure 1
The crystal structure of complex (I), showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

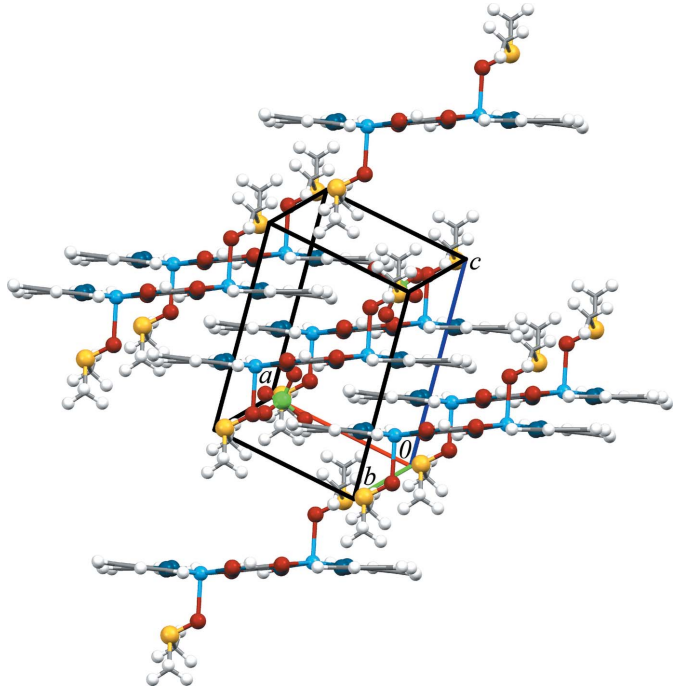


Figure 2
The crystal packing of complex (I).

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5O···O6	0.92 (5)	2.12 (5)	2.912 (3)	144 (4)
C4—H4···O2^{ii}	0.95	2.42	3.359 (3)	171
C7—H7···O2^{ii}	0.95	2.31	3.226 (3)	162
C3—H3···O7^{iii}	0.95	2.50	3.239 (3)	134
C13—H13A···O7^{iv}	0.98	2.56	3.409 (3)	145
C13—H13C···O8^{v}	0.98	2.48	3.346 (3)	148
C13—H13B···O8^{vi}	0.98	2.65	3.442 (3)	138
C12—H12A···O9	0.98	2.36	3.175 (3)	140
C8—H8···O9^{ii}	0.95	2.56	3.462 (3)	159
C12—H12B···O9^{vi}	0.98	2.59	3.470 (3)	150

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

4. Database survey

A search in the Cambridge Structural Database (Version 5.35, May 2014; Groom & Allen, 2014) shows that there are seven reports devoted to the study of crystal structures of oxalodihydroxamic acid and its complexes. In the reported crystal structures of oxalodihydroxamic acid and its salts, the compound crystallized only in the *trans*-form. The bond lengths in oxalodihydroxamic acid itself and in its ammonium and thallium salts do not differ significantly [C—C bonds are in the range 1.51 (2)–1.528 (3) Å, C=O 1.231 (3)–1.248 (3) Å, C—N 1.310 (4)–1.33 (2) Å while the N—O bond lengths vary from 1.36 (2) to 1.388 (1) Å; Lowe-Ma & Decker, 1986; Sameena Begum *et al.*, 1987, 1988; Huang *et al.*, 1991; Marsh, 1989). Only two structures of coordination compounds with dihydroxyoxamidato ligands were found. Both involved anionic mononuclear Ni^{II} complexes with ligands derived from doubly or triply deprotonated oxalodihydroxamic acid. In one of these complexes (Moroz *et al.*, 2006), the dihydroxyoxamidato trianion acts as a simple bidentate chelating ligand forming a square-planar complex. In the second (Świątek-Kozłowska *et al.*, 2000), a square planar Ni^{II} complex again forms, but the dihydroxyoxamidato ligand also forms bridges to the potassium counter-ions generating a polymeric system. The structure presented here is the first example in which a dihydroxyoxamidato anion acts as a bridging ligand between two transition metals. The lack of crystal data for complexes with other transition metal cations may be associated with the ease of hydrolysis of the oxalodihydroxamic acid initiated by a metal salt solution.

5. Synthesis and crystallization

To the warm mixture containing 0.060 g (0.5 mmol) of oxalodihydroxamic acid and 0.370 g (1 mmol) of $Cu(ClO_4)_2\cdot 6H_2O$ in 10 ml of DMSO the solution of 2,2′-bipyridine (0.156 g, 1 mmol) in 10 ml of methanol was added upon stirring. The resulted solution was stirred for 1 h and then left for slow evaporation.

The resulting blue crystals suitable for X-ray analysis were isolated after one week. The crystals were washed with small amounts of 2-propanol and dried in air, yielding 0.255 g (28%) of the title compound.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_2H_2N_2O_4)(C_{10}H_8N_2)_2(C_2H_6OS)_2](ClO_4)_2$
M_r	912.66
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	7.3641 (2), 10.3759 (5), 12.1358 (5)
α, β, γ (°)	68.853 (2), 84.803 (3), 87.825 (3)
V (Å^3)	861.27 (6)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.59
Crystal size (mm)	0.13 × 0.12 × 0.12
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (*SORTAV*; Blessing, 1995)
T_{min}, T_{max}	0.789, 0.835
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18205, 3943, 3351
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.087, 1.11
No. of reflections	3943
No. of parameters	241
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, −0.55

Computer programs: *COLLECT* (Bruker, 2004), *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The OH hydrogen atom was located from a difference Fourier map and was refined isotropically. Other hydrogen atoms were positioned geometrically and were constrained to ride on their parent atoms, with C—H = 0.95–0.98 Å, and U_{iso} = 1.2–1.5 U_{eq}(parent atom). The highest peak is located 0.99 Å from atom Cu1 and the deepest hole is located 0.82 Å from atom Cu1.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2004). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Buvailo, A. I., Pavlishchuk, A. V., Penkova, L. V., Kotova, N. V. & Haukka, M. (2012). *Acta Cryst.* E**68**, m1480–m1481.
Dobosz, A., Dudarenko, N. M., Fritsky, I. O., Głowiak, T., Karaczyn, A., Kozłowski, H., Sliva, T. Yu. & Świątek-Kozłowska, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 743–750.
Duda, A. M., Karaczyn, A., Kozłowski, H., Fritsky, I. O., Głowiak, T., Prisyazhnaya, E. V., Sliva, T. Yu. & Świątek-Kozłowska, J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3853–3860.

Fritsky, I. O., Świątek-Kozłowska, J., Dobosz, A., Sliva, T. Y. & Dudarenko, N. M. (2004). *Inorg. Chim. Acta*, **357**, 3746–3752.
Golenya, I. A., Gumienna-Kontecka, E., Haukka, M., Korsun, O. M., Kalugin, O. N. & Fritsky, I. O. (2014). *CrystEngComm*, **16**, 1904–1918.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Gumienna-Kontecka, E., Golenya, I. A., Szebesczyk, A., Haukka, M., Krämer, R. & Fritsky, I. O. (2013). *Inorg. Chem.* **52**, 7633–7644.
Huang, S.-H., Wang, R.-J. & Mak, T. C. W. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1379–1381.
Jankolovits, J., Andolina, C. M., Kampf, J. W., Raymond, K. N. & Pecoraro, V. L. (2011). *Angew. Chem. Int. Ed.* **50**, 9660–9664.
Krämer, R. & Fritsky, I. O. (2000). *Eur. J. Org. Chem.* pp. 3505–3510.
Lim, C.-S., Jankolovits, J., Zhao, P., Kampf, J. W. & Pecoraro, V. L. (2011). *Inorg. Chem.* **50**, 4832–4841.
Lowe-Ma, C. K. & Decker, D. L. (1986). *Acta Cryst.* C**42**, 1648–1649.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Marmion, C. J., Griffith, D. & Nolan, K. B. (2004). *Eur. J. Inorg. Chem.* pp. 3003–3016.
Marsh, R. E. (1989). *Acta Cryst.* C**45**, 347.
Mezei, G., Zaleski, C. M. & Pecoraro, V. L. (2007). *Chem. Rev.* **107**, 4933–5003.
Moroz, Y. S., Gumienna-Kontecka, E., Fritsky, I. O., Dudarenko, N. M. & Świątek-Kozłowska, J. (2006). *Acta Cryst.* C**62**, m498–m500.
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.
Pavlishchuk, A. V., Kolotilov, S. V., Fritsky, I. O., Zeller, M., Addison, A. W. & Hunter, A. D. (2011*b*). *Acta Cryst.* C**67**, m255–m265.
Pavlishchuk, A. V., Kolotilov, S. V., Zeller, M., Shvets, O. V., Fritsky, I. O., Lofland, S. E., Addison, A. W. & Hunter, A. D. (2011*a*). *Eur. J. Inorg. Chem.* pp. 4826–4836.
Pavlishchuk, A. V., Kolotilov, S. V., Zeller, M., Thompson, L. K. & Addison, A. W. (2014). *Inorg. Chem.* **53**, 1320–1330.
Pavlishchuk, A. V., Kolotilov, S. V., Zeller, M., Thompson, L. K., Fritsky, I. O., Addison, A. W. & Hunter, A. D. (2010). *Eur. J. Inorg. Chem.* pp. 4851–4858.
Safyanova, I. S., Golenya, I. A., Pavlenko, V. A., Gumienna-Kontecka, E., Pekhnyo, V. I., Bon, V. V. & Fritsky, I. O. (2015). *Z. Anorg. Allg. Chem.* **641**, 2326–2332.
Sameena Begum, A., Jain, V. K., Khetrapal, C. L. & Shivaprakash, N. C. (1987). *J. Crystallogr. Spectrosc. Res.* **17**, 545–555.
Sameena Begum, A., Jain, V. K., Ramakumar, S. & Khetrapal, C. L. (1988). *Acta Cryst.* C**44**, 1047–1049.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Strotmeyer, K. P., Fritsky, I. O., Ott, R., Pritzkow, H. & Krämer, R. (2003). *Supramol. Chem.* **15**, 529–547.
Świątek-Kozłowska, J., Fritsky, I. O., Dobosz, A., Karaczyn, A., Dudarenko, N. M., Sliva, T. Yu., Gumienna-Kontecka, E. & Jerzykiewicz, L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 4064–4068.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2016). E**72**, 147-150 [doi:10.1107/S2056989016000050]

Crystal structure of μ-oxalodihydroxamato-bis[(2,2′-bipyridyl)(dimethyl sulfoxide-κO)copper(II)] bis(perchlorate)

Irina A. Odarich, Anna V. Pavlishchuk, Valentina A. Kalibabchuk and Matti Haukka

Computing details

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

μ-Oxalodihydroxamato-bis[(2,2′-bipyridyl)(dimethyl sulfoxide-κO)copper(II)] bis(perchlorate)

Crystal data

$[Cu_2(C_2H_2N_2O_4)(C_{10}H_8N_2)_2(C_2H_6OS)_2](ClO_4)_2$
M_r = 912.66
Triclinic, $P\overline{1}$
a = 7.3641 (2) Å
b = 10.3759 (5) Å
c = 12.1358 (5) Å
α = 68.853 (2)°
β = 84.803 (3)°
γ = 87.825 (3)°
V = 861.27 (6) Å^3
Z = 1
$F(000)$ = 464
D_x = 1.760 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 26719 reflections
θ = 1.0–27.5°
μ = 1.59 mm^{-1}
T = 100 K
Block, pale blue
0.13 × 0.12 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.789, T_{max} = 0.835
18205 measured reflections
3943 independent reflections
3351 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 27.5°, θ_{min} = 2.8°
h = −8→9
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.087
S = 1.11
3943 reflections
241 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.7097P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.81268 (4)	0.11133 (3)	0.38671 (2)	0.01840 (10)
Cl1	0.71265 (8)	−0.30071 (6)	0.19039 (5)	0.02481 (14)
S1	0.85060 (7)	0.28499 (6)	0.10324 (5)	0.01997 (14)
O1	0.6724 (2)	−0.05948 (17)	0.41752 (15)	0.0210 (3)
O2	0.7106 (2)	0.23761 (17)	0.21002 (14)	0.0221 (4)
O5	0.4262 (2)	−0.26749 (18)	0.48100 (16)	0.0243 (4)
H5O	0.528 (6)	−0.253 (5)	0.428 (4)	0.083 (14)*
O6	0.6917 (3)	−0.3371 (2)	0.31798 (18)	0.0383 (5)
O7	0.5444 (3)	−0.3243 (2)	0.1500 (2)	0.0423 (5)
O8	0.8557 (3)	−0.3841 (2)	0.16071 (18)	0.0344 (4)
O9	0.7598 (3)	−0.15753 (19)	0.13534 (19)	0.0365 (5)
N1	0.9922 (3)	0.2580 (2)	0.36990 (17)	0.0192 (4)
N2	1.0297 (3)	0.0299 (2)	0.32626 (17)	0.0192 (4)
N3	0.3959 (3)	−0.1523 (2)	0.51515 (17)	0.0192 (4)
C1	0.9598 (3)	0.3726 (3)	0.3950 (2)	0.0238 (5)
H1	0.8409	0.3883	0.4252	0.029*
C2	1.0948 (3)	0.4694 (3)	0.3781 (2)	0.0255 (5)
H2	1.0683	0.5499	0.3967	0.031*
C3	1.2673 (3)	0.4473 (3)	0.3342 (2)	0.0257 (5)
H3	1.3624	0.5108	0.3248	0.031*
C4	1.3010 (3)	0.3309 (2)	0.3038 (2)	0.0222 (5)
H4	1.4180	0.3153	0.2708	0.027*
C5	1.1604 (3)	0.2381 (2)	0.3224 (2)	0.0199 (5)
C6	1.1790 (3)	0.1118 (2)	0.2922 (2)	0.0203 (5)
C7	1.3330 (3)	0.0781 (3)	0.2340 (2)	0.0241 (5)
H7	1.4356	0.1376	0.2100	0.029*
C8	1.3359 (3)	−0.0434 (3)	0.2112 (2)	0.0261 (5)
H8	1.4398	−0.0679	0.1705	0.031*
C9	1.1844 (3)	−0.1290 (3)	0.2487 (2)	0.0249 (5)
H9	1.1846	−0.2140	0.2358	0.030*
C10	1.0341 (3)	−0.0888 (2)	0.3050 (2)	0.0231 (5)
H10	0.9300	−0.1469	0.3295	0.028*
C11	0.5220 (3)	−0.0590 (2)	0.4801 (2)	0.0183 (5)
C12	0.8329 (4)	0.1655 (3)	0.0300 (2)	0.0290 (6)
H12A	0.8580	0.0719	0.0845	0.044*
H12B	0.9215	0.1893	−0.0395	0.044*
H12C	0.7095	0.1696	0.0047	0.044*
C13	0.7529 (4)	0.4328 (3)	−0.0024 (2)	0.0266 (5)
H13A	0.6320	0.4095	−0.0173	0.040*

H13B	0.8315	0.4622	−0.0766	0.040*
H13C	0.7414	0.5081	0.0286	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01496 (15)	0.02100 (16)	0.01911 (16)	−0.00278 (10)	0.00203 (10)	−0.00758 (12)
Cl1	0.0209 (3)	0.0239 (3)	0.0307 (3)	−0.0023 (2)	0.0016 (2)	−0.0117 (2)
S1	0.0164 (3)	0.0234 (3)	0.0179 (3)	−0.0026 (2)	0.0010 (2)	−0.0050 (2)
O1	0.0169 (8)	0.0230 (8)	0.0234 (9)	−0.0041 (6)	0.0043 (6)	−0.0097 (7)
O2	0.0165 (8)	0.0291 (9)	0.0187 (8)	−0.0036 (7)	0.0033 (6)	−0.0069 (7)
O5	0.0229 (9)	0.0232 (9)	0.0297 (10)	−0.0029 (7)	0.0045 (7)	−0.0143 (8)
O6	0.0423 (12)	0.0437 (12)	0.0292 (10)	0.0059 (9)	0.0046 (9)	−0.0157 (9)
O7	0.0267 (10)	0.0498 (13)	0.0519 (13)	−0.0114 (9)	−0.0070 (9)	−0.0181 (11)
O8	0.0354 (11)	0.0327 (10)	0.0356 (11)	0.0075 (8)	0.0041 (8)	−0.0153 (9)
O9	0.0344 (11)	0.0241 (10)	0.0488 (13)	−0.0064 (8)	0.0063 (9)	−0.0120 (9)
N1	0.0182 (9)	0.0218 (10)	0.0167 (9)	−0.0023 (7)	0.0003 (7)	−0.0061 (8)
N2	0.0169 (9)	0.0204 (10)	0.0195 (10)	−0.0008 (7)	−0.0016 (8)	−0.0062 (8)
N3	0.0190 (10)	0.0186 (9)	0.0207 (10)	−0.0015 (7)	0.0004 (8)	−0.0083 (8)
C1	0.0218 (12)	0.0263 (13)	0.0236 (12)	−0.0007 (9)	0.0007 (10)	−0.0099 (10)
C2	0.0274 (13)	0.0210 (12)	0.0271 (13)	−0.0035 (10)	0.0017 (10)	−0.0082 (10)
C3	0.0254 (13)	0.0233 (12)	0.0264 (13)	−0.0074 (10)	−0.0024 (10)	−0.0057 (10)
C4	0.0175 (11)	0.0247 (12)	0.0214 (12)	−0.0029 (9)	0.0001 (9)	−0.0050 (10)
C5	0.0189 (11)	0.0239 (12)	0.0153 (11)	0.0005 (9)	−0.0026 (9)	−0.0050 (9)
C6	0.0179 (11)	0.0229 (12)	0.0187 (11)	−0.0020 (9)	−0.0012 (9)	−0.0058 (9)
C7	0.0173 (11)	0.0294 (13)	0.0236 (13)	−0.0014 (9)	0.0000 (9)	−0.0075 (10)
C8	0.0210 (12)	0.0315 (13)	0.0255 (13)	0.0029 (10)	0.0026 (10)	−0.0113 (11)
C9	0.0264 (13)	0.0253 (13)	0.0248 (13)	0.0029 (10)	−0.0018 (10)	−0.0115 (10)
C10	0.0224 (12)	0.0225 (12)	0.0240 (12)	−0.0004 (9)	−0.0026 (10)	−0.0076 (10)
C11	0.0179 (11)	0.0195 (11)	0.0164 (11)	−0.0001 (9)	−0.0019 (9)	−0.0051 (9)
C12	0.0349 (14)	0.0279 (13)	0.0244 (13)	−0.0011 (11)	0.0054 (11)	−0.0114 (11)
C13	0.0306 (13)	0.0220 (12)	0.0243 (13)	0.0015 (10)	−0.0041 (10)	−0.0046 (10)

Geometric parameters (Å, º)

Cu1—O1	1.9848 (16)	C2—C3	1.376 (4)
Cu1—N2	1.985 (2)	C2—H2	0.9500
Cu1—N3^{i}	1.986 (2)	C3—C4	1.393 (4)
Cu1—N1	1.9966 (19)	C3—H3	0.9500
Cu1—O2	2.2516 (16)	C4—C5	1.388 (3)
Cl1—O9	1.4336 (19)	C4—H4	0.9500
Cl1—O7	1.4339 (19)	C5—C6	1.481 (3)
Cl1—O8	1.4401 (19)	C6—C7	1.382 (3)
Cl1—O6	1.450 (2)	C7—C8	1.384 (4)
S1—O2	1.5234 (17)	C7—H7	0.9500
S1—C12	1.781 (3)	C8—C9	1.390 (4)
S1—C13	1.783 (2)	C8—H8	0.9500
O1—C11	1.286 (3)	C9—C10	1.378 (4)

O5—N3	1.404 (3)	C9—H9	0.9500
O5—H5O	0.92 (5)	C10—H10	0.9500
N1—C1	1.338 (3)	C11—C11^{i}	1.486 (5)
N1—C5	1.359 (3)	C12—H12A	0.9800
N2—C10	1.345 (3)	C12—H12B	0.9800
N2—C6	1.355 (3)	C12—H12C	0.9800
N3—C11	1.296 (3)	C13—H13A	0.9800
N3—Cu1^{i}	1.986 (2)	C13—H13B	0.9800
C1—C2	1.389 (3)	C13—H13C	0.9800
C1—H1	0.9500		

O1—Cu1—N2	90.36 (7)	C2—C3—H3	120.4
O1—Cu1—N3^{i}	82.73 (7)	C4—C3—H3	120.4
N2—Cu1—N3^{i}	165.41 (8)	C5—C4—C3	118.8 (2)
O1—Cu1—N1	168.93 (7)	C5—C4—H4	120.6
N2—Cu1—N1	81.76 (8)	C3—C4—H4	120.6
N3^{i}—Cu1—N1	103.13 (8)	N1—C5—C4	121.6 (2)
O1—Cu1—O2	98.04 (6)	N1—C5—C6	114.7 (2)
N2—Cu1—O2	97.53 (7)	C4—C5—C6	123.7 (2)
N3^{i}—Cu1—O2	96.15 (7)	N2—C6—C7	121.8 (2)
N1—Cu1—O2	90.72 (7)	N2—C6—C5	114.2 (2)
O9—Cl1—O7	109.44 (13)	C7—C6—C5	124.1 (2)
O9—Cl1—O8	109.53 (12)	C6—C7—C8	119.1 (2)
O7—Cl1—O8	110.04 (13)	C6—C7—H7	120.4
O9—Cl1—O6	109.19 (13)	C8—C7—H7	120.4
O7—Cl1—O6	109.47 (13)	C7—C8—C9	119.0 (2)
O8—Cl1—O6	109.16 (12)	C7—C8—H8	120.5
O2—S1—C12	105.19 (11)	C9—C8—H8	120.5
O2—S1—C13	105.82 (11)	C10—C9—C8	119.1 (2)
C12—S1—C13	98.84 (13)	C10—C9—H9	120.5
C11—O1—Cu1	110.68 (14)	C8—C9—H9	120.5
S1—O2—Cu1	117.43 (9)	N2—C10—C9	122.2 (2)
N3—O5—H5O	110 (3)	N2—C10—H10	118.9
C1—N1—C5	119.0 (2)	C9—C10—H10	118.9
C1—N1—Cu1	126.77 (16)	O1—C11—N3	127.6 (2)
C5—N1—Cu1	114.11 (16)	O1—C11—C11^{i}	119.6 (2)
C10—N2—C6	118.8 (2)	N3—C11—C11^{i}	112.8 (2)
C10—N2—Cu1	126.04 (16)	S1—C12—H12A	109.5
C6—N2—Cu1	114.74 (16)	S1—C12—H12B	109.5
C11—N3—O5	116.51 (19)	H12A—C12—H12B	109.5
C11—N3—Cu1^{i}	114.16 (16)	S1—C12—H12C	109.5
O5—N3—Cu1^{i}	129.32 (14)	H12A—C12—H12C	109.5
N1—C1—C2	122.0 (2)	H12B—C12—H12C	109.5
N1—C1—H1	119.0	S1—C13—H13A	109.5
C2—C1—H1	119.0	S1—C13—H13B	109.5
C3—C2—C1	119.3 (2)	H13A—C13—H13B	109.5
C3—C2—H2	120.4	S1—C13—H13C	109.5

C1—C2—H2	120.4	H13A—C13—H13C	109.5
C2—C3—C4	119.2 (2)	H13B—C13—H13C	109.5

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*O*···O6	0.92 (5)	2.12 (5)	2.912 (3)	144 (4)
C4—H4···O2^{ii}	0.95	2.42	3.359 (3)	171
C7—H7···O2^{ii}	0.95	2.31	3.226 (3)	162
C3—H3···O7^{iii}	0.95	2.50	3.239 (3)	134
C13—H13*A*···O7^{iv}	0.98	2.56	3.409 (3)	145
C13—H13*C*···O8^{v}	0.98	2.48	3.346 (3)	148
C13—H13*B*···O8^{vi}	0.98	2.65	3.442 (3)	138
C12—H12*A*···O9	0.98	2.36	3.175 (3)	140
C8—H8···O9^{ii}	0.95	2.56	3.462 (3)	159
C12—H12*B*···O9^{vi}	0.98	2.59	3.470 (3)	150

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) *x*+1, *y*+1, *z*; (iv) −*x*+1, −*y*, −*z*; (v) *x*, *y*+1, *z*; (vi) −*x*+2, −*y*, −*z*.