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A cofacial binuclear copper(II) complex with a bridging 1,4-dithiane ligand

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Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.005 Å; R factor = 0.050; wR factor = 0.110; data-to-parameter ratio = 12.7.

The molecule of (μ-1,4-dithiane-κ^2S:S')bis{μ-3,3′-[naphthalene-2,7-diylbis(methylene)]bis(pentane-2,4-dionato)-κ^4O,O':O'',O'''}dicopper(II), $[Cu_2(C_{22}H_{22}O_4)(C_4H_8S_2)]$, lies on an inversion center, with a Cu···Cu distance of 8.130 (1) Å. The Cu^{II} centers have square-pyramidal coordination geometry, with Cu—O distances in the range 1.905 (2)–1.925 (2) Å and a Cu—S distance of 2.8088 (10) Å. The host binuclear complex is distorted from a rectangular shape. The inversion symmetry of the molecule requires that the two coordination planes be parallel. However, they are 'slipped': the normals to the two coordination planes at the Cu atoms are 1.865 (1) Å apart. Another measure of this 'slipping' is provided by the four CH_2 groups, whose C atoms form a parallelogram with interior angles of 87.2 (3) and 92.8 (3)°. The two chelate rings tilt differently from the coordination plane, with one Cu atom lying only 0.0131 (5) Å out of one C_3O_2 mean plane, but 0.4416 (5) Å out of the other. Those two chelate planes form a dihedral angle of 11.2 (4)°. This relatively large deviation is believed to be due to the large size of the 1,4-dithiane guest.

Related literature

$Cu_2(NBA)_2$ {$NBAH_2$ is 3,3′-[naphthalene-2,7-diylbis(methylene)]bis(pentane-2,4-dione)} forms a crystalline solvate with two $CHCl_3$ molecules, in which the Cu···Cu distance is 7.349 (1) Å at room temperature (Maverick *et al.*, 1986) and 7.298 (1) Å at 100 K (Burton *et al.*, 2002). With μ-Dabco (1,4-diazabicyclo[2.2.2]octane), the Cu···Cu distance is 7.403 (4) Å (Maverick *et al.*, 1986), with μ-2,5-dimethylpyrazine it is 7.559 (2) and 7.596 (2) Å (Maverick *et al.*, 1990), and with μ-2-methylpyrazine it is 7.4801 (8) Å (Maverick *et al.*, 2001). For related literature, see: Martin *et al.* (1959).

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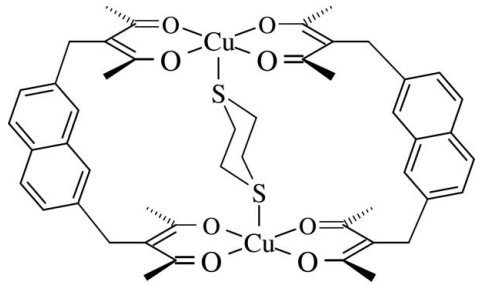

Experimental

Crystal data

$[Cu_2(C_{22}H_{22}O_4)(C_4H_8S_2)]$
M_r = 948.10
Monoclinic, $P2_1/c$
a = 7.758 (2) Å
b = 28.981 (7) Å
c = 9.640 (3) Å
β = 97.840 (15)°
V = 2147.1 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.14 mm^{-1}
T = 120 K
0.15 × 0.08 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.878, T_{max} = 0.924
10982 measured reflections
3491 independent reflections
2598 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.110
S = 1.06
3491 reflections
275 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2036).

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supplementary materials

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A cofacial binuclear copper(II) complex with a bridging 1,4-dithiane ligand

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Comment

Our group has previously prepared binuclear metal complexes derived from polydentate liands, which have been shown to intramolecularly bind bridging substrate molecules, similar to those produced by several other flexible binucleating macrocycles. This work was undertaken in an attempt to associate and quantify the binding between di-sulfur bases and their previously studied nitrogen analogues, see Related Literature section.

The molecule is centrosymmetric, and inclusion of the 1,4-dithiane molecule organizes the host such that the Cu···Cu distance, 8.130 (1) Å, is longer than in complexes with other guests, see Related Literature section. Several distortions take place in this organization. The $Cu_2(NBA)_2$ unit is not rectangular, but slipped such that the four CH_2 groups (C6, C17 and their inversion equivalents) form a parallelogram with sides 7.578 (5) and 9.570 (5) Å, and interior angles differing from orthogonality by 2.8 (3)°. This involves a slippage of the coordination planes horizontally by 1.865 (1) Å.

The coordination sphere is square pyramidal, with distances given in the Abstract and geometric details table. The two chelate rings tilt differently from the coordination plane, with Cu1 lying only 0.0131 (5) Å out of the best plane O1/O2/C2/C3/C4, but 0.4416 (5) Å out of the best plane O3/O4/C19/C20/C21. Those two planes form a dihedral angle of 11.2 (4)°. The Cu—S bond is tilted away from O1 and O2 (O—Cu—S angles 98.91 (8) and 96.32 (7)°) and toward O3 and O4 (angles 86.77 (7) and 87.66 (7)°), and forms an angle of 20.15 (5)° with the Cu···Cu vector.

Experimental

The $NBAH_2$, (2,7-naphthalenediylbis(methylene)bis(acetylacetone)) ligand was prepared previously by the general nucleophilic substitution method outlined by Martin *et al.* (1959). The $Cu_2(NBA)_2$ was also prepared by previously published procedures, see Related Literature section. Bis(3,3'-(naphthalene-2,7-diylbis(methylene)bis(2,4-pentanedionato)))\ dicopper(μ-1,4-dithiane) was prepared by combining a 5.05 mMolar chloroform solution of $Cu_2(NBA)_2$ with a 1.02 Molar chloroform solution of 1,4-dithiane. The resulting mixture was layered with acetonitrile and afforded light blue (turquoise) crystals of $Cu_2(NBA)_2$(μ-1,4-dithiane) after standing for 5 days.

Refinement

H atoms were placed in idealized positions with C—H distances 0.95 − 0.99 Å and thereafter treated as riding. U_{iso} for H was assigned as 1.2 times U_{eq} of the attached C atoms (1.5 for methyl). A torsional parameter was refined for each methyl group.

Figures

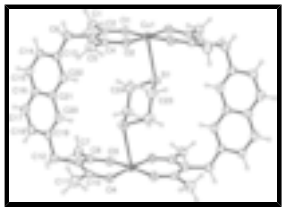


Fig. 1. Numbering scheme and ellipsoids at the 50% level. H atoms are represented with arbitrary radius.

(μ-1,4-Dithiane-κ^2*S*:*S*')bis[μ-3,3'-(naphthalene-2,7- diyldimethylene)bis(pentane-2,4-dionato)-κ^4*O*,*O*':*O*'',*O*''']dicopper,

Crystal data

$[Cu_2(C_{22}H_{22}O_4)(C_4H_8S_2)]$	F_{000} = 988
M_r = 948.10	D_x = 1.466 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 6304 reflections
a = 7.758 (2) Å	θ = 2.5–25.0º
b = 28.981 (7) Å	μ = 1.14 mm^{-1}
c = 9.640 (3) Å	T = 120 K
β = 97.840 (15)º	Prism, light blue
V = 2147.1 (10) Å^3	0.15 × 0.08 × 0.07 mm
Z = 2	

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler	3491 independent reflections
Radiation source: fine-focus sealed tube	2598 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.046
T = 120 K	θ_{max} = 25.0º
ω scans with κ offsets	θ_{min} = 2.5º
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	h = −9→9
T_{min} = 0.878, T_{max} = 0.924	k = −33→34
10982 measured reflections	l = −11→11

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.050	H-atom parameters constrained
$wR(F^2)$ = 0.110	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 2.9798P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3491 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
275 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.88337 (6)	0.458966 (15)	0.80517 (5)	0.02939 (16)
S1	0.66505 (12)	0.46085 (3)	0.54758 (10)	0.0331 (3)
O1	1.0347 (3)	0.50850 (8)	0.7737 (2)	0.0290 (6)
O2	0.7427 (3)	0.49798 (8)	0.9033 (2)	0.0291 (6)
O3	0.2550 (3)	0.59178 (8)	0.1455 (2)	0.0300 (6)
O4	−0.0323 (3)	0.58236 (8)	0.2801 (2)	0.0291 (6)
C1	1.1720 (4)	0.58089 (13)	0.7810 (4)	0.0356 (10)
H1A	1.2465	0.5895	0.8676	0.053*
H1B	1.1232	0.6088	0.7336	0.053*
H1C	1.2411	0.5642	0.7194	0.053*
C2	1.0269 (5)	0.55050 (12)	0.8153 (4)	0.0289 (9)
C3	0.8971 (4)	0.56851 (12)	0.8897 (4)	0.0280 (9)
C4	0.7629 (4)	0.54102 (13)	0.9297 (4)	0.0285 (9)
C5	0.6320 (4)	0.56102 (12)	1.0147 (4)	0.0340 (10)
H5A	0.5341	0.5396	1.0141	0.051*
H5B	0.5897	0.5906	0.9740	0.051*
H5C	0.6871	0.5659	1.1112	0.051*
C6	0.9059 (4)	0.61985 (11)	0.9282 (4)	0.0293 (9)
H6A	0.8458	0.6243	1.0114	0.035*
H6B	1.0296	0.6282	0.9556	0.035*
C7	0.3945 (5)	0.66348 (12)	0.1506 (4)	0.0393 (10)
H7A	0.5020	0.6625	0.2171	0.059*
H7B	0.3499	0.6951	0.1435	0.059*
H7C	0.4187	0.6531	0.0585	0.059*
C8	0.2612 (4)	0.63233 (13)	0.2010 (4)	0.0296 (9)
C9	0.1539 (4)	0.64831 (12)	0.2977 (4)	0.0257 (9)

C10	0.0089 (4)	0.62301 (13)	0.3266 (4)	0.0294 (9)
C11	−0.1178 (5)	0.64297 (13)	0.4144 (4)	0.0398 (10)
H11A	−0.2097	0.6204	0.4234	0.060*
H11B	−0.1695	0.6710	0.3699	0.060*
H11C	−0.0570	0.6505	0.5076	0.060*
C12	0.1908 (4)	0.69621 (12)	0.3596 (4)	0.0317 (9)
H12A	0.1820	0.7187	0.2817	0.038*
H12B	0.0985	0.7039	0.4173	0.038*
C13	0.8278 (4)	0.65323 (12)	0.8151 (4)	0.0282 (9)
C14	0.9166 (5)	0.69515 (11)	0.7956 (4)	0.0317 (9)
H14	1.0252	0.7011	0.8511	0.038*
C15	0.8490 (5)	0.72711 (12)	0.6989 (4)	0.0324 (9)
H15	0.9119	0.7547	0.6881	0.039*
C16	0.6881 (4)	0.71991 (12)	0.6148 (4)	0.0285 (9)
C17	0.6175 (4)	0.75160 (12)	0.5128 (4)	0.0305 (9)
H17	0.6788	0.7793	0.4998	0.037*
C18	0.4621 (5)	0.74330 (12)	0.4318 (4)	0.0323 (9)
H18	0.4176	0.7652	0.3626	0.039*
C19	0.3664 (4)	0.70273 (12)	0.4493 (4)	0.0288 (9)
C20	0.4350 (4)	0.67094 (12)	0.5462 (4)	0.0285 (9)
H20	0.3729	0.6432	0.5565	0.034*
C21	0.5968 (4)	0.67833 (12)	0.6320 (4)	0.0271 (9)
C22	0.6716 (4)	0.64566 (12)	0.7320 (4)	0.0303 (9)
H22	0.6117	0.6175	0.7420	0.036*
C23	0.4616 (5)	0.46546 (13)	0.6187 (4)	0.0360 (10)
H23A	0.4343	0.4351	0.6577	0.043*
H23B	0.4763	0.4879	0.6968	0.043*
C24	0.6918 (5)	0.51949 (12)	0.4876 (4)	0.0369 (10)
H24A	0.7030	0.5407	0.5688	0.044*
H24B	0.8002	0.5215	0.4444	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0288 (3)	0.0309 (3)	0.0285 (3)	−0.0002 (2)	0.00385 (19)	−0.0009 (2)
S1	0.0315 (6)	0.0372 (6)	0.0301 (6)	0.0030 (5)	0.0023 (4)	0.0026 (5)
O1	0.0273 (14)	0.0293 (15)	0.0310 (16)	−0.0012 (11)	0.0069 (11)	−0.0013 (12)
O2	0.0309 (15)	0.0271 (15)	0.0299 (16)	−0.0005 (11)	0.0066 (12)	−0.0040 (13)
O3	0.0332 (15)	0.0310 (15)	0.0260 (16)	−0.0016 (12)	0.0053 (12)	−0.0006 (12)
O4	0.0316 (14)	0.0269 (14)	0.0281 (15)	0.0012 (12)	0.0008 (12)	−0.0017 (13)
C1	0.036 (2)	0.038 (2)	0.034 (2)	−0.0012 (19)	0.0103 (19)	−0.004 (2)
C2	0.026 (2)	0.036 (2)	0.022 (2)	0.0000 (18)	−0.0056 (17)	0.0004 (19)
C3	0.025 (2)	0.033 (2)	0.025 (2)	0.0034 (18)	0.0019 (17)	−0.0008 (19)
C4	0.030 (2)	0.034 (2)	0.019 (2)	0.003 (2)	−0.0028 (16)	−0.001 (2)
C5	0.030 (2)	0.036 (2)	0.036 (2)	0.0006 (18)	0.0068 (19)	−0.001 (2)
C6	0.030 (2)	0.031 (2)	0.026 (2)	−0.0019 (17)	0.0003 (17)	−0.0024 (19)
C7	0.044 (3)	0.034 (2)	0.041 (3)	−0.0044 (19)	0.011 (2)	0.001 (2)
C8	0.031 (2)	0.033 (2)	0.023 (2)	−0.0018 (18)	−0.0048 (18)	0.0065 (19)

C9	0.022 (2)	0.026 (2)	0.027 (2)	0.0017 (17)	−0.0013 (17)	0.0027 (18)
C10	0.030 (2)	0.038 (2)	0.018 (2)	0.0090 (19)	−0.0032 (17)	0.0033 (19)
C11	0.037 (2)	0.041 (2)	0.043 (3)	−0.004 (2)	0.010 (2)	−0.002 (2)
C12	0.032 (2)	0.029 (2)	0.034 (2)	0.0052 (17)	0.0032 (18)	0.0004 (19)
C13	0.030 (2)	0.030 (2)	0.025 (2)	−0.0011 (18)	0.0009 (18)	−0.0041 (19)
C14	0.036 (2)	0.026 (2)	0.031 (2)	−0.0062 (19)	−0.0021 (19)	−0.005 (2)
C15	0.038 (2)	0.027 (2)	0.032 (2)	−0.0063 (18)	0.0036 (19)	−0.005 (2)
C16	0.027 (2)	0.032 (2)	0.025 (2)	0.0016 (19)	0.0014 (18)	0.0009 (19)
C17	0.031 (2)	0.027 (2)	0.034 (2)	−0.0059 (18)	0.0080 (19)	0.001 (2)
C18	0.036 (2)	0.031 (2)	0.029 (2)	0.0044 (19)	0.0024 (19)	0.0053 (19)
C19	0.030 (2)	0.030 (2)	0.026 (2)	0.0016 (18)	0.0029 (18)	−0.0034 (19)
C20	0.031 (2)	0.024 (2)	0.030 (2)	−0.0033 (17)	0.0058 (19)	−0.0018 (19)
C21	0.031 (2)	0.024 (2)	0.025 (2)	0.0025 (17)	0.0016 (18)	−0.0039 (18)
C22	0.038 (2)	0.024 (2)	0.029 (2)	−0.0057 (18)	0.0058 (19)	−0.0019 (19)
C23	0.033 (2)	0.043 (2)	0.032 (2)	−0.005 (2)	0.0045 (18)	0.008 (2)
C24	0.035 (2)	0.043 (2)	0.033 (2)	−0.0076 (19)	0.0058 (19)	0.001 (2)

Geometric parameters (Å, °)

Cu1—O1	1.905 (2)	C9—C10	1.402 (5)
Cu1—O2	1.910 (2)	C9—C12	1.523 (5)
Cu1—O3^{i}	1.918 (2)	C10—C11	1.499 (5)
Cu1—O4^{i}	1.925 (2)	C11—H11A	0.9800
Cu1—S1	2.8088 (10)	C11—H11B	0.9800
S1—C23	1.809 (4)	C11—H11C	0.9800
S1—C24	1.816 (4)	C12—C19	1.522 (5)
O1—C2	1.286 (4)	C12—H12A	0.9900
O2—C4	1.278 (4)	C12—H12B	0.9900
O3—C8	1.289 (4)	C13—C22	1.376 (5)
O3—Cu1^{i}	1.918 (2)	C13—C14	1.422 (5)
O4—C10	1.285 (4)	C14—C15	1.367 (5)
O4—Cu1^{i}	1.925 (2)	C14—H14	0.9500
C1—C2	1.502 (5)	C15—C16	1.408 (5)
C1—H1A	0.9800	C15—H15	0.9500
C1—H1B	0.9800	C16—C17	1.401 (5)
C1—H1C	0.9800	C16—C21	1.419 (5)
C2—C3	1.413 (5)	C17—C18	1.365 (5)
C3—C4	1.406 (5)	C17—H17	0.9500
C3—C6	1.533 (5)	C18—C19	1.413 (5)
C4—C5	1.505 (4)	C18—H18	0.9500
C5—H5A	0.9800	C19—C20	1.367 (5)
C5—H5B	0.9800	C20—C21	1.422 (5)
C5—H5C	0.9800	C20—H20	0.9500
C6—C13	1.520 (5)	C21—C22	1.418 (5)
C6—H6A	0.9900	C22—H22	0.9500
C6—H6B	0.9900	C23—C24^{i}	1.525 (5)
C7—C8	1.502 (5)	C23—H23A	0.9900
C7—H7A	0.9800	C23—H23B	0.9900

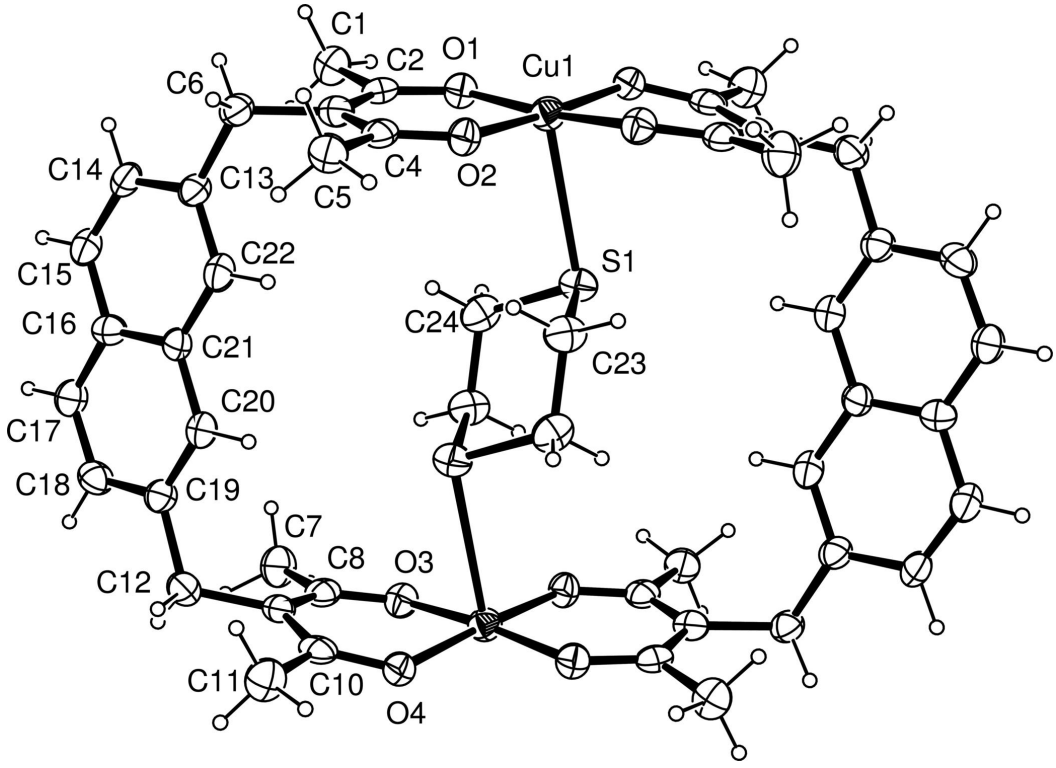
C7—H7B	0.9800	C24—C23^{i}	1.525 (5)
C7—H7C	0.9800	C24—H24A	0.9900
C8—C9	1.410 (5)	C24—H24B	0.9900
O1—Cu1—O2	92.23 (10)	O4—C10—C11	113.5 (3)
O1—Cu1—O3^{i}	174.31 (10)	C9—C10—C11	121.1 (3)
O2—Cu1—O3^{i}	87.38 (10)	C10—C11—H11A	109.5
O1—Cu1—O4^{i}	88.97 (10)	C10—C11—H11B	109.5
O2—Cu1—O4^{i}	175.62 (10)	H11A—C11—H11B	109.5
O3^{i}—Cu1—O4^{i}	91.01 (10)	C10—C11—H11C	109.5
O1—Cu1—S1	98.91 (8)	H11A—C11—H11C	109.5
O2—Cu1—S1	96.32 (7)	H11B—C11—H11C	109.5
O3^{i}—Cu1—S1	86.77 (7)	C19—C12—C9	116.2 (3)
O4^{i}—Cu1—S1	87.66 (7)	C19—C12—H12A	108.2
C23—S1—C24	101.26 (17)	C9—C12—H12A	108.2
C23—S1—Cu1	96.79 (13)	C19—C12—H12B	108.2
C24—S1—Cu1	102.62 (13)	C9—C12—H12B	108.2
C2—O1—Cu1	127.4 (2)	H12A—C12—H12B	107.4
C4—O2—Cu1	127.8 (2)	C22—C13—C14	117.6 (3)
C8—O3—Cu1^{i}	126.0 (2)	C22—C13—C6	123.3 (3)
C10—O4—Cu1^{i}	125.7 (2)	C14—C13—C6	119.1 (3)
C2—C1—H1A	109.5	C15—C14—C13	121.4 (3)
C2—C1—H1B	109.5	C15—C14—H14	119.3
H1A—C1—H1B	109.5	C13—C14—H14	119.3
C2—C1—H1C	109.5	C14—C15—C16	121.3 (3)
H1A—C1—H1C	109.5	C14—C15—H15	119.4
H1B—C1—H1C	109.5	C16—C15—H15	119.4
O1—C2—C3	125.1 (3)	C17—C16—C15	122.5 (3)
O1—C2—C1	114.7 (3)	C17—C16—C21	119.0 (3)
C3—C2—C1	120.2 (3)	C15—C16—C21	118.4 (3)
C4—C3—C2	122.4 (3)	C18—C17—C16	121.0 (3)
C4—C3—C6	119.6 (3)	C18—C17—H17	119.5
C2—C3—C6	118.0 (3)	C16—C17—H17	119.5
O2—C4—C3	125.0 (3)	C17—C18—C19	121.1 (3)
O2—C4—C5	114.2 (3)	C17—C18—H18	119.5
C3—C4—C5	120.7 (3)	C19—C18—H18	119.5
C4—C5—H5A	109.5	C20—C19—C18	118.7 (3)
C4—C5—H5B	109.5	C20—C19—C12	122.6 (3)
H5A—C5—H5B	109.5	C18—C19—C12	118.7 (3)
C4—C5—H5C	109.5	C19—C20—C21	121.8 (3)
H5A—C5—H5C	109.5	C19—C20—H20	119.1
H5B—C5—H5C	109.5	C21—C20—H20	119.1
C13—C6—C3	116.3 (3)	C22—C21—C16	118.8 (3)
C13—C6—H6A	108.2	C22—C21—C20	122.8 (3)
C3—C6—H6A	108.2	C16—C21—C20	118.4 (3)
C13—C6—H6B	108.2	C13—C22—C21	122.4 (3)
C3—C6—H6B	108.2	C13—C22—H22	118.8
H6A—C6—H6B	107.4	C21—C22—H22	118.8

C8—C7—H7A	109.5	$C24^{i}$—C23—S1	114.1 (3)
C8—C7—H7B	109.5	$C24^{i}$—C23—H23A	108.7
H7A—C7—H7B	109.5	S1—C23—H23A	108.7
C8—C7—H7C	109.5	$C24^{i}$—C23—H23B	108.7
H7A—C7—H7C	109.5	S1—C23—H23B	108.7
H7B—C7—H7C	109.5	H23A—C23—H23B	107.6
O3—C8—C9	125.5 (3)	$C23^{i}$—C24—S1	111.7 (3)
O3—C8—C7	113.7 (3)	$C23^{i}$—C24—H24A	109.3
C9—C8—C7	120.7 (3)	S1—C24—H24A	109.3
C10—C9—C8	121.4 (3)	$C23^{i}$—C24—H24B	109.3
C10—C9—C12	120.8 (3)	S1—C24—H24B	109.3
C8—C9—C12	117.5 (3)	H24A—C24—H24B	107.9
O4—C10—C9	125.4 (3)		
O1—Cu1—S1—C23	−125.86 (14)	C12—C9—C10—O4	−179.5 (3)
O2—Cu1—S1—C23	−32.59 (14)	C8—C9—C10—C11	−171.8 (3)
$O3^{i}$—Cu1—S1—C23	54.41 (14)	C12—C9—C10—C11	2.4 (5)
$O4^{i}$—Cu1—S1—C23	145.55 (14)	C10—C9—C12—C19	121.8 (4)
O1—Cu1—S1—C24	−22.68 (15)	C8—C9—C12—C19	−63.8 (4)
O2—Cu1—S1—C24	70.59 (14)	C3—C6—C13—C22	43.2 (5)
$O3^{i}$—Cu1—S1—C24	157.59 (15)	C3—C6—C13—C14	−138.7 (3)
$O4^{i}$—Cu1—S1—C24	−111.27 (15)	C22—C13—C14—C15	0.5 (5)
O2—Cu1—O1—C2	1.7 (3)	C6—C13—C14—C15	−177.6 (3)
$O4^{i}$—Cu1—O1—C2	−174.1 (3)	C13—C14—C15—C16	0.3 (5)
S1—Cu1—O1—C2	98.4 (3)	C14—C15—C16—C17	−178.6 (3)
O1—Cu1—O2—C4	−0.5 (3)	C14—C15—C16—C21	−0.3 (5)
$O3^{i}$—Cu1—O2—C4	173.8 (3)	C15—C16—C17—C18	179.2 (3)
S1—Cu1—O2—C4	−99.7 (3)	C21—C16—C17—C18	0.9 (5)
Cu1—O1—C2—C3	−2.6 (5)	C16—C17—C18—C19	0.7 (5)
Cu1—O1—C2—C1	176.5 (2)	C17—C18—C19—C20	−2.1 (5)
O1—C2—C3—C4	1.9 (5)	C17—C18—C19—C12	177.8 (3)
C1—C2—C3—C4	−177.1 (3)	C9—C12—C19—C20	−43.3 (5)
O1—C2—C3—C6	−178.6 (3)	C9—C12—C19—C18	136.8 (3)
C1—C2—C3—C6	2.4 (5)	C18—C19—C20—C21	1.9 (5)
Cu1—O2—C4—C3	0.1 (5)	C12—C19—C20—C21	−178.0 (3)
Cu1—O2—C4—C5	−177.7 (2)	C17—C16—C21—C22	177.9 (3)
C2—C3—C4—O2	−0.6 (6)	C15—C16—C21—C22	−0.5 (5)
C6—C3—C4—O2	179.9 (3)	C17—C16—C21—C20	−1.1 (5)
C2—C3—C4—C5	177.1 (3)	C15—C16—C21—C20	−179.5 (3)
C6—C3—C4—C5	−2.4 (5)	C19—C20—C21—C22	−179.2 (3)
C4—C3—C6—C13	−97.4 (4)	C19—C20—C21—C16	−0.3 (5)
C2—C3—C6—C13	83.1 (4)	C14—C13—C22—C21	−1.4 (5)
$Cu1^{i}$—O3—C8—C9	−7.1 (5)	C6—C13—C22—C21	176.7 (3)
$Cu1^{i}$—O3—C8—C7	174.3 (2)	C16—C21—C22—C13	1.4 (5)
O3—C8—C9—C10	−10.2 (6)	C20—C21—C22—C13	−179.7 (3)
C7—C8—C9—C10	168.3 (3)	C24—S1—C23—$C24^{i}$	59.9 (3)

O3—C8—C9—C12	175.4 (3)	Cu1—S1—C23—C24^{i}	164.3 (2)
C7—C8—C9—C12	−6.1 (5)	C23—S1—C24—C23^{i}	−58.2 (3)
Cu1^{i}—O4—C10—C9	14.3 (5)	Cu1—S1—C24—C23^{i}	−157.9 (2)
Cu1^{i}—O4—C10—C11	−167.5 (2)	S1—C24—C23^{i}—S1^{i}	66.0 (3)
C8—C9—C10—O4	6.3 (5)		

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

Fig. 1


C1
C2
O1
Cu1
C6
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O2
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C22
S1
C16
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C21
C23
C20
C17
C18
C19
C7
C8
O3
C12
C11
C10
O4