Table 2. *Selected geometric parameters (Å, °)*

Cu1—Cu2	3.1242 (7)	Cu2 -N1	1.957 (4)
Cu1—O1	2.026 (3)	Cu2—N2	1.997 (4)
Cu1—O2	2.356 (3)	O1—C1	1.319 (5)
Cu1—O3	1.951 (2)	O2—C11	1.303 (5)
Cu2—O1	2.008 (3)	O3—C18	1.265 (6)
Cu2—O2	1.922 (3)	O4—C18	1.236 (7)
Cu2—O4	2.265 (3)		
O1—Cu1—O2	73.6 (1)	N1—Cu2—N2	94.0 (2)
O1—Cu1—O3	89.2 (1)	Cu1—O1—Cu2	101.5 (1)
O2—Cu1—O3	92.3 (1)	Cu2—O1—C1	122.8 (3)
O1—Cu2—O2	84.3 (1)	Cu2—O2—C11	124.4 (3)
O1—Cu2—O4	90.7 (1)	Cu1—O3—C18	134.1 (3)
O1—Cu2—N1	89.6 (1)	Cu2—O4—C18	122.4 (2)
O1—Cu2—N2	167.7 (1)	Cu2—N1—C7	123.2 (4)
O2—Cu2—O4	90.4 (1)	Cu2—N1—C8	119.4 (3)
O2—Cu2—N1	173.0 (1)	Cu2—N2—C10	122.3 (3)
O2—Cu2—N2	91.4 (2)	Cu2—N2—C17	121.3 (4)
O4—Cu2—N1	93.1 (1)	O3—C18—O4	127.4 (3)
O4—Cu2—N2	100.9 (1)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2- H2⋯O3^i	0.950	2.522	3.125 (6)	121.4 (3)
C21—H211⋯O3^i	0.906	2.542	3.408 (6)	160.3 (4)

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

All non-H atoms were refined with anisotropic displacement parameters. The H7, H17, H81, H82, H91, H92, H101, H102, H191, H192, H193, H201, H202, H211 and H212 atoms were taken from difference maps, while other H atoms were placed geometrically 0.95 Å from their parent C atoms and then a riding model was used for all H atoms with $U_{iso}(H) = 1.3U_{eq}(C)$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

Enraf–Nonius (1994). *CAD-4 Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Ercan, F. & Atakol, O. (1998). *Acta Cryst.* C54, 1268–1270.
Ercan, F., Ülkü, D., Atakol, O. & Dinçer, F. N. (1998). *Acta Cryst.* C54, 1787–1790.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Fukuhara, C., Tsuneyoshi, K., Matsumoto, N., Kida, S., Mikuriya, M. & Mori, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3473–3479.
Gerli, A., Hagen, K. S. & Marzilli, L. (1991). *Inorg. Chem.* 30, 4673–4676.
Spek, A. L. (1990). *Acta Cryst.* A46, C-34.

Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* University of Utrecht, The Netherlands.
Ülkü, D., Ercan, F., Atakol, O. & Dinçer, F. N. (1997). *Acta Cryst.* C53, 1056–1057.
Ülkü, D., Tahir, M. N., Atakol, O. & Nazır, H. (1997). *Acta Cryst.* C53, 872–874.

Copper(II) 2-thiopheneglyoxylate adducts with pyridine derivatives

KAZUYUKI NAKASA, HIROO NAKAGAWA, YOSHIYUKI KANI, MASANOBU TSUCHIMOTO AND SHIGERU OHBA

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan. E-mail: ohba@chem.keio.ac.jp

Abstract

In the crystals of *trans*-bis(pyridine-*N*)bis(2-thiopheneglyoxylato-O^1,O^2)copper(II), [Cu(C$_6$H$_3$O$_3$S)$_2$(C$_5$H$_5$N)$_2$], there is a mononuclear Cu^{II} complex molecule. In the crystal of *catena*-poly[[[bis(2-thiopheneglyoxylato-O^1,O^2)copper(II)]-μ-(2-thiopheneglyoxylato-O^1:$O^{1'},O^2$)-[bis(3-methylpyridine-*N*)copper(II)]-μ-(2-thiophenegly-oxylato-O^1,O^2:$O^{1'}$)] monohydrate], {[Cu$_2$(C$_6$H$_3$O$_3$S)$_4$-(C$_6$H$_7$N)$_2$]·H$_2$O}$_n$, there is a zigzag polymer chain where the Cu^{II} atoms are bridged by the thiopheneglyoxylate ions. In the crystal of *cis*-bis(4-methylpyridine-*N*)bis(2-thiopheneglyoxylato-O^1,O^2)copper(II), [Cu(C$_6$H$_3$O$_3$S)$_2$(C$_6$H$_7$N)$_2$], there is a mononuclear Cu^{II} complex. The coordination geometry around the Cu atoms is distorted octahedral. Each thiopheneglyoxylate ion adopts a flattened structure and forms a five-membered chelate ring with the Cu atom.

Comment

Dimeric copper(II) benzoylformates adopt a cage structure and show an abnormally large antiferromagnetic spin-exchange interaction between the Cu atoms (Harada *et al.*, 1997). In the present study, 2-thiopheneglyoxylic acid was selected as another α-keto acid to prepare a binuclear copper(II) complex with pyridine derivatives as axial ligands. However, the compounds

obtained are either monomeric or polymeric. This is a result of the planar conformation of the 2-thiophene-glyoxylate ion, and the keto O atom is involved in the coordination, as observed in [Cu(C₄H₃SCOCOO)₂] and *trans*-[Cu(C₄H₃SCOCOO)₂(H₂O)₂] (Arnaud *et al.*, 1986). In the copper(II) benzoylformates, PhCOCOO⁻ ions adopt a twisted conformation: the phenyl group is coplanar with the carbonyl moiety and the Ph—C(=O) plane is almost perpendicular to the COO moiety, which bridges the two Cu atoms. The benzoylformate ion does not prefer a planar conformation because one of the phenyl H atoms will be very close to one of the carboxyl O atoms. The twisted conformation of the α-keto carboxylic acid is essential for the formation of a binuclear Cuᴵᴵ complex, because the keto O atom is free from coordination.

monohydrate], (II), there are two independent Cu atoms which lie on centers of symmetry. The Cu1 atom is surrounded by six O atoms, with the longest bond of 2.243 (4) Å for Cu1—O8, while the Cu2 atom is surrounded by two N and four O atoms, with the longest bond of 2.388 (4) Å for Cu2—O10. The magnetic susceptibility measurement of (II) at 90–

Fig. 1. The molecular structure of (I), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of radius 0.1 Å.

(I)

(II)

·H₂O

(III)

In the crystals of *trans*-bis(pyridine)bis(2-thiophene-glyoxylato)copper(II), (I), there is a mononuclear Cuᴵᴵ complex molecule. In *catena*-poly[[[bis(2-thiophenegly-oxylato)copper(II)]-μ-(2-thiopheneglyoxylato)-[bis(3-methylpyridine)copper(II)]-μ-(2-thiopheneglyoxylato)]

Fig. 2. The molecular structure of (II), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of radius 0.1 Å. [Symmetry codes: (i) ½ − x, ½ − y, 1 − z; (ii) 1 − x, 1 − y, 1 − z.]

300 K did not indicate any spin-exchange interaction between the Cu atoms in the polymeric zigzag chain. In *cis*-bis(4-methylpyridine)bis(2-thiopheneglyoxylato)-copper(II), (III), the Cu1 atom lies on a crystallographic twofold axis and the 4-methylpyridine ligands are in *cis* positions.
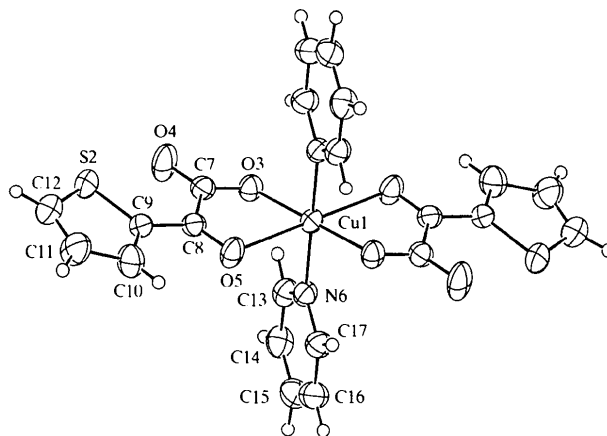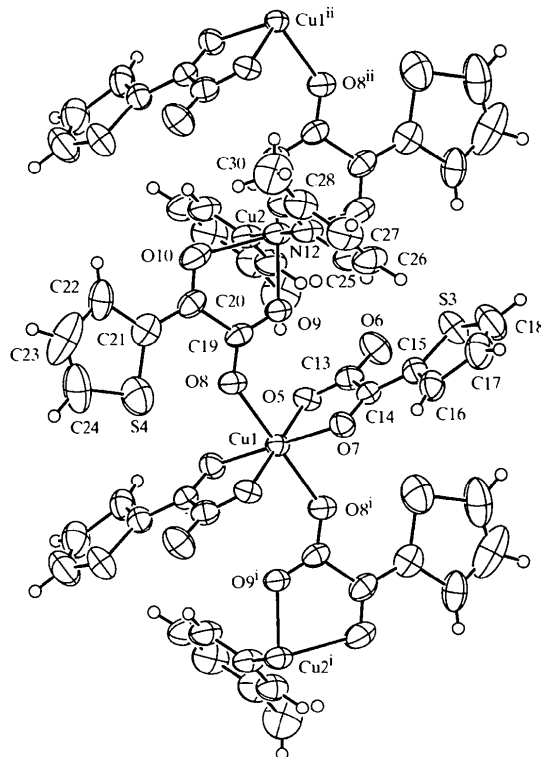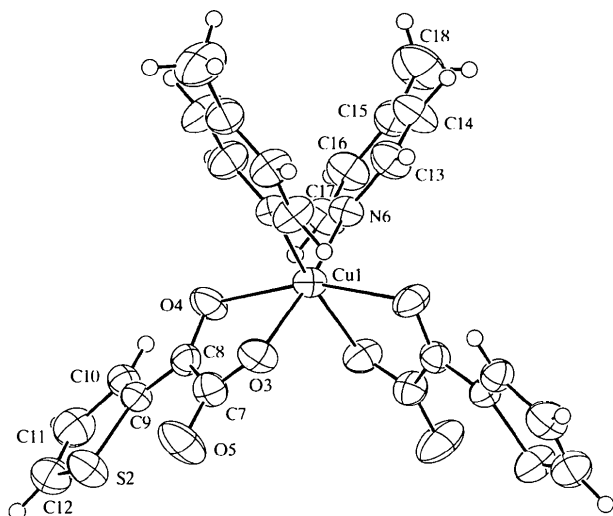

Fig. 3. The molecular structure of (III), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

2-Thiopheneglyoxylic acid (313 mg, 2.0 mmol) and $CuCO_3$·-$Cu(OH)_2$·H_2O (120 mg, 0.5 mmol) were suspended in aqueous acetonitrile (2:3, 60 ml) and the solution was evaporated to dryness. The pale-green residue was dissolved in methanol, from which pale-green prisms of *trans*-$[Cu(C_4H_3SCOCOO)_2(H_2O)_2]$ were grown. Crystals of (I), (II) and (III) were obtained from methanol solutions by adding pyridine (py), 3-Me-py or 4-Me-py, respectively.

Compound (I)

Crystal data

$[Cu(C_6H_3O_3S)_2(C_5H_5N)_2]$
$M_r = 532.04$
Monoclinic
$C2/c$
$a = 13.150(2)$ Å
$b = 11.545(2)$ Å
$c = 14.565(2)$ Å
$\beta = 102.02(1)°$
$V = 2162.7(6)$ Å^3
$Z = 4$
$D_x = 1.634$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.6$–$15.0°$
$\mu = 1.247$ mm^{-1}
$T = 297$ K
Prism
$0.30 \times 0.25 \times 0.20$ mm
Blue

Data collection

Rigaku AFC-5 diffractometer
$R_{int} = 0.017$
$\theta_{max} = 27.5°$

θ–2θ scans
Absorption correction: none
2594 measured reflections
2489 independent reflections
1932 reflections with $|F_o| > 3\sigma(|F_o|)$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 15$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.039$
$wR = 0.040$
$S = 1.401$
1932 reflections
151 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu1	1/4	1/4	1/2	0.0365(1)
S2†	0.12628(7)	0.42807(7)	0.82542(6)	0.0561(3)
O3	0.1869(2)	0.3923(2)	0.5341(1)	0.0410(6)
O4	0.1360(2)	0.4964(2)	0.6437(2)	0.078(1)
O5	0.1937(2)	0.2028(2)	0.6438(1)	0.0510(8)
N6	0.1077(2)	0.1945(2)	0.4283(2)	0.0386(8)
C7	0.1628(2)	0.4060(2)	0.6131(2)	0.0412(9)
C8	0.1691(2)	0.2950(2)	0.6748(2)	0.0385(9)
C9	0.1476(2)	0.3026(2)	0.7689(2)	0.0398(9)
C10‡	0.1498(2)	0.2016(3)	0.8271(2)	0.058(1)
C11	0.1318(3)	0.2400(3)	0.9169(2)	0.065(1)
C12	0.1189(3)	0.3558(3)	0.9236(2)	0.064(1)
C13	0.0323(2)	0.2693(3)	0.3887(2)	0.045(1)
C14	−0.0647(2)	0.2325(3)	0.3423(2)	0.052(1)
C15	−0.0858(2)	0.1165(3)	0.3368(2)	0.056(1)
C16	−0.0100(2)	0.0391(3)	0.3774(2)	0.054(1)
C17	0.0859(2)	0.0815(3)	0.4226(2)	0.047(1)

† Site occupancy = 0.938.   ‡ Site occupancy = 1.167.   (This is an artifact of the disorder of the thiophene ring; C 90% and S 10%, see *Experimental.*)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Cu1—O3	1.951(2)	O3—C7	1.264(4)
Cu1—O5	2.424(3)	O4—C7	1.216(4)
Cu1—N6	2.047(3)	O5—C8	1.226(4)
O3—Cu1—O5	75.3(1)	Cu1—O3—C7	122.5(2)
O3—Cu1—N6	90.1(1)	Cu1—O5—C8	106.0(2)
O5—Cu1—N6	87.7(1)		

Compound (II)

Crystal data

$[Cu_2(C_6H_3O_3S)_4(C_6H_7N)_2]$·-$H_2O$
$M_r = 951.96$
Monoclinic
$C2/c$
$a = 20.160(3)$ Å
$b = 9.000(2)$ Å
$c = 24.497(3)$ Å
$\beta = 118.47(1)°$
$V = 3907.2(12)$ Å^3
$Z = 4$
$D_x = 1.618$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 1.370$ mm^{-1}
$T = 298$ K
Plate
$0.55 \times 0.30 \times 0.20$ mm
Dark green

Data collection

Rigaku AFC-5 diffractom-
eter
ω scans
Absorption correction:
  by integration (Coppens
  et al., 1965)
  $T_{min} = 0.582$, $T_{max} = 0.673$
4934 measured reflections
4481 independent reflections
3347 reflections with
  $|F_o| > 3\sigma(|F_o|)$

$R_{int} = 0.020$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 12$
$l = -32 \rightarrow 32$
3 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.050$
$S = 1.643$
3347 reflections
264 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Extinction correction: none
Scattering factors from *Inter-
national Tables for X-ray
Crystallography* (Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	1/4	1/4	1/2	0.0465 (3)
Cu2	1/2	1/2	1/2	0.0564 (4)
S3†	0.4315 (1)	0.6639 (2)	0.66976 (9)	0.0735 (9)
S4	0.2229 (1)	0.2579 (2)	0.31081 (8)	0.1094 (9)
O5	0.3498 (2)	0.2290 (3)	0.5687 (1)	0.051 (1)
O6	0.4394 (2)	0.3552 (4)	0.6482 (2)	0.066 (2)
O7	0.2626 (2)	0.4652 (3)	0.5337 (1)	0.055 (1)
O8	0.2919 (2)	0.3237 (4)	0.4344 (1)	0.076 (2)
O9	0.4011 (2)	0.4387 (3)	0.4922 (1)	0.055 (1)
O10	0.4270 (2)	0.4316 (4)	0.3934 (2)	0.084 (2)
O11	0	0.3486 (6)	1/4	0.130 (4)
N12	0.4618 (2)	0.7070 (4)	0.4778 (2)	0.062 (2)
C13	0.3776 (2)	0.3436 (5)	0.6015 (2)	0.054 (2)
C14	0.3254 (2)	0.4830 (5)	0.5788 (2)	0.051 (2)
C15	0.3491 (2)	0.6256 (5)	0.6088 (2)	0.054 (2)
C16‡	0.2942 (2)	0.7666 (3)	0.5821 (1)	0.074 (1)
C17	0.3455 (4)	0.8834 (6)	0.6266 (3)	0.101 (3)
C18	0.4133 (4)	0.8356 (7)	0.6705 (3)	0.103 (3)
C19	0.3518 (2)	0.3828 (5)	0.4430 (2)	0.053 (2)
C20	0.3659 (3)	0.3845 (5)	0.3854 (2)	0.062 (2)
C21	0.3096 (3)	0.3296 (5)	0.3260 (2)	0.068 (2)
C22	0.3240 (3)	0.3275 (6)	0.2716 (2)	0.076 (3)
C23	0.2568 (6)	0.2663 (9)	0.2232 (4)	0.154 (6)
C24	0.2015 (4)	0.2250 (8)	0.2357 (3)	0.118 (4)
C25	0.4291 (3)	0.7741 (5)	0.5076 (3)	0.078 (3)
C26	0.3979 (3)	0.9136 (6)	0.4911 (3)	0.086 (3)
C27	0.3988 (3)	0.9833 (6)	0.4416 (3)	0.088 (3)
C28	0.4328 (3)	0.9176 (6)	0.4099 (3)	0.073 (3)
C29	0.4641 (3)	0.7770 (5)	0.4302 (2)	0.068 (2)
C30	0.4376 (4)	0.9910 (7)	0.3573 (3)	0.110 (4)

† Site occupancy = 0.688. ‡ Site occupancy = 1.833. (This is an artifact of the disorder of the thiophene ring; C 50% and S 50%, see *Experimental*.)

Table 4. *Selected geometric parameters (Å, °) for (II)*

Cu1—O5	1.920 (4)	O5—C13	1.263 (6)
Cu1—O7	2.073 (4)	O6—C13	1.231 (6)
Cu1—O8	2.243 (4)	O7—C14	1.231 (5)
Cu2—O9	1.988 (4)	O8—C19	1.243 (6)
Cu2—O10	2.388 (4)	O9—C19	1.246 (6)
Cu2—N12	1.990 (4)	O10—C20	1.226 (6)

O5—Cu1—O7	82.2 (2)	Cu1—O5—C13	116.0 (3)
O5—Cu1—O8	93.5 (2)	Cu1—O7—C14	110.9 (3)
O7—Cu1—O8	89.6 (2)	Cu1—O8—C19	132.3 (3)
O9—Cu2—O10	75.9 (2)	Cu2—O9—C19	120.4 (3)
O9—Cu2—N12	89.6 (2)	Cu2—O10—C20	108.2 (3)
O10—Cu2—N12	89.2 (2)		

Table 5. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O6^i	0.960	1.979	2.859 (6)	151.2

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (III)

Crystal data

[Cu(C$_6$H$_3$O$_3$S)$_2$(C$_6$H$_7$N)$_2$]
$M_r = 560.10$
Orthorhombic
$Pnca$
$a = 11.894$ (2) Å
$b = 18.092$ (3) Å
$c = 11.452$ (2) Å
$V = 2464.3$ (7) Å^3
$Z = 4$
$D_x = 1.510$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 10–15°$
$\mu = 1.098$ mm^{-1}
$T = 299$ K
Prism
$0.45 \times 0.40 \times 0.25$ mm
Dark green

Data collection

Rigaku AFC-5 diffractom-
eter
θ–2θ scans
Absorption correction:
  by integration (Coppens
  et al., 1965)
  $T_{min} = 0.577$, $T_{max} = 0.746$
2835 measured reflections
2835 independent reflections

1894 reflections with
  $|F_o| > 3\sigma(|F_o|)$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 15$
3 standard reflections
  every 100 reflections
  intensity decay: 3%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.049$
$S = 1.421$
1894 reflections
159 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *Inter-
national Tables for X-ray
Crystallography* (Vol. IV)

Table 6. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	1/4	0	0.40594 (5)	0.0374 (2)
S2	0.1596 (1)	0.23901 (6)	0.7155 (1)	0.0607 (4)
O3	0.3359 (2)	0.0510 (1)	0.5301 (2)	0.0472 (9)
O4	0.1492 (2)	0.1109 (1)	0.4392 (2)	0.050 (1)
O5	0.3262 (2)	0.1318 (2)	0.6755 (3)	0.074 (1)
N6	0.1358 (2)	−0.0332 (2)	0.2858 (3)	0.039 (1)
C7	0.2900 (3)	0.1032 (2)	0.5861 (4)	0.043 (1)
C8	0.1800 (3)	0.1340 (2)	0.5345 (3)	0.039 (1)
C9	0.1137 (3)	0.1892 (2)	0.5960 (3)	0.040 (1)

C10	0.0030 (3)	0.2073 (2)	0.5676 (3)	0.041 (1)
C11	−0.0387 (3)	0.2615 (3)	0.6453 (4)	0.059 (2)
C12	0.0353 (4)	0.2832 (2)	0.7263 (4)	0.062 (2)
C13	0.1586 (3)	−0.0812 (2)	0.2005 (4)	0.056 (2)
C14	0.0792 (4)	−0.1035 (3)	0.1221 (4)	0.066 (2)
C15	−0.0291 (4)	−0.0758 (2)	0.1280 (4)	0.055 (2)
C16	−0.0511 (3)	−0.0266 (2)	0.2160 (4)	0.055 (1)
C17	0.0312 (3)	−0.0073 (2)	0.2937 (3)	0.050 (1)
C18	−0.1192 (4)	−0.0980 (3)	0.0416 (4)	0.086 (2)

Table 7. *Selected geometric parameters (Å, °) for (III)*

Cu1—O3	1.979 (3)	O3—C7	1.266 (5)
Cu1—O4	2.368 (3)	O4—C8	1.224 (5)
Cu1—N6	2.024 (3)	O5—C7	1.225 (6)
O3—Cu1—O4	75.6 (1)	N6—Cu1—N6^i	94.4 (2)
O3—Cu1—N6	166.6 (2)	Cu1—O3—C7	119.3 (3)
O4—Cu1—N6	91.2 (2)	Cu1—O4—C8	106.4 (3)

Symmetry code: (i) $\frac{1}{2} - x, -y, z$.

The space group of (III) is *Pnca*, the *cab* setting of *Pbcn*. Disorder was observed in the thiophene rings in (I) and (II). Assuming that it has two possible orientations, and the S and C atoms share the same positions, their site-occupation factors being estimated as reported by Pelletier & Brisse (1994). For example, the S3 and C16 positions in (II) are occupied by both $_{16}$S and $_6$C atoms with 50% probabilities; the site-occupation factors are estimated as $(16 \times 0.5 + 6 \times 0.5)/16 = 0.688$ for S3 and $(16 \times 0.5 + 6 \times 0.5)/6 = 1.833$ for C16 position. The long C15—C16 distance of 1.604 (5) Å is an artifact of the disorder. In (II), the O atom of the water of crystallization lies on a twofold axis, and the H atom was located from difference synthesis. The positions of all the other H atoms were calculated geometrically. A riding refinement was made, with C—H and O—H distances of 0.96 Å, and U_{iso}(H) = 0.1 Å^2 for (I), and 0.2 Å^2 for (II) and (III).

For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structures: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1077). Services for accessing these data are described at the back of the journal.

References

Arnaud, C., Faure, R. & Loiseleur, H. (1986). *Acta Cryst.* C42, 814–816.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* 18, 1035–1038.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1996). *CRYSTAN-GM*. Version 6.3.3. *A Computer Program for the Solution and Refinement of Crystal Structures*. MacScience, Japan.

Harada, A., Tsuchimoto, M., Ohba, S., Iwasawa, K. & Tokii, T. (1997). *Acta Cryst.* B53, 654–661.

Pelletier, M. & Brisse, F. (1994). *Acta Cryst.* C50, 1942–1945.

Rigaku Corporation (1993). *AFC/MSC Diffractometer Control System*. Rigaku Corporation, Tokyo, Japan.

μ-Oxo-bis{bis[2,2'-bi(1H-imidazole-N³)]-oxorhenium(V)} tetrachloride hexahydrate

SUZANNE BÉLANGER AND ANDRÉ L. BEAUCHAMP

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: beauchmp@chimie.umontreal.ca

Abstract

The basic structural unit of the title compound, [{ReO(C$_6$H$_6$N$_4$)$_2$}$_2$O]Cl$_4$·6H$_2$O, consists of a linear [Re$_2$O$_3$(biimidazole)$_4$]$^{4+}$ cation whose O=Re—O—Re=O backbone lies on a twofold rotation axis. Octahedral coordination about each Re centre is completed by two chelating biimidazole ligands perpendicular to the backbone. Three Cl$^-$ anions are hydrogen bonded to the coordinated biimidazole ligands *via* N—H··Cl bonds. The fourth anion is disordered over two positions and is connected to the rest of the structure *via* a chain of crystallization water molecules.

Comment

The structure resolution of the title compound, (I), raised considerable difficulties. The orthorhombic Laue symmetry and reflection conditions (*hkl*, $h + k = 2n$; 0*kl*, $l = 2n$; *h*0*l*, $l = 2n$) were compatible with space groups *Ccc*2 (No. 37) and *Cccm* (No. 66). In both cases, an [Re$_2$O$_3$(BiimH$_2$)$_4$]$^{4+}$ cation with a linear O=Re—O—Re=O backbone was initially identified on a crystallographic twofold axis. However, for *Cccm*, the biimidazole ligands (BiimH$_2$) were all disordered and no sensible model could be unravelled for the Cl$^-$/H$_2$O region. On the other hand, in *Ccc*2, the structure could be satisfactorily solved with only mild disorder.

(I)
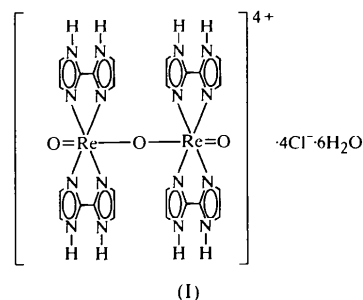
The cation occupies special position 4*c* and the biimidazole ligands are ordered. In the Δ*F* map phased on this model, electron density high enough to correspond