Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)

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

	x	y	z	U_{eq}
Co	1/2	0.70161 (10)	1/4	0.0415 (7)
Cl	0.43316 (10)	0.60460 (17)	0.14763 (13)	0.0823 (13)
N1	0.4208 (2)	0.7900 (4)	0.3173 (3)	0.036 (3)
N2	0.3132 (2)	0.8848 (4)	0.3152 (3)	0.042 (3)
N3	0.5023 (3)	1.0632 (4)	0.1401 (3)	0.045 (3)
C1	0.3755 (3)	0.7485 (4)	0.3856 (4)	0.039 (3)
C2	0.3905 (3)	0.6643 (5)	0.4509 (4)	0.043 (4)
C3	0.3351 (3)	0.6440 (5)	0.5111 (4)	0.055 (4)
C4	0.2676 (3)	0.7022 (6)	0.5082 (4)	0.064 (5)
C5	0.2531 (3)	0.7834 (5)	0.4444 (4)	0.055 (4)
C6	0.3083 (3)	0.8057 (5)	0.3849 (4)	0.041 (4)
C7	0.3812 (3)	0.8747 (4)	0.2779 (4)	0.039 (3)
C8	0.4067 (3)	0.9453 (4)	0.2027 (4)	0.037 (3)
C9	0.3621 (3)	0.9624 (5)	0.1256 (4)	0.052 (4)
C10	0.3899 (3)	1.0302 (5)	0.0583 (4)	0.061 (4)
C11	0.4579 (4)	1.0785 (5)	0.0673 (4)	0.055 (4)
C12	0.4763 (3)	0.9994 (4)	0.2069 (4)	0.039 (4)
C13	0.1790 (4)	1.0639 (5)	0.2097 (5)	0.070 (5)
C14	0.1332 (4)	1.2463 (6)	0.2501 (5)	0.089 (6)
C15	0.0777 (4)	1.1432 (6)	0.1186 (6)	0.105 (6)
N4	0.1315 (3)	1.1478 (4)	0.1919 (3)	0.053 (3)
O	0.2255 (2)	1.0618 (3)	0.2701 (3)	0.069 (3)

Table 2. Selected geometric parameters ($\mathring{A}$, °)

Co—Cl	2.2300 (18)	Co—N1	2.033 (4)
Cl—Co—Cl^i	118.12 (10)	Cl^i—Co—N1	108.08 (13)
Cl—Co—N1	102.61 (13)	N1—Co—N1^i	118.13 (18)

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

The title structure was solved by the heavy-atom method; subsequent Fourier syntheses based on the heavy atom revealed the positions of all the non-H atoms. Least-squares refinement including anisotropic parameters for the non-H atoms was performed. H atoms were placed at calculated positions with $U = U$(attached atom) + 0.01 $\mathring{A}$.

Data collection: CAD-4-PC Software (Enraf–Nonius, 1992). Cell refinement: CAD-4-PC Software. Data reduction: NRC-VAX DATRD2 (Gabe, Le Page, White & Lee, 1987). Program(s) used to solve structure: NRCVAX SOLVER. Program(s) used to refine structure: NRCVAX LSTSQ. Molecular graphics: NRCVAX. Software used to prepare material for publication: NRCVAX TABLES.

References

Bernarducci, E., Bharadwaj, P. K., Krogh-Jesperson, K., Potenza, J. A. & Schugar, H. J. (1983). J. Am. Chem. Soc. 105, 3860–3866.
Cheng, K. L. (1989). MS thesis, National Taiwan University, Taiwan.
Enraf–Nonius (1992). CAD-4-PC Software. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). Acta Cryst. A43, S-294.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Knapp, S., Keenan, T. P., Zhang, X., Fikar, R., Potenza, J. A. & Schugar, H. J. (1987). J. Am. Chem. Soc. 109, 1882–1883.

Larson, A. C. (1970). Crystallographic Computing, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351–359.

CuW(py)2(H2O)2O2F4 and CuW(py)4O2F4

Shiv Halasyamani, Kevin R. Heier, Charlotte L. Stern and Kenneth R. Poeppelmeier*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, USA. E-mail: krp@nwu.edu
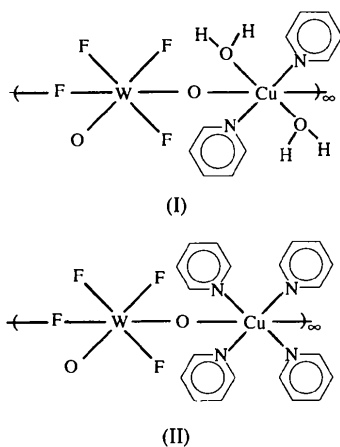
Abstract

Two new Cu^{II}/W^{VI} oxyfluorides, catena-poly[(trifluoro-oxotungsten)-μ-fluoro-[diaquabis(pyridine-N)copper]-μ-oxo] or catena-poly[(difluoro-cis-dioxotungsten)-μ-fluoro-[diaquabis(pyridine-N)copper]-μ-fluoro], [CuW-O2F4(C5H5N)2(H2O)2], (I), and catena-poly[(trifluoro-oxotungsten)-μ-fluoro-[tetrakis(pyridine-N)copper]-μ-oxo] or catena-poly[(difluoro-cis-dioxotungsten)-μ-fluoro-[tetrakis(pyridine-N)copper]-μ-fluoro], [CuW-O2F4(C5H5N)4], (II), have been synthesized. The first complex, (I), contains one-dimensional chains of alternating $[Cu(py)_2(H_2O)_2(O/F)_{2/2}]^{0.66+}$ cations and $[W(O/F)_4(O/F)_{2/2}]^{0.66-}$ anions. The corner-linked octahedra form infinite and parallel chains that run along the b axis. The second compound, (II), contains one-dimensional chains of alternating $[Cu(py)_4(O/F)_{2/2}]^{0.66+}$ cations and $[W(O/F)_4(O/F)_{2/2}]^{0.66-}$ anions. The corner-linked octahedra form infinite and non-intersecting chains that switch between [110] and [1$\bar{1}$0] every $c/2$.

Comment

Two new complexes containing the $[WO_2F_4]^{2-}$ anion, CuW(py)2(H2O)2O2F4, (I), and CuW(py)4O2F4, (II), have been synthesized. For (I), the Cu^{II} cation is axially Jahn–Teller distorted with four 'short' equatorial distances [Cu—NC5H5 ave = 2.02 (1) and Cu—OH2 ave = 2.00 (1) $\mathring{A}$] and two 'long' bonds [Cu—$X1_{ax}$ = 2.356 (7) and Cu—$X2_{ax}$ = 2.363 (7) $\mathring{A}$], with $X1$ and $X2$ disordered 33% O/67% F. The Cu^{II} octahedra are linked to W^{VI} through the axial ligands. Each W^{VI} atom is coordinated by two O and four F atoms [W—($X3$—$X6$)$_{eq,ave}$ = 1.885 (7) $\mathring{A}$ and W—($X1,X2$)$_{ax,ave}$ = 1.866 (7) $\mathring{A}$], with $X1$—$X6$ disordered 33% O/67% F. Inter- and intra-chain hydrogen bonding (Fig. 2) occurs between H2O and O/F [O7—H$\cdots$$X5(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ = 2.61 (1) $\mathring{A}$ (inter-

chain), O7—H$\cdots$X5 = 2.69(1) Å (intra-chain), O8—H$\cdots$X6($\frac{3}{2}$ + x, $\frac{1}{2}$ + y, $\frac{3}{2}$ + z) = 2.63(1) Å (inter-chain), and O8—H$\cdots$X6(x, 1 + y, z) = 2.65(1) Å (intra-chain)]. Complex (I) is also hypercentric (Lipson & Woolfson, 1952), with all atoms residing on general positions in the centrosymmetric space group, $P2_1/n$.

(I)

(II)

The second Cu^{II}/W^{VI} complex, $CuW(py)_4O_2F_4$, (II), is structurally similar to $CuNb(py)_4OF_5$ (Halasyamani, Willis, Stern, Lundquist, Wong & Poeppelmeier, 1996). Compound (II) also contains d^9 Jahn–Teller distorted Cu^{II}. The Cu^{II} atoms are equatorially coordinated to four

pyridines [Cu—$NC_5H_{5\,eq,ave}$ = 2.04(1) Å] and axially to O and F atoms [Cu—$X1_{ax}$ = 2.364(5) Å]. The W^{VI} cation is also octahedrally coordinated, linked to two

Fig. 3. Polyhedral and ball-and-stick packing diagram of (I). The copper octahedra are dark and the tungsten octahedra are light. In the ball-and-stick figure, the Cu^{II} atoms are filled circles and the W^{VI} atoms are dark outlined circles.
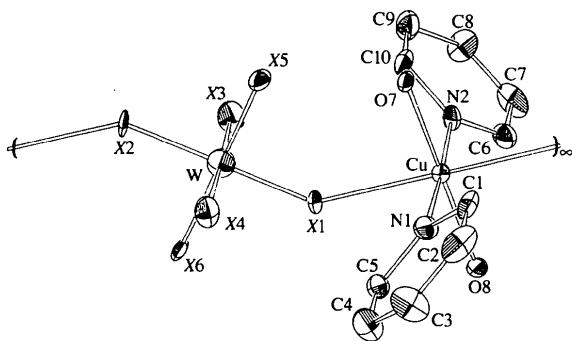

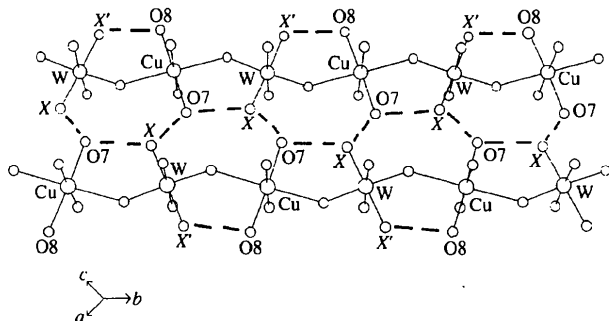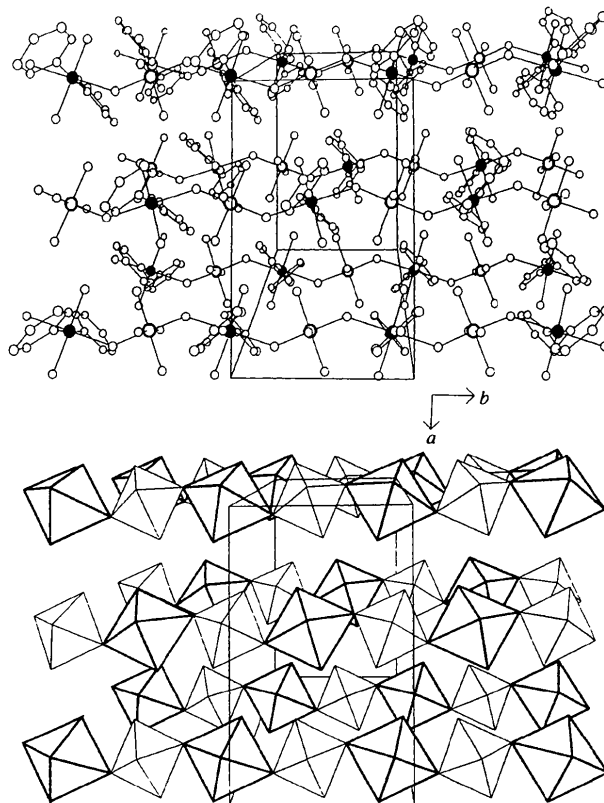Fig. 1. *ORTEP*II (Johnson, 1976) (50% probability ellipsoids) of (I). X1–X6 are disordered 33% O/67% F.

Fig. 2. Ball-and-stick diagram of (I) with dashed lines indicating hydrogen bonding. X = 33% O5/67% F5 and X' = 33% O6/67% F6.

Fig. 4. *ORTEP*II (Johnson, 1976) (50% probability ellipsoids) of (II). The ligands around tungsten, X1–X3, are disordered 33% O/67% F.

Fig. 5. Polyhedral and ball-and-stick diagrams of (II). The copper octahedra are dark and the tungsten octahedra are light. In the ball-and-stick figure, the Cu^{II} atoms are filled circles and the W^{VI} atoms are dark outlined circles.
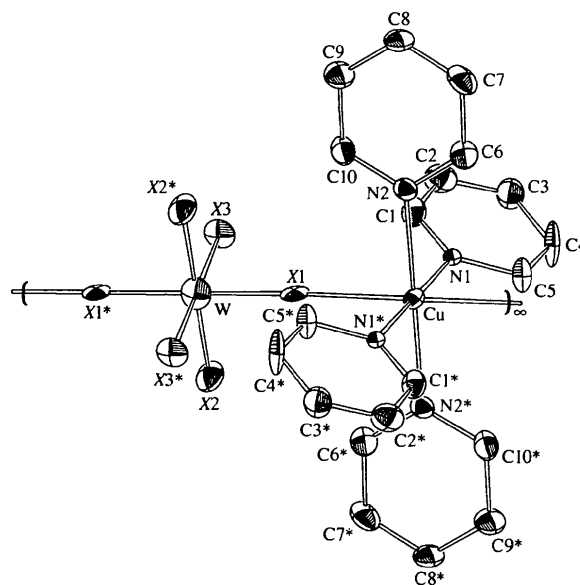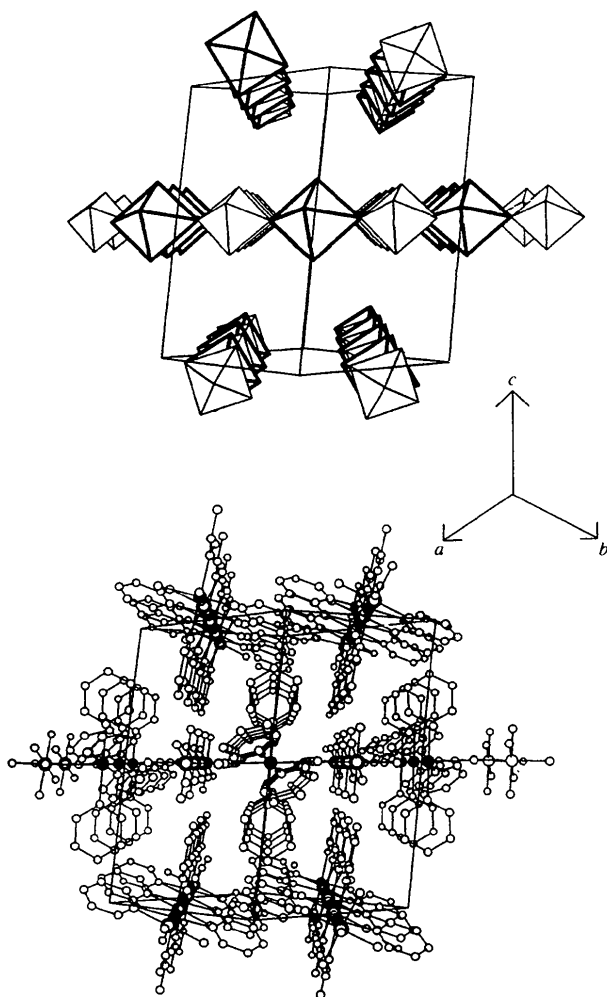
O and four F atoms, W—$(X2,X3)_{eq,ave}$ = 1.87 (1) Å and W—$(X1,X3)_{ax,ave}$ = 1.887 (5) Å, with $X1$–$X3$ disordered 33% O/67% F.

The W—O/F bond distances are consistent with those in $Na_2WO_2F_4$ and $Cs_2WO_2F_4$ (Vlasse, Mountou, Cervera-Marzal, Chaminade & Hagenmuller, 1982; Srivastava & Ackerman, 1992). The remaining distances and angles are in agreement with accepted values. For the pyridine rings, the C—C bond distances range from 1.36 (2) to 1.40 (2) Å. The average C—C distance is 1.37 (2) Å for both complexes.

Magnetic susceptibility measurements indicated (I) and (II) are paramagnetic d^9 Cu^{II} systems with μ(eff) = 1.85 and 1.80 BM, respectively. IR measurements on (I) and (II) revealed two W—O stretches, symmetric and anti-symmetric, corresponding to cis-oxygen coordination around the tungsten (Griffith & Wickins, 1968).

Experimental

Complex (I) was synthesized by placing 4.0 × 10⁻² g (5 × 10⁻⁴ mol) CuO (Aldrich, 99.5%) and 5.8 × 10⁻² g (2.5 × 10⁻⁴ mol) WO₃ (Aldrich, 99.99%) in a teflon pouch (Gier & Stucky, 1991). To the pouch, 4.3 × 10⁻² g (1.4 × 10⁻³ mol) (HF)$_x$.pyridine (Aldrich, pyridinium polyhydrogen fluoride, 70% HF by weight, x = 9.2), 8.0 × 10⁻¹ g (1 × 10⁻² mol) pyridine (Aldrich, 99%) and 6.3 × 10⁻² g (3.5 × 10⁻³ mol) H₂O were added. Compound (II) was synthesized by placing 4.0 × 10⁻² g (5 × 10⁻⁴ mol) CuO (Aldrich, 99.5%) and 5.8 × 10⁻² g (2.5 × 10⁻⁴ mol) WO₃ (Aldrich, 99.99%) in a separate teflon pouch (Gier & Stucky, 1991). To the pouch, 1.7 × 10⁻¹ g (5.5 × 10⁻³ mol) (HF)$_x$.pyridine (Aldrich, pyridinium polyhydrogen fluoride, 70% HF by weight, x = 9.2), 8.0 × 10⁻¹ g (1 × 10⁻² mol) pyridine (Aldrich, 99%) and 6.3 × 10⁻² g (3.5 × 10⁻³ mol) H₂O were added. The pouches were sealed and placed in a 2000 ml autoclave filled with 600 ml of H₂O. The autoclave was heated for 24 h at 423 K and cooled to room temperature over an additional 24 h. The pouches were opened in air and the products recovered by filtration. (I) and (II) crystallized separately as light-blue and dark-blue crystals, respectively. The synthesis of (II) resulted in a 50% yield of a single-phase dark-blue crystalline product, while the synthesis of (I) produced a 30% yield of the desired light-blue crystals as a mixture with (II).

Compound (I)

Crystal data

[CuWO₂F₄(C₅H₅N)₂(H₂O)₂]	Mo $K\alpha$ radiation
M_r = 549.62	λ = 0.7107 Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
a = 11.500 (4) Å	θ = 10.0–11.8°
b = 7.970 (2) Å	μ = 9.31 mm⁻¹
c = 16.521 (3) Å	T = 153.2 K
β = 103.06 (2)°	Plate
V = 1475.1 (6) Å³	0.36 × 0.34 × 0.10 mm
Z = 4	Light blue
D_x = 2.475 Mg m⁻³	
D_m = 2.43 (5) Mg m⁻³	
D_m measured by flotation	

Data collection

CAD-4 diffractometer	R_{int} = 0.02
ω/θ scans	θ_{max} = 22.97°
Absorption correction:	h = 0 → 12
analytical (de Meulenaer	k = 0 → 8
& Tompa, 1965)	l = −18 → 17
T_{min} = 0.09, T_{max} = 0.42	3 standard reflections
2355 measured reflections	every 90 reflections
2237 independent reflections	intensity decay: −1.4%
1603 reflections with	
$I > 3\sigma(I)$	

Refinement

Refinement on F	$\Delta\rho_{max}$ = 1.8 e Å⁻³
R = 0.040	$\Delta\rho_{min}$ = −2.3 e Å⁻³
wR = 0.047	Extinction correction:
S = 3.41	Zachariasen (1967) type
1603 reflections	2 Gaussian isotropic
200 parameters	Extinction coefficient:
H atoms not refined	9.65251

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.015$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) 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}
W	0.49702 (4)	0.10511 (6)	0.74633 (3)	0.0252 (2)
Cu	0.4988 (1)	0.6023 (2)	0.74419 (8)	0.0141 (3)
X1†	0.5558 (5)	0.3198 (7)	0.7383 (4)	0.021 (2)
X2	0.4412 (6)	−0.1151 (7)	0.7507 (4)	0.022 (2)
X3	0.4363 (6)	0.0995 (8)	0.6312 (4)	0.027 (2)
X4	0.5617 (6)	0.1029 (8)	0.8608 (4)	0.026 (2)
X5	0.3544 (5)	0.1933 (8)	0.7648 (4)	0.028 (2)
X6	0.6454 (5)	0.0136 (7)	0.7307 (4)	0.023 (2)
O7	0.3482 (5)	0.5287 (9)	0.7727 (4)	0.017 (2)
O8	0.6533 (5)	0.6836 (9)	0.7206 (4)	0.018 (2)
N1	0.5721 (7)	0.603 (1)	0.8668 (6)	0.020 (3)
N2	0.4238 (8)	0.598 (1)	0.6204 (6)	0.018 (3)
C1	0.5296 (9)	0.703 (1)	0.9189 (6)	0.022 (3)
C2	0.577 (1)	0.706 (2)	1.0030 (7)	0.034 (4)
C3	0.675 (1)	0.602 (2)	1.0358 (7)	0.036 (4)
C4	0.717 (1)	0.499 (2)	0.9831 (7)	0.033 (3)
C5	0.6656 (9)	0.503 (1)	0.9006 (7)	0.021 (3)
C6	0.4582 (9)	0.705 (1)	0.5683 (7)	0.023 (3)
C7	0.4140 (10)	0.701 (2)	0.4838 (7)	0.033 (4)
C8	0.327 (1)	0.580 (2)	0.4505 (7)	0.034 (4)
C9	0.291 (1)	0.474 (1)	0.5043 (7)	0.031 (3)
C10	0.3399 (9)	0.482 (1)	0.5872 (7)	0.024 (3)

† X represents the 33/67% disordered O/F positions.

Table 2. *Selected geometric parameters ($\mathring{A}$, °) for (I)*

W—X1	1.855 (6)	Cu—O7	1.984 (6)
W—X2	1.876 (6)	Cu—O8	2.010 (7)
W—X3	1.872 (6)	Cu—N1	2.010 (9)
W—X4	1.870 (6)	Cu—N2	2.033 (9)
W—X5	1.872 (6)	Cu—X1	2.356 (7)
W—X6	1.926 (6)	Cu—X2	2.363 (7)
X1—W—X2	177.4 (3)	O7—Cu—O8	177.1 (3)
X1—W—X3	90.4 (3)	O7—Cu—N1	87.2 (3)
X1—W—X5	90.7 (3)	O8—Cu—N2	90.2 (3)
X2—W—X3	87.9 (3)	N1—Cu—N2	179.0 (3)
X2—W—X5	91.4 (3)	O8—Cu—X2^i	89.3 (4)
X3—W—X4	177.6 (3)	N2—Cu—X2^i	90.5 (5)
X3—W—X5	92.0 (3)	X1—Cu—X2^i	179.2 (2)
X4—W—X5	90.1 (3)	W—X1—Cu	140.1 (5)
X5—W—X6	178.4 (3)	W—X2—Cu	140.7 (5)

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

Compound (II)

Crystal data

[CuWO$_2$F$_4$(C$_5$H$_5$N)$_4$]
$M_r = 671.79$
Monoclinic
$C2/c$
$a = 10.450$ (2) $\mathring{A}$
$b = 13.396$ (3) $\mathring{A}$
$c = 16.067$ (7) $\mathring{A}$
$\beta = 97.33$ (2)°
$V = 2230.8$ (10) $\mathring{A}^3$
$Z = 4$
$D_x = 2.00$ Mg m^{-3}
$D_m = 1.90$ (5) Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ $\mathring{A}$
Cell parameters from 25 reflections
$\theta = 10.0–11.9°$
$\mu = 6.17$ mm^{-1}
$T = 153.2$ K
Faceted
0.34 × 0.33 × 0.26 mm
Blue

Data collection

CAD-4 diffractometer
ω/θ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.15$, $T_{max} = 0.25$
2167 measured reflections
2049 independent reflections
1730 reflections with
$I > 3\sigma(I)$

$R_{int} = 0.04$
$\theta_{max} = 24.97°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 19$
3 standard reflections
every 90 reflections
intensity decay: −0.9%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.050$
$S = 4.45$
1730 reflections
149 parameters
H atoms not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.10$

$\Delta\rho_{max} = 1.0$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -2.3$ e $\mathring{A}^{-3}$
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 25.49971
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) 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}
W	0	1/2	0	0.0299 (2)
Cu	1/4	1/4	0	0.0161 (3)
X1†	0.1185 (4)	0.3931 (3)	0.0020 (2)	0.021 (1)
X2	0.0477 (5)	0.5452 (4)	−0.1007 (3)	0.033 (1)
X3	0.1291 (4)	0.5811 (4)	0.0579 (3)	0.026 (1)
N1	0.4070 (5)	0.3346 (5)	0.0347 (3)	0.016 (2)
N2	0.2394 (6)	0.2289 (5)	0.1266 (4)	0.020 (2)
C1	0.4042 (7)	0.4153 (6)	0.0823 (5)	0.024 (2)
C2	0.5128 (9)	0.4689 (7)	0.1134 (5)	0.033 (2)
C3	0.6310 (8)	0.4394 (7)	0.0920 (5)	0.033 (2)
C4	0.6370 (7)	0.3573 (6)	0.0399 (6)	0.037 (3)
C5	0.5246 (7)	0.3071 (6)	0.0111 (5)	0.026 (2)
C6	0.3089 (7)	0.1570 (6)	0.1670 (5)	0.025 (2)
C7	0.3115 (8)	0.1420 (6)	0.2521 (5)	0.031 (2)
C8	0.2385 (8)	0.2026 (7)	0.2969 (5)	0.031 (2)
C9	0.1679 (8)	0.2777 (7)	0.2557 (5)	0.032 (2)
C10	0.1688 (8)	0.2885 (6)	0.1706 (5)	0.027 (2)

† X represents the 33/67% disordered O/F positions.

Table 4. *Selected geometric parameters ($\mathring{A}$, °) for (II)*

W—X1	1.891 (4)	Cu—X1	2.364 (5)
W—X2	1.855 (5)	Cu—N1	2.014 (6)
W—X3	1.883 (4)	Cu—N2	2.071 (6)
X1—W—X1^i	180.0	X1—Cu—N2	89.8 (2)
X2—W—X2^i	180.0	N1—Cu—N2	87.1 (2)
X3—W—X3^i	180.0	W—X1—Cu	174.9 (3)
X1—Cu—N1	89.8 (2)		

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

Based on charge balance and IR evidence, the individual [WO$_2$F$_4$]$^{2-}$ groups exhibit *cis*-oxygen coordination; however, in the refinements, it was assumed that oxygen and fluorine are disordered around tungsten. For (I), although the site symmetry of tungsten is consistent with an ordered model, no evidence for ordering was observed. In (II), both the Cu^{II} and W^{VI} atoms reside on inversion centers, requiring disorder of the O/F positions. Subsequently the '*X*' ligands are disordered 33%O/67%F. The disordered O atoms (positions and U^{ij}'s)

were constrained to equal the respective F-atom values. The remaining non-H atoms were refined anisotropically. Pyridine H atoms were fixed at ideal positions with isotropic displacement parameters equal to 1.2 times the value of the C atom to which it is bonded. For (I), the H atoms on the water molecules, associated with O7 and O8 were not located. Neutral atom scattering factors were taken from Cromer & Waber (1974).

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *DIRDIF*94 (Beurskens *et al.*, 1994) for (I); *DIRDIF*92 (Beurskens *et al.*, 1992) for (II). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structures: *SAPI*91 (Fan, 1991) for (I); *SHELXS*86 (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israél, R. & Smits, J. M. M. (1994). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Gier, T. E. & Stucky, G. D. (1991). *Nature (London)*, **349**, 508–510.

Griffith, W. P. & Wickins, T. D. (1968). *J. Chem. Soc. A*, pp. 400–404.

Halasyamani, P., Willis, M. J., Stern, C. L., Lundquist P. M., Wong, G. K. & Poeppelmeier, K. R. (1996). *Inorg. Chem.* **35**, 1367–1371.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lipson, H. & Woolfson, M. M. (1952). *Acta Cryst.* **5**, 680–682.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Srivastava, A. M. & Ackerman, J. F. (1992). *J. Solid State Chem.* **98**, 144–150.

Vlasse, M., Mountou, J. M., Cervera-Marzal, M., Chaminade, J. P. & Hagenmuller, P. (1982). *Rev. Chim. Miner.* **19**, 58–64.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Bis(barium disaccharinate triglyme)†

CHRISTIAN NÄTHER, TIM HAUCK AND HANS BOCK

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany. E-mail: bock@bock.anorg.chemie.uni-frankfurt.de
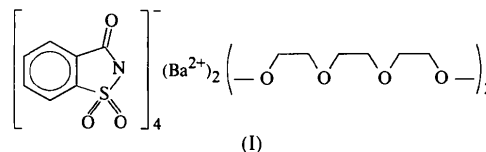
Abstract

The crystal structure of $[Ba(C_7H_4NO_3S)_2(C_8H_{18}O_4)]_2$ has been determined at 150 K. The structure contains dimers of barium disaccharinate, in which each barium dication is surrounded by three saccharinate anions and one triglyme molecule. The asymmetric unit contains two crystallographically independent saccharinate anions, of which one is coordinated to the barium dication by both sulfonyl O atoms, whereas both are coordinated *via* their amide groups. With four additional contacts to the triglyme O atoms, the Ba^{2+} centres achieve a tenfold coordination sphere.

Comment

Detailed structure investigations of crystalline organobarium complexes are rather rare, presumably due to the difficulties associated with their preparation caused by the low reactivity of barium metal. The saccharinate anion was selected because of its excellent complexation properties. The numerous structures of saccharinate salts reported in the literature usually contain transition metal ions and only a few structures containing alkaline or alkaline earth cations are reported. Representative examples are magnesium disaccharinate heptahydrate, sodium saccharinate 2/3-hydrate (Jovanovski & Kamenar, 1982) or dipotassium sodium trisaccharinate monohydrate (Malik, Haider, Hossain & Hursthouse, 1984).

The title compound, (I), crystallizes as a dimeric complex composed of two barium dications, four saccharinate anions and two triglyme molecules. Each barium centre is surrounded by three saccharinate anions and one triglyme molecule. Two of the saccharinate anions coordinate *via* their amide groups and the third *via* the sulfonyl O atoms. The barium dication is located within an irregular polyhedron and exhibits coordination num-

(I)