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'	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 $U_{\rm iso}$(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*.

The authors are grateful to Professor T. Tokii of Saga University for the magnetic susceptibility measurements.

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.* C**42**, 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.* B**53**, 654–661.

Pelletier, M. & Brisse, F. (1994). *Acta Cryst.* C**50**, 1942–1945.

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

Acta Cryst. (1999). C**55**, 517–521

μ-Oxo-bis{bis[2,2′-bi(1H-imidazole-N^3)]-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

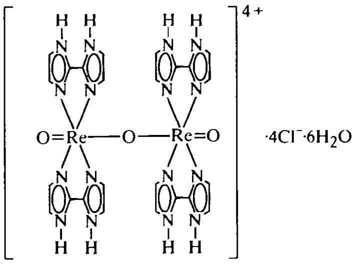
(*Received 29 June 1998; accepted 17 November 1998*)

Abstract

The basic structural unit of the title compound, $[\{ReO(C_6H_6N_4)_2\}_2O]Cl_4\cdot6H_2O$, consists of a linear $[Re_2O_3(biimidazole)_4]^{4+}$ 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*, $h+k = 2n$; $0kl$, $l = 2n$; $h0l$, $l = 2n$) were compatible with space groups *Ccc*2 (No. 37) and *Cccm* (No. 66). In both cases, an $[Re_2O_3(BiimH_2)_4]^{4+}$ 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_2O 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 ΔF map phased on this model, electron density high enough to correspond to full Cl^- ions was detected on a special position 4*b* (Cl1) and on a general position (Cl2), for a total of three Cl^- ions per cation. One anion (*i.e.* one half-anion per asymmetric unit) was still missing to balance the charge of $[Re_2O_3(BiimH_2)_4]^{4+}$. Among the remaining residual peaks, mainly due to lattice water molecules, one had to be attributed to a disordered Cl^- ion. To make the assignments, peak height and hydrogen-bonding environment were considered. The Cl3/O30 site was found to be occupied randomly by a Cl^- anion and a solvent molecule. Water molecules O10 and O40 were ordered, but O20 was disordered on two neighbouring sites (O20*a* and O20*b*).

The $[Re_2O_3(BiimH_2)_4]^{4+}$ cation is shown in Fig. 1, with important bond lengths and angles in Table 2. The O═Re—O—Re═O backbone is, by symmetry, perfectly linear. The terminal Re1═O1 and Re2═O2 bonds have respective lengths of 1.65 (2) and 1.74 (2) Å, reflecting a higher bond order than for the bridging bonds [Re1—O3 1.92 (3) and Re2—O3 1.89 (3) Å]. The Re—N3*n* distances [range 2.108 (8)–2.134 (7) Å] are normal.

The N31, N32, N31′ and N32′ atoms are coplanar, but Re1 is displaced from this plane by 0.148 (6) Å on the O1 side. The plane defined by N33, N34, N33′ and N34′ shows a barely significant tetrahedral deformation, the atoms being alternatively displaced by 0.022 (7) Å on each side of their mean plane, while Re2 is found 0.129 (7) Å from this plane, towards O2. This reflects the high bond order for the terminal oxo ligands, which also leads to values of *ca* 94° for the O1═Re1—N3*n* and O2═Re2—N3*n* angles, a deviation from the ideal angle of 90° commonly observed for monomeric $[ReO(OR)L_4]^{n+}$ complexes with monodentate imidazoles (Bélanger & Beauchamp, 1996, 1997).

Three types of oxo-bridged dirhenium(V) compounds have been characterized by X-ray diffraction: $Re_2O_3Cl_4L_4$ (where *L* = pyridine, 3,5-dimethylpyrazole or 1-methylimidazole) (Lock & Turner, 1978; Fortin & Beauchamp, 1998; Backes-Dahmann & Enemark, 1987; Pearson & Beauchamp, 1994), $[Re_2O_3(CN)_8]^{4-}$ (Shandles *et al.*, 1971) and $Re_2O_3(L^4)_2$ (where L^4 is a dianionic tetradentate amino–phenol ligand) (Fletcher & Skapski, 1972). The bridging Re—O bond lengths in these compounds are similar to those observed here. The average value for our terminal Re═O bond lengths (1.69 Å) is typical of such systems, but there is no obvious explanation for their apparently significant difference of 0.09 (3) Å.

The N31—Re1—N32 and N33—Re2—N34 angles [77.2 (3) and 77.8 (3)°, respectively] are in agreement with those reported for octahedral complexes with neutral chelating biimidazole and bibenzimidazole (Rasmussen *et al.*, 1986; Boinnard *et al.*, 1990; García *et al.*, 1990; Esteruelas *et al.*, 1994). As expected, coordination does not take place along the lone pair; the Re—N3*n*—C2*n* angles inside the five-membered chelate ring vary from 112.6 (6) to 114.8 (6)°, while the external Re—N3*n*—C4*n* angles are between 138.2 (6) and 139.6 (7)°. The angles within the imidazole rings are normal. Tension resulting from bidentate coordination is reflected, however, in the difference between the external N1*n*—C2*n*—C2*n*′ angles [132.4 (10)–133.9 (9)°] and the internal N3*n*—C2*n*—C2*n*′ angles [116.6 (8)–119.2 (8)°] of the chelate ring. The two crystallographically independent biimidazole ligands are roughly planar, with a dihedral angle of 0.9 (1)° between the imidazole units. However, the planes of the aromatic rings deviate from their respective ReN_4 coordination plane by *ca* 3.5°.

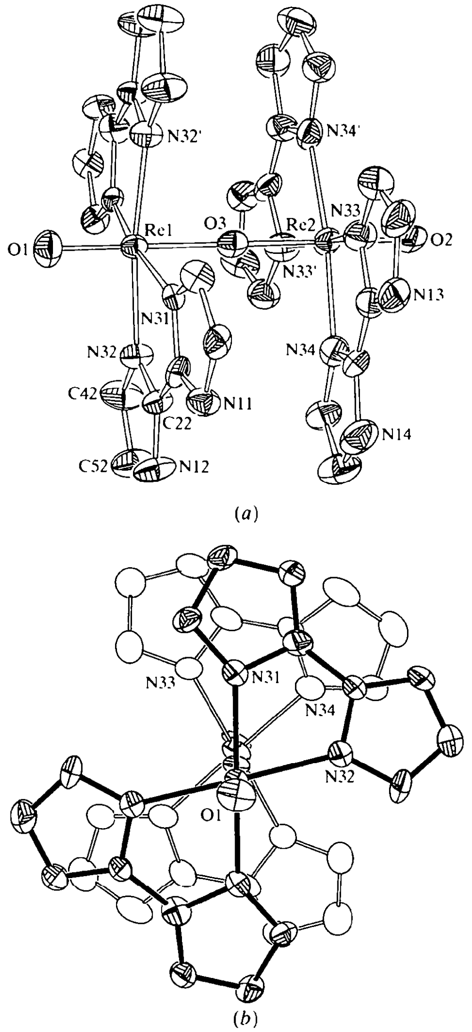


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[Re_2O_3(BiimH_2)_4]^{4+}$ cation. A twofold rotation axis runs through the O═Re—O—Re═O backbone. Ellipsoids correspond to 50% probability and H atoms have been omitted. (*a*) Atoms in the five-membered rings of the biimidazole ligands are labelled sequentially N1*j*—C2*j*—N3*j*—C4*j*—C5*j*, as shown for ring *j* = 2 in the lower left side; the primed ligands are related to the unprimed ones by the twofold axis. (*b*) The same molecule viewed down the O═Re—O—Re═O direction.

The cations participate in an extended network of hydrogen bonds (Fig. 2 and Table 3). A chloride anion (Cl1), lying on a twofold rotation axis, bonds two cations *via* the biimidazole N11—H11 and N12—H12 groups. Each of these N—H groups simultaneously participates in a hydrogen bond with a water molecule (O10), located roughly in the same plane as the aromatic rings. This water molecule interacts with Cl2, a non-disordered chloride, which serves as a proton acceptor from the N13—H13 and N14—H14 groups of the second biimidazole ligand. The O10 and Cl2 atoms are hydrogen bonded to a chain of crystallization water molecules running parallel to the O═Re—O—Re═O axis in the cell. This chain contains a disordered chloride anion (Cl3), which shares the same site as a water molecule (O30), generating further disorder in the position of a nearby water molecule, which can adopt two positions (O20*a* or O20*b*) depending on the nature (Cl or O) of the neighbouring site. This chain is centred on a twofold rotation axis, with water molecule O40 in the middle of an approximate tetrahedron formed by O30, Cl3, O20*a* and O20*b*. Between each pair of O40 solvent molecules, there is one O20*b*· · ·Cl3 and one O20*a*· · ·O30 segment, but these are interchanged randomly in the crystal to generate the disorder.

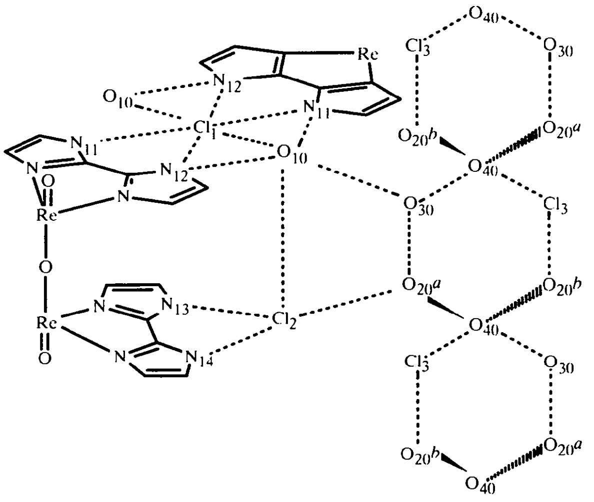


Fig. 2. Schematic representation of the hydrogen-bond network involving the dinuclear cations, chloride anions and crystallization water molecules.

Experimental

$ReOCl_3(PPh_3)_2$ was prepared according to the literature (Chatt & Rowe, 1962) using $HReO_4$ (prepared from $KReO_4$ by ion-exchange chromatography on a DOWEX 50X2-200 resin) rather than $KReO_4$ as starting material. All chemicals were purchased from Aldrich. The IR spectrum was recorded on a Perkin–Elmer 1705 FT spectrophotometer. Microanalyses were performed at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal. The solid-state ^{13}C CP–MAS spectrum was recorded on a Bruker AMX-300 spectrometer and externally referenced to the aromatic hexamethylbenzene C atoms (δ 132.1 p.p.m.). The variable-temperature ^1H NMR spectra were recorded in DMSO-d_6 (δ 2.49 p.p.m.) on a Bruker ARX-400 spectrometer. The ligand $BiimH_2{\cdot}0.5HCl$ was prepared by bubbling NH_3 gas through a 40% aqueous glyoxal solution, as described by Fieselmann *et al.* (1978). It was recrystallized using a modification of the method of Kirchner & Krebs (1987) for $BiimH_2$. The bulk sample was dissolved in 1 *M* HCl and the solution was stirred with activated charcoal for 30 min. The mixture was then filtered and the resulting colourless solution neutralized with 1.5 *M* NH_4OH. The beige solid was filtered, washed with water, ethanol and ether. ^1H NMR (298 K, DMSO-d_6, p.p.m.): 12.66 (*s*, N—H), 7.11 (*s*, broad, C—H), 6.99 (*s*, broad, C—H); ^1H NMR (343 K, DMSO-d_6, p.p.m.): 7.06 (*s*, sharp, C—H); ^{13}C NMR (CP–MAS): 139.2 (C2, C2′), 129.1 and 126.8 (C4, C4′), 120.6 and 118.7 (C5, C5′); analysis calculated for $C_6H_{6.5}Cl_{0.5}N_4$: C 47.97, H 4.33, N 37.32%; experimental: C 47.83, H 4.24, N 37.01%. $[Re_2O_3(BiimH_2)_4]Cl_4{\cdot}6H_2O$ was prepared as follows: to a suspension of $BiimH_2{\cdot}0.5HCl$ (0.063 g, 0.377 mmol) in acetone (10 ml), 0.4 ml (0.48 mmol) of an aqueous 1.2 *M* HCl solution was added, followed by $ReOCl_3(PPh_3)_2$ (0.106 g, 0.13 mmol) and 5 ml of deionized water. The yellow suspension was stirred for 22 h, after which time the dark-green mixture was filtered in order to remove a fraction (0.038 g) of unreacted $ReOCl_3(PPh_3)_2$. The green filtrate was evaporated to dryness, and the sample redissolved in a small amount of acetone. The poorly soluble PPh_3 was filtered off and the dark-green filtrate was left to crystallize in the refrigerator, where the orange crystalline plates used for the crystal structure determination formed after a few days. IR (cm^{-1}): 785 (*s*) and/or 772 (*s*), ν(Re═O).

Crystal data

$[Re_2O_3(C_6H_6N_4)_4]Cl_4{\cdot}6H_2O$
M_r = 1206.88
Orthorhombic
*Ccc*2
a = 13.855 (4) Å
b = 21.573 (6) Å
c = 13.163 (4) Å
V = 3934 (2) Å^3
Z = 4
D_x = 2.037 Mg m^{-3}
D_m not measured

Cu *K*α radiation
λ = 1.54056 Å
Cell parameters from 25 reflections
θ = 20–25°
μ = 14.6 mm^{-1}
T = 295 (2) K
Plate
0.23 × 0.14 × 0.05 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration (Gabe *et al.*, 1989)
T_{min} = 0.16, T_{max} = 0.51
13 752 measured reflections
3751 independent reflections

2332 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 69.9°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 26$
$l = -16 \rightarrow 16$
5 standard reflections
frequency: 60 min
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.086$
$S = 0.60$
3751 reflections
256 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.080P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.04$
$\Delta\rho_{\rm max} = 0.75$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.96$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: $1.06(8) \times 10^{-4}$
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.30 (2)

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

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

	x	y	z	$U_{\rm eq}$
Re1	3/4	3/4	1.14497 (2)	0.0231 (2)
Re2	3/4	3/4	0.85511 (3)	0.0306 (2)
O1	3/4	3/4	1.2704 (13)	0.040 (4)
O2	3/4	3/4	0.7229 (13)	0.033 (4)
O3	3/4	3/4	0.999 (2)	0.0284 (12)
N11	0.9986 (6)	0.6434 (3)	1.1239 (6)	0.032 (2)
C21	0.9050 (7)	0.6575 (5)	1.1285 (9)	0.031 (2)
N31	0.8944 (6)	0.7199 (3)	1.1334 (6)	0.024 (2)
C41	0.9865 (6)	0.7452 (4)	1.1315 (7)	0.031 (2)
C51	1.0508 (7)	0.6983 (5)	1.1245 (8)	0.031 (2)
N12	0.8008 (6)	0.5616 (3)	1.1250 (8)	0.041 (2)
C22	0.8187 (7)	0.6217 (4)	1.1288 (7)	0.027 (2)
N32	0.7358 (5)	0.6524 (3)	1.1340 (7)	0.031 (2)
C42	0.6639 (8)	0.6094 (4)	1.1327 (9)	0.046 (3)
C52	0.7019 (8)	0.5537 (5)	1.1268 (10)	0.048 (3)
N13	1.0473 (7)	0.7313 (4)	0.8764 (7)	0.039 (2)
C23	0.9546 (8)	0.7159 (4)	0.8712 (8)	0.035 (2)
N33	0.9003 (6)	0.7677 (4)	0.8666 (9)	0.036 (2)
C43	0.9622 (8)	0.8164 (5)	0.8712 (8)	0.043 (2)
C53	1.0542 (8)	0.7943 (5)	0.8767 (10)	0.047 (3)
N14	0.9351 (6)	0.5995 (4)	0.8743 (7)	0.050 (2)
C24	0.9047 (7)	0.6586 (4)	0.8693 (10)	0.034 (2)
N34	0.8087 (6)	0.6587 (3)	0.8633 (6)	0.034 (2)
C44	0.7765 (7)	0.5984 (5)	0.8639 (8)	0.039 (2)
C54	0.8548 (9)	0.5618 (4)	0.8684 (10)	0.055 (3)
Cl1	1	1/2	1.0834 (4)	0.073 (2)
Cl2	1.1622 (2)	0.60751 (12)	0.8796 (3)	0.0531 (7)
Cl3†	1.4132 (3)	0.5983 (2)	1.1381 (4)	0.0726 (14)
O30†	1.4132 (3)	0.5983 (2)	1.1381 (4)	0.0726 (14)
O10	1.1964 (8)	0.5860 (5)	1.1156 (8)	0.084 (3)
O20*a*†	1.378 (5)	0.564 (2)	0.925 (5)	0.080 (7)
O20*b*†	1.376 (5)	0.543 (2)	0.910 (5)	0.080 (7)
O40	1/2	1/2	1.2737 (13)	0.108 (6)

† Site occupancy = 0.50.

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

Re1—O1	1.65 (2)	Re2—O2	1.74 (2)
Re1—O3	1.92 (3)	Re2—O3	1.89 (3)
Re1—N31	2.108 (8)	Re2—N33	2.122 (9)
Re1—N32	2.119 (7)	Re2—N34	2.134 (7)
O1—Re1—O3	180	O2—Re2—O3	180
O1—Re1—N31	94.1 (2)	O2—Re2—N33	94.1 (3)
O3—Re1—N31	85.9 (2)	O3—Re2—N33	85.9 (3)
O1—Re1—N32	93.9 (2)	O2—Re2—N34	92.9 (2)
O3—Re1—N32	86.1 (2)	O3—Re2—N34	87.1 (2)
N31$^{\rm i}$—Re1—N31	171.7 (5)	N33—Re2—N33$^{\rm i}$	171.8 (6)
N31$^{\rm i}$—Re1—N32	102.3 (3)	N33—Re2—N34$^{\rm i}$	101.8 (3)
N31—Re1—N32	77.2 (3)	N33$^{\rm i}$—Re2—N34$^{\rm i}$	77.8 (3)
N32—Re1—N32$^{\rm i}$	172.2 (5)	N34$^{\rm i}$—Re2—N34	174.2 (5)
Re1—O3—Re2	180		

Symmetry code: (i) $\frac{3}{2} - x, \frac{3}{2} - y, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$\cdots$Cl1	0.86	2.37	3.139 (7)	149
N12—H12$\cdots$Cl1	0.86	2.34	3.112 (8)	150
N13—H13$\cdots$Cl2	0.86	2.32	3.109 (9)	153
N14—H14$\cdots$Cl2	0.86	2.37	3.152 (10)	151
N11—H11$\cdots$O10	0.86	2.45	3.010 (13)	123
N12—H12$\cdots$O10$^{\rm i}$	0.86	2.62	3.186 (13)	125
O20*a*$\cdots$Cl2			3.20 (7)	
O20*b*$\cdots$Cl2			3.30 (7)	
O20*a*$\cdots$O30			2.94 (7)	
O20*b*$\cdots$Cl3			3.27 (6)	
Cl3$\cdots$O40$^{\rm ii}$			3.021 (11)	
O30$\cdots$O40$^{\rm ii}$			3.021 (11)	
O10$\cdots$Cl3			3.029 (12)	
O10$\cdots$O30			3.029 (12)	
O10$\cdots$Cl1			3.321 (12)	
O10$\cdots$Cl2			3.176 (10)	
O20*a*$\cdots$Cl2			3.20 (7)	
O20*b*$\cdots$Cl2			3.30 (7)	
O20*a*$\cdots$O40$^{\rm iii}$			2.95 (5)	
O20*b*$\cdots$O40$^{\rm iii}$			2.65 (6)	

Symmetry codes: (i) $2 - x, 1 - y, z$; (ii) $1 + x, y, z$; (iii) $1 + x, 1 - y, z - \frac{1}{2}$.

For the absorption correction, the crystal faces were indexed and the distances to a reference point within the crystal were measured carefully. The transmission factor was calculated on the basis of this geometry by Gaussian integration (grid 20 × 20 × 20) using the *ABSN* program of the *NRCVAX* package (Gabe *et al.*, 1989). All non-H atoms were refined anisotropically. The H atoms of biimidazole were introduced at idealized positions and allowed to ride on their respective non-H atom [C—H = 0.93 Å, N—H = 0.86 Å and U(H) = 1.3U(C/N)]. Those of the water molecules were neglected. The Cl3 and O30 atoms were refined with common atomic coordinates and displacement parameters. Residual electron-density peaks of 0.96–0.40 e Å^{-3} remained near the Re atoms. The general background was below ±0.30 e Å^{-3}.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC Crystallographic Computer Programs* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in the *NRCVAX* package. Software used to prepare material for publication: *SHELXL*93.

Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR (Ministère de l'Éducation du Québec). The authors thank M. Simard for help with the data collection, and S. Bilodeau and R. Mayer for running the variable temperature and CP–MAS spectra.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1428). Services for accessing these data are described at the back of the journal.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM/360*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.

Backes-Dahmann, G. & Enemark, J. H. (1987). *Inorg. Chem.* **26**, 3960–3962.

Bélanger, S. & Beauchamp, A. L. (1996). *Inorg. Chem.* **35**, 7836–7844.

Bélanger, S. & Beauchamp, A. L. (1997). *Inorg. Chem.* **36**, 3640–3647.

Boinnard, D., Cassoux, P., Petrouleas, V., Savariault, J. M. & Tuchagues, J. P. (1990). *Inorg. Chem.* **29**, 4114–4122.

Chatt, J. & Rowe, G. A. (1962). *J. Chem. Soc.* pp. 4019–4033.

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

Esteruelas, M. E., Lahoz, F. J., Oro, L. A., Oñate, E. & Ruiz, N. (1994). *Inorg. Chem.* **33**, 787–792.

Fieselmann, B. F., Hendrickson, D. N. & Stucky, G. D. (1978). *Inorg. Chem.* **17**, 2078–2083.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fletcher, J. R. & Skapski, A. C. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1073–1078.

Fortin, S. & Beauchamp, A. L. (1998). *Inorg. Chim. Acta*, **279**, 159–164.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

García, M. P., Lopez, A. M., Esteruelas, M. A., Lahoz, F. J. & Oro, L. A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3465–3472.

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

Kirchner, C. & Krebs, B. (1987). *Inorg. Chem.* **26**, 3569–3576.

Lock, C. J. L. & Turner, G. (1978). *Can. J. Chem.* **56**, 179–188.

Pearson, C. & Beauchamp, A. L. (1994). *Acta Cryst.* C**50**, 42–44.

Rasmussen, P. G., Anderson, J. E., Bailey, O. H., Tamres, M. & Bayo, J. C. (1986). *J. Am. Chem. Soc.* **107**, 279–281.

Shandles, R., Schlemper, E. O. & Murmann, R. K. (1971). *Inorg. Chem.* **10**, 2785–2789.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 521–523

$K_2[MoO_3(C_2O_4)]\cdot H_2O$

Yong-Heng Xing,[a] Zuo Wang,[a] Ji-Qing Xu,[a]* Dong-Mei Li,[a] Ren-Zhang Wang,[a] Wei-Ming Bu,[b] Ling Ye,[b] Xing Yan,[c] Yong-Hua Lin[c] and Heng-Qing Jia[c]

[a]*Department of Chemistry, Jilin University, Changchun, Jilin 130023, People's Republic of China,* [b]*Key Laboratory for Supramolecular Structure and Spectroscopy, Jilin University, Changchun, Jilin 130023, People's Republic of China, and* [c]*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, People's Republic of China. E-mail: xjq@mail.jlu.edu.cn*

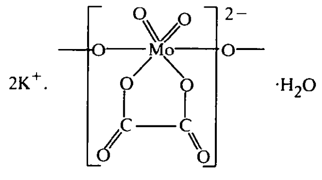
(*Received 9 July 1998; accepted 11 November 1998*)

Abstract

In the title compound, *catena*-poly[dipotassium [[(oxalato-*O*,*O*′)dioxomolybdate]-μ-oxo] monohydrate], oxalate acts as a bidentate ligand coordinating to each Mo atom through the two deprotonated carboxylate groups. The coordination polyhedron of molybdenum is distorted octahedral and there are infinite chains in the structure. Principal dimensions are: Mo—O(terminal) 1.560 (3) and 1.739 (3) Å, Mo—O(bridging) 2.046 (4) and 2.410 (4) Å, and Mo—O(carboxylate) 1.949 (3) and 2.113 (3) Å.

Comment

Oxalate is an important organic ligand, which is coordinated to many metals in complexes exhibiting different structural characteristics, such as $[Cu_2(\mu\text{-ox})_2(\mu\text{-pyz})(pyz)_2]_n$ (pyz is pyrazine; Kitagawa *et al.*, 1995), $[Cu(en)_2][Cu(ox)_2]$ (Oshio & Nagashima, 1992), $(Ph_4P)_2[(VO)_2(H_2O)_2(C_2O_4)_3]\cdot 4H_2O$ and $(Ph_4P)[VOCl(C_2O_4)]$ (Salta *et al.*, 1996), *etc.* In order to further understand the structure of the complexes containing the oxalate ligand, we have decided to turn our attention to molybdenum(VI) oxalate complexes. This is because molybdenum in the V and VI oxidation states forms a considerable number of oxo complexes (Cruywagen *et al.*, 1986). Few of these have been unequivocally characterized structurally, but it is important to do so in many cases. The point of particular interest in such compounds is the different structural arrangements which have an effect on intramolecular bond distances and angles. We report here an infinite-chain molybdenum–oxalate compound, (1).



(1)

It was found that $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$, (2), which was structurally characterized by X-ray diffraction (Cotton *et al.*, 1964), and (1) were considered to have a similar coordination mode for molybdenum. Structure analysis shows that in the anion of (1), the various Mo—O bond lengths and O—Mo—O bond angles vary considerably. The six oxygen ligands of each Mo atom are of three types, namely, terminal, bridging and oxalate, with respective Mo—O bond lengths of 1.560 (3)–1.739 (3), 2.046 (4)–2.410 (4) and 1.949 (3)–2.113 (3) Å, and angles ranging from 164.01 (14) to 76.85 (14)°. A comparison of (1) with (2) showed that one Mo—O(terminal) bond distance [1.560 (3) Å] in (1) is shorter than that in (2) (average 1.69 Å), however, another Mo—O(terminal) bond distance [1.739 (3) Å] is longer than that in (2). Therefore, the Mo—O(bridging) bond distances of (1) are longer than in (2) (1.876 Å), and their corresponding angles are considerably differ-

Acta Crystallographica Section C
ISSN 0108-2701 © 1999