4312 reflections
307 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 3.2317P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Gd—O4	2.414 (3)	Gd—O1*B*	2.531 (3)
Gd—O6	2.422 (3)	Gd—N5	2.546 (3)
Gd—O5	2.462 (3)	Gd—N4	2.583 (3)
Gd—O2*A*	2.497 (3)	Gd—O2*B*	2.606 (3)
Gd—N6	2.530 (3)	Gd—O1*A*	2.695 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*B*···O3*A*	0.922	1.847	2.754 (4)	167
O4—H4*B*···O3*A*	0.894	1.843	2.733 (4)	174
O5—H5*B*···O3*B*	1.041	1.670	2.700 (4)	170
O6—H6*A*···O3*C*	1.069	2.054	3.052 (4)	154
O4—H4*A*···O1*C*	1.070	1.834	2.809 (4)	149
O5—H5*A*···O1*A*	1.009	1.832	2.816 (4)	164

After positioning the detector 26 mm from the crystal, the data collection was performed by recording 90 images, while applying a 180° scan on φ (2° steps). Data are 95% complete to 2θ (52.6°). The H atoms of the ligand were included as riding atoms at calculated positions (U = 1.2 times that of the corresponding C atom). The H atoms of the water molecules were introduced into the calculation from positions found on the final difference Fourier map and were not refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997). Cell refinement: *DENZO*. Data reduction: *DENZO*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1321). Services for accessing these data are described at the back of the journal.

References

Backer-Dirks, J. J. D., Cooke, J. E., Galas, A. M. R., Ghotra, J. S., Gray, C. J., Hart, F. A. & Hursthouse, M. B. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2191–2198.

Bruker (1997). *SHELXTL*. Release 5. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA.

Constable, E. C., Chotalia, R. & Tocher, D. A. (1992). *J. Chem. Soc. Chem. Commun.* pp. 771–773.

Fréchette, M. & Bensimon, C. (1995). *Inorg. Chem.* **34**, 3520–3527.

Frost, G. H., Hart, F. A., Heath, C. & Hursthouse, M. B. (1969). *J. Chem. Soc. Chem. Commun.* pp. 1421–1422.

Harrowfield, J. McB., Kepert, D. L., Patrick, J. M. & White, J. M. (1983). *Aust. J. Chem.* **36**, 483–492.

Holtz, R. C. & Thompson, L. C. (1988). *Inorg. Chem.* **27**, 4640–4644.

Kepert, C. J., Weimin, L., Skelton, B. W. & White, A. H. (1994). *Aust. J. Chem.* **47**, 365–384.

Mallet, C., Thummel, R. P. & Hery, C. (1993). *Inorg. Chim. Acta*, **210**, 223–231.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276. *Macromolecular Crystallography, Part A*, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Radonovitch, L. J. & Glick, M. D. (1971). *Inorg. Chem.* **10**, 1463–1468.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON. Multipurpose Crystallographic Tool*. University of Utrecht, The Netherlands.

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Di-μ-oxo-bis[(2,2′-bipyridine)(difluoroacetato)oxomolybdenum(V)] dihydrate

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Abstract

The structure of the title complex, $[Mo_2O_4(C_2HF_2O_2)_2(C_{10}H_8N_2)_2]\cdot 2H_2O$, is reported. The structure consists of the Mo_2O_4 core, with each metal center bonded to terminal and bridging oxo ligands, a monodentate difluoroacetate ligand and a chelating 2,2′-bipyridine group. The water molecules are each hydrogen bonded to a terminal oxo ligand and a difluoroacetate carbonyl group. The product, a result of accidental air oxidation, is similar in structure to other Mo_2O_4 complexes with similar ligation.

Comment

For some years we have been interested in the nature of the quadruply bonded dimolybdenum(II) carboxylates in solution (Webb & Dong, 1982; Islam *et al.*, 1990; Snowden *et al.*, 1993; Webb *et al.*, 1995). These complexes are often quite labile to substitution, and their solution chemistry is often richer and more complex than might be expected from solid-state studies. The chemistry of these complexes is also affected by carboxylate basicity (Webb *et al.*, 1995).

We were interested in examining the chemistry of $Mo_2(O_2CCHF_2)_4$ with 2,2′-bipyridine in comparison with an earlier study involving trifluoroacetate (Matonic *et al.*, 1991). ^{19}F NMR studies indicate that 2,2′-bipyridine forms several complexes with $Mo_2(O_2CCHF_2)_4$ in DMSO or acetonitrile, and that the species in solution change with the bipyridine:Mo_2 ratio; NMR evidence also suggests that free difluoroacetate is not produced in the reaction. However, it has not proven possible to date to identify any of the species in solution. We therefore set out to crystallize one or more complexes for comparison with the earlier trifluoroacetate study. From reaction mixtures, we could isolate a mixture of three different solids (white, orange–red and dark).

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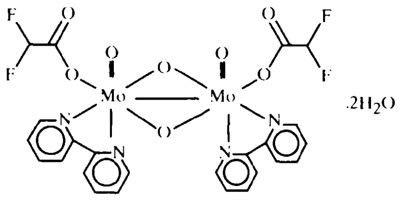
Only the orange–red product appeared to be crystalline and proved to be the title compound, (I), an oxidation product. Dulebohn *et al.* (1991) have noted that similar Mo^V species are easily produced by oxidation of other dimolybdenum(II) complexes in the presence of 2,2′-bipyridine and its substituted derivatives.



(I)

The title compound, shown in Fig. 1, contains the well known Mo_2O_4 core, with a crystallographic twofold axis bisecting the metal–metal bond. The coordination sphere of each Mo atom also includes one chelating 2,2′-bipyridine and one monodentate difluoroacetate. Two waters of hydration also appear, which are hydrogen bonded to a terminal oxo ligand and to the carbonyl O atom of a difluoroacetate ligand. The latter interaction is somewhat shorter than the former [2.00 (5) *versus* 2.29 (7) Å]. The geometry of the Mo_2O_4 core is quite comparable to that found in other Mo_2O_4 complexes (Beck *et al.*, 1984; Cotton & Morehouse, 1965; Delbaere & Prout, 1971; Drew & Kay, 1971; Dulebohn *et al.*, 1991; Gatehouse & Nunn, 1976; Glowiak *et al.*, 1975; Jezowska-Trzebiatowska *et al.*, 1977). The Mo—N distances are similar to those reported in three Mo_2O_4(bipyridine derivative)$_2X_2$ complexes, where X represents a monodentate anionic ligand. When X is Cl (Beck *et al.*, 1984; Dulebohn *et al.*, 1991), the Mo—N distances are more nearly equal than those found here, and when X is OP(O)H$_2$ (Gatehouse & Nunn, 1976), the Mo—N distances are almost identical to those found here. The average Mo–hypophosphite O distance [2.09 (1) Å] is slightly shorter than the Mo–carboxyl O distance in the present compound [2.138 (2) Å]. Either differing steric requirements of difluoroacetate compared to hypophosphite or differing ligand–ligand basicities toward Mo^V could account for this small difference in bond distance.

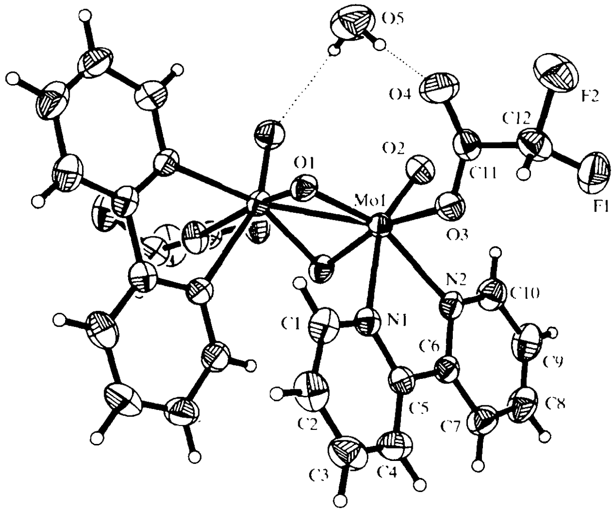


Fig. 1. The structure of (I) with 50% probability ellipsoids. Only one of the symmetry-equivalent water molecules is shown.

Experimental

In a test tube under argon, $Mo_2(O_2CCHF_2)_4$ (Webb *et al.*, 1995) (0.0127 g, 0.022 mmol) was dissolved in 4.0 ml redistilled acetonitrile. A solution of 2,2′-bipyridine (0.0075 g, 0.048 mmol) in 4 ml heptane was layered over the acetonitrile solution. The tube was capped under argon and left at room temperature for several days. Crystals formed at the interface and were recovered by filtration and dried.

Crystal data

$[Mo_2O_4(C_2HF_2O_2)_2(C_{10}H_8N_2)_2]\cdot 2H_2O$
$M_r = 794.34$
Monoclinic
$C2/c$
$a = 16.734 (3)$ Å
$b = 10.267 (2)$ Å
$c = 17.173 (4)$ Å
$\beta = 110.34 (2)°$
$V = 2766.3 (9)$ Å^3
$Z = 4$
$D_x = 1.907$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.60–14.82°$
$\mu = 1.00$ mm^{-1}
$T = 294 (2)$ K
Block
0.28 × 0.20 × 0.20 mm
Orange–red

Data collection

Siemens $R3m$ diffractometer
$2\theta-\omega$ scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Siemens, 1994)
$T_{min} = 0.724$, $T_{max} = 0.843$
2540 measured reflections
2451 independent reflections

2167 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.05°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 12$
$l = -20 \rightarrow 19$
2 standard reflections every 98 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.060$
$S = 1.12$
2451 reflections
207 parameters
H atoms: water H atoms refined, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 3.9966P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mo1—O2	1.690 (2)	Mo1—N2	2.236 (2)
Mo1—O1	1.911 (2)	Mo1—N1	2.318 (2)
Mo1—O1^{i}	1.948 (2)	Mo1—Mo1^{i}	2.5601 (7)
Mo1—O3	2.138 (2)		
O2—Mo1—O1	113.02 (9)	O1—Mo1—N1	84.63 (8)
O2—Mo1—O1^{i}	105.08 (9)	O1^{i}—Mo1—N1	87.03 (8)
O1—Mo1—O1^{i}	92.09 (8)	O3—Mo1—N1	74.79 (8)
O2—Mo1—O3	91.07 (9)	N2—Mo1—N1	70.50 (8)
O1—Mo1—O3	89.83 (8)	O2—Mo1—Mo1^{i}	100.89 (7)
O1^{i}—Mo1—O3	161.46 (8)	O1—Mo1—Mo1^{i}	49.06 (6)
O2—Mo1—N2	92.04 (9)	O1^{i}—Mo1—Mo1^{i}	47.82 (5)
O1—Mo1—N2	154.83 (9)	O3—Mo1—Mo1^{i}	138.69 (6)
O1^{i}—Mo1—N2	83.09 (8)	N2—Mo1—Mo1^{i}	130.90 (6)
O3—Mo1—N2	87.35 (8)	N1—Mo1—Mo1^{i}	101.10 (5)
O2—Mo1—N1	157.67 (9)	Mo1—O1—Mo1^{i}	83.12 (7)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O4	0.85 (5)	2.00 (5)	2.832 (4)	169 (5)
O5—H5*B*···O2^{i}	0.91 (7)	2.29 (7)	3.138 (4)	154 (6)

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

Data collection: *P3/PC Diffractometer Control Program* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Control Program*. Data reduction: *SHELXTL* (Siemens, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1424). Services for accessing these data are described at the back of the journal.

References

Beck, J., Hiller, W., Schweda, E. & Strähle, J. (1984). *Z. Naturforsch. Teil B*, **39**, 1110–1113.

Cotton, F. A. & Morehouse, S. M. (1965). *Inorg. Chem.* **4**, 1377–1381.

Delbaere, L. T. J. & Prout, C. K. (1971). *Chem. Commun.* p. 162.

Drew, M. G. B. & Kay, A. (1971). *J. Chem. Soc. A*, pp. 1846–1850.

Dulebohn, J. I., Stamatakos, T. C., Ward, D. L. & Nocera, D. G. (1991). *Polyhedron*, **10**, 2813–2820.

Gatehouse, B. M. & Nunn, E. K. (1976). *Acta Cryst.* B**32**, 2627–2630.

Glowiak, T., Sabat, M., Sabat, H. & Rudolf, M. F. (1975). *J. Chem. Soc. Chem. Commun.* p. 712.

Islam, M. Q., Hill, W. E. & Webb, T. R. (1990). *J. Fluorine Chem.* **48**, 429–440.

Jezowska-Trzebiatowska, B., Glowiak, T., Rudolf, M. F., Sabat, M. & Sabat, J. (1977). *Russ. J. Inorg. Chem.* **22**, 1590–1597.

Matonic, J. H., Chen, C.-J., Perlepes, S. P., Dunbar, K. R. & Christou, G. (1991). *J. Am. Chem. Soc.* **113**, 8169–8171.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1989). *P3/PC Diffractometer Control Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Snowden, K. J., Webb, T. R. & Snoddy, B. (1993). *Inorg. Chem.* **32**, 3541–3545.

Webb, T. R. & Dong, T.-Y. (1982). *Inorg. Chem.* **21**, 114–116.

Webb, T. R., Pollard, J. D., Goodloe, G. W. & McKee, M. L. (1995). *Inorg. Chim. Acta*, **229**, 127–133.