A dinuclear oxomolybdenum(V) compound with picolinate ligands

Nobuo Okabe,* Noriko Isomoto and Mamiko Odoko

Faculty of Pharmaceutical Sciences, Kinki University, Kokawae 3-4-1, Higashiosaka, Osaka 577-8502, Japan

Correspondence e-mail: okabe@phar.kindai.ac.jp

The title compound, diaquadi-μ_2-oxo-dioxobis(pyridine-2-carboxylato-O,N)molybdenum(V) monohydrate, [Mo$_2$O$_2$-(C$_6$H$_4$NO$_2$)$_2$(H$_2$O)$_2$]·H$_2$O, is a dinuclear complex which consists of two Mo^V atoms connected together by a metal–metal single bond and two bridging oxo groups. Each Mo^V atom has a distorted octahedral geometry and is coordinated by three oxo groups, one O atom of the water molecule, and the O and N atoms of one picolinate anion.

Comment

Picolinic acid (pyridine-2-carboxylic acid) is a well known terminal tryptophan metabolite (Mahler & Cordes, 1971). It has biological activity to induce apotosis in leukemia HL-60 cells, which is cell death characterized by DNA fragmentation (Ogata *et al.*, 2000). Molybdenum is a well known biologically essential metal and serves as a component of molybdenum enzymes. It also has antitumor activity for leukemia and lymphomas (Hall *et al.*, 2000). We intended to prepare hybrid complexes of these bioactive substances and determine their structures.

(I)
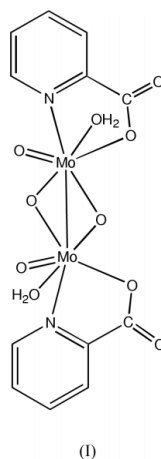
The structure of (I) is a dinuclear complex, as illustrated in Fig. 1. Selected bond lengths and angles are given in Table 1. Each Mo^V atom of the complex has a pseudo-octahedral [MoO$_5$N] geometry which is defined by three oxo ligands, one O atom of a water ligand, and O and N atoms of picolinate. The Mo^V atoms are bridged by two oxo groups with Mo—O distances of 1.928 (2)–1.956 (3) Å, and two other oxo O atoms are coordinated at short distances [Mo1—O5 1.683 (3) Å and Mo2—O5 1.688 (3) Å]. The Mo atoms are also joined by a Mo—Mo single bond with a short distance [Mo1—Mo2 2.5538 (5) Å]. Similar oxo bridges, short Mo–O distances, and
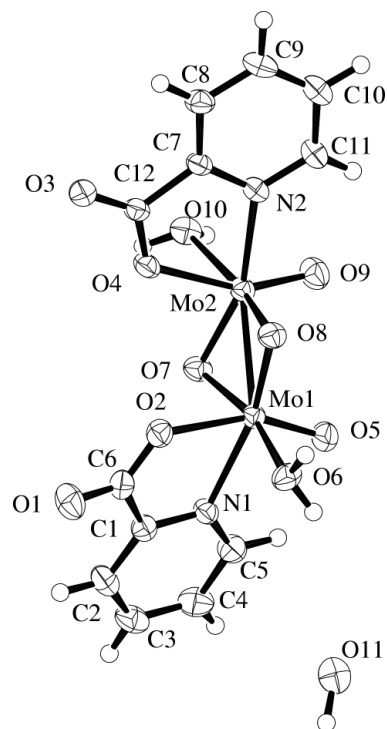
Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to the 50% probability level.

an Mo—Mo single bond are observed in a decanuclear oxomolybdenum(V,VI) cluster with 4-isopropylpyridine (Modec *et al.*, 2001). The geometrical parameters around Mo^V in this 4-isopropylpyridine complex and in the title compound are similar to each other. The coordination of N and O atoms of picolinate to a metal is a common feature for all metal complexes of this ligand: Ni^{II} and Zn^{II} (Takenaka *et al.*, 1970), Cu^{II} (Faure *et al.*, 1973), Mn^{II} (Okabe & Koizumi, 1998) and Cd^{II} (Odoko *et al.*, 2001). The crystal structure is stabilized by stacking of picolinate rings and by O—H···O hydrogen bonds (Table 2), in which the coordinated and the hydrate water molecules act as the hydrogen donors, and the O atoms of the bridging oxo groups and carboxylate group of picolinate act as acceptors.

Experimental

The orange plate crystals were obtained by slow evaporation from a 90% ethanol–water solution of picolinic acid (pyridine-2-carboxylic acid) and molybdenum(V) chloride (4:1 molar ratio).

Crystal data

[Mo$_2$O$_2$(C$_6$H$_4$NO$_2$)$_2$(H$_2$O)$_2$]·H$_2$O	$Z = 2$
$M_r = 554.13$	$D_x = 2.126$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo Kα radiation
$a = 9.260 (2)$ Å	Cell parameters from 25
$b = 12.145 (2)$ Å	reflections
$c = 8.261 (1)$ Å	$\theta = 14.8-15.0°$
$\alpha = 98.02 (1)°$	$\mu = 1.51$ mm^{-1}
$\beta = 101.89 (1)°$	$T = 296.2$ K
$\gamma = 103.68 (1)°$	Prismatic, orange
$V = 865.8 (3)$ Å^3	$0.3 \times 0.3 \times 0.2$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.011$
ω–2θ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = 0 \rightarrow 12$
(North *et al.*, 1968)	$k = -15 \rightarrow 15$
$T_{min} = 0.627$, $T_{max} = 0.739$	$l = -10 \rightarrow 10$
4227 measured reflections	3 standard reflections
3977 independent reflections	every 150 reflections
3473 reflections with $I > 2\sigma(I)$	intensity decay: 0.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{max} = -0.001$
$S = 0.92$	$\Delta\rho_{max} = 0.81$ e Å^{-3}
3473 reflections	$\Delta\rho_{min} = -0.52$ e Å^{-3}
245 parameters	Extinction correction: *SHELXL*97
H-atom parameters not refined	Extinction coefficient: 0.0050 (12)

Table 1
Selected geometric parameters (Å, °).

Mo1—Mo2	2.5538 (5)	Mo2—O8	1.956 (3)
Mo1—O2	2.155 (2)	Mo2—O9	1.688 (3)
Mo1—O5	1.683 (3)	Mo2—O10	2.187 (3)
Mo1—O6	2.156 (3)	Mo2—N2	2.242 (2)
Mo1—O7	1.934 (3)	O1—C6	1.243 (4)
Mo1—O8	1.941 (2)	O2—C6	1.267 (4)
Mo1—N1	2.234 (3)	O3—C12	1.215 (4)
Mo2—O4	2.144 (2)	O4—C12	1.278 (3)
Mo2—O7	1.928 (2)		
O2—Mo1—O5	157.3 (1)	O4—Mo2—N2	72.43 (9)
O2—Mo1—O6	77.23 (9)	O7—Mo2—O8	94.70 (10)
O2—Mo1—O7	86.28 (9)	O7—Mo2—O9	109.0 (1)
O2—Mo1—O8	90.43 (9)	O7—Mo2—O10	86.13 (10)
O2—Mo1—N1	72.44 (8)	O7—Mo2—N2	159.8 (1)
O5—Mo1—O6	91.1 (1)	O8—Mo2—O9	105.7 (1)
O5—Mo1—O7	103.5 (1)	O8—Mo2—O10	164.87 (9)
O5—Mo1—O8	108.7 (1)	O8—Mo2—N2	88.02 (9)
O5—Mo1—N1	87.8 (1)	O9—Mo2—O10	88.2 (1)
O6—Mo1—O7	163.30 (10)	O9—Mo2—N2	89.4 (1)
O6—Mo1—O8	87.83 (9)	O10—Mo2—N2	86.16 (9)
O6—Mo1—N1	87.07 (9)	Mo1—O2—C6	121.6 (2)
O7—Mo1—O8	95.01 (10)	Mo2—O4—C12	123.0 (2)
O7—Mo1—N1	85.42 (10)	Mo1—O7—Mo2	82.81 (8)
O8—Mo1—N1	162.81 (10)	Mo1—O8—Mo2	81.88 (8)
O4—Mo2—O7	87.56 (9)	Mo1—N1—C1	116.5 (2)
O4—Mo2—O8	89.06 (9)	Mo1—N1—C5	124.5 (2)
O4—Mo2—O9	156.4 (1)	Mo2—N2—C7	116.1 (2)
O4—Mo2—O10	75.87 (9)	Mo2—N2—C11	124.5 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H12···O3^i	0.905	1.699	2.594 (3)	169
O6—H13···O8^{ii}	0.929	1.772	2.654 (3)	158
O10—H14···O11^{iii}	0.928	1.730	2.643 (3)	167
O10—H15···O1^{iv}	0.888	1.805	2.658 (2)	160
O11—H16···O1^v	0.985	1.980	2.953 (4)	169
O11—H17···O7^{vi}	0.903	1.835	2.733 (3)	173

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, -z$; (iii) $x - 1, y, z$; (iv) $x, y, 1 + z$; (v) $1 - x, 1 - y, -z$; (vi) $1 - x, 1 - y, 1 - z$.

The unit cell is not in its conventional reduced form. All H atoms were located from difference Fourier maps, and were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation and Rigaku Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data

reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku Corporation, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF94 Program System.* Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands.

Das, N. & Dash, A. C. (1993). *Indian J. Chem. Sect. A*, **32**, 531–535.

Faure, P. R., Loiseleur, H. & Thomas-David, G. (1973). *Acta Cryst.* B**29**, 1890–1893.

Hall, I. H., Lackey, C. B., Kistler, T. D., Durham, R. W., Russel, J. M. & Grimes, R. N. (2000). *Anticancer Res.* **20**, 2345–2354.

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

Mahler, H. R. & Cordes, E. H. (1971). *Biological Chemistry*, 2nd ed., pp. 801–803. New York: Harper and Row Publishers.

Modec, B., Brenčič, J. V. & Giester, G. (2001). *Acta Cryst.* C**57**, 246–247.

Molecular Structure Corporation & Rigaku Corporation (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN* (Version 1.10). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, 3–9–12 Akishima, Tokyo, Japan.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Odoko, M., Isomoto, N. & Okabe, N. (2001). *Acta Cryst.* E**57**, m371–m372.

Ogata, S., Takeuchi, M., Fujita, H., Shibata, K., Okumura, K. & Taguchi, H. (2000). *Biosci. Biotechnol. Biochem.* **64**, 327–332.

Okabe, N. & Koizumi, M. (1998). *Acta Cryst.* C**54**, 288–290.

Sheldrick, G. M. (1997). *SHELXL.* University of Göttingen, Germany.

Takenaka, A., Utsumi, H., Yamamoto, T., Furusaki, A. & Nitta, I. (1970). *Nippon Kagaku Zasshi*, **91**, 921–927.