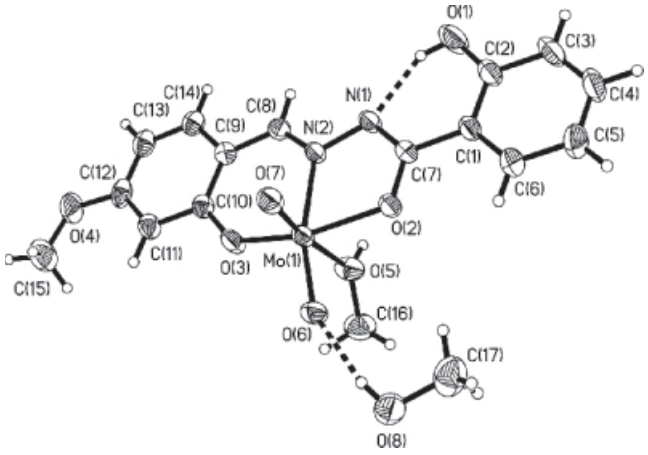
Crystal structure of [*N′*-(2-hydroxy-4-methoxybenzylidene)-2-hydroxybenzohydrazido](methanol)dioxomolybdenum(VI) methanol solvate, $C_{16}H_{16}MoN_2O_7{\cdot}CH_3OH$, $C_{17}H_{20}MoN_2O_8$

Xiao-Chuan Jia[*, I], Jing Li[I], Yuan-Yuan Liu[II], Na Wang[I] and Hui Zhang[I]

[I] Tianjin Entry-Exit Inspection and Quarantine Bureau, Tianjin 300201, P. R. China
[II] Tianjin Chest Hospital, Tianjin 300051, P. R. China

Received October 13, 2012, accepted December 03, 2012, available online April 12, 2013, CCDC no. 1267/3935



Abstract

$C_{17}H_{20}MoN_2O_8$, triclinic, $P\bar{1}$ (no. 2), a = 6.9004(7) Å, b = 10.225(1) Å, c = 14.332(2) Å, α = 79.346(2)°, β = 82.660(2)°, γ = 77.576(1)°, V = 966.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.0318, $wR_{ref}(F^2)$ = 0.0813, T = 298 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.17×0.20×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.26 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD area-detector, ω
$2\theta_{max}$:	52.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5423, 3910
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3723
$N(param)_{refined}$:	261
Programs:	SADABS [10], SAINT [11], SHELX [12]

Source of material

2-Hydroxy-4-methoxybenzaldehyde (1.0 mmol, 0.152 g) and 2-hydroxybenzohydrazide (1.0 mmol, 0.152 g) were mixed and stirred in methanol (20 mL) at room temperature for 30 min. To this mixture was further added a methanolic solution (20 mL) of molybdenyl(IV)oxide-*bis*(2,4-pentanedionate) (1.0 mmol, 0.326 g). Finally the mixture was stirred at room temperature for 30 min to give a yellow solution. Yellow block-shaped single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution for several days.

Experimental details

H5 attached to O5 was located from a difference Fourier map and refined isotropically, with O–H distance restrained to 0.85(1) Å. The remaining H atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H distances of 0.93-0.96 Å, O–H distances of 0.82 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(O and C_{methyl}).

Discussion

Molybdenum complexes have been attracted considerable attention for their catalytic properties [1-3] as well as electro-chemical aspects [4-6]. In this paper, the crystal structure of a new molybdenum complex, synthesized from *N′*-(2-hydroxy-4-methoxybenzylidene)-2-hydroxybenzohydrazide, is reported. The molecular structure of the complex is shown in the figure. The asymmetric unit of the title structure contains a mononuclear dioxomolybdenum complex and a methanol molecule. The Mo atom is in an octahedral coordination. The equatorial plane of the coordination is defined by the phenolate O, imine N, and enolate O atoms of the hydrazone ligand and one double bonded oxo ligand. The two axial positions of the coordination are occupied by one methanol O atom and the other oxo ligand. The Mo atom is displaced out of the equatorial plane by 0.320(1) Å. There is an intramolecular O1–H1···N1 hydrogen bond, which supports the planarity of the hydrazone ligand. The dihedral angle between the C(1)–C(6) and C(9)–C(14) benzene rings is 3.5(2)°. The coordinate bond lengths and angles are comparable to those observed in similar complexes [7-9]. A hydrogen bonded, one-dimensional polymer along [100] is constructed in the title structure by the methanol solvate molecule which donates a hydrogen bond to the oxo ligand O6 and accepts a hydrogen bond from the OH function of a methanol ligand (O5') of an adjacent complex.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	–0.2788	1.0748	0.2850	0.131
H(8)	2*i*	0.7958	0.7808	0.1220	0.118
H(3)	2*i*	–0.3431	1.4061	0.2071	0.090
H(4)	2*i*	–0.1012	1.5159	0.1283	0.096
H(5A)	2*i*	0.2188	1.4015	0.1004	0.100
H(6)	2*i*	0.3003	1.1704	0.1536	0.079
H(8A)	2*i*	–0.2238	0.7507	0.3548	0.051
H(11)	2*i*	0.3345	0.3085	0.3647	0.065
H(13)	2*i*	–0.2378	0.3105	0.4610	0.071
H(14)	2*i*	–0.3143	0.5403	0.4207	0.063
H(15A)	2*i*	0.3295	0.0858	0.3782	0.139
H(15B)	2*i*	0.2724	–0.0157	0.4686	0.139
H(15C)	2*i*	0.3524	0.1121	0.4802	0.139
H(16A)	2*i*	0.4303	0.7490	0.0181	0.125
H(16B)	2*i*	0.2648	0.6739	0.0019	0.125
H(16C)	2*i*	0.4360	0.5974	0.0657	0.125

* Correspondence author (e-mail: xiaochuanjia2012@163.com)

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(17A)	2*i*	0.6423	0.9715	0.0945	0.153
H(17B)	2*i*	0.7401	0.9696	–0.0103	0.153
H(17C)	2*i*	0.8469	1.0174	0.0638	0.153
H(5)	2*i*	0.114(2)	0.752(4)	0.118(3)	0.080

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	2*i*	0.35617(3)	0.74116(2)	0.27042(2)	0.0310(1)	0.0350(1)	0.0571(2)	–0.00148(9)	–0.00089(9)	–0.0058(1)
N(1)	2*i*	–0.0557(3)	0.9299(2)	0.2820(2)	0.039(1)	0.034(1)	0.061(2)	0.0004(9)	–0.002(1)	–0.009(1)
N(2)	2*i*	0.0291(3)	0.7910(2)	0.3024(2)	0.036(1)	0.033(1)	0.049(1)	–0.0027(9)	–0.0024(9)	–0.0063(9)
O(1)	2*i*	–0.3202(4)	1.1567(3)	0.2715(3)	0.055(2)	0.057(2)	0.135(3)	0.011(1)	0.006(2)	–0.011(2)
O(2)	2*i*	0.2651(3)	0.9381(2)	0.2203(2)	0.040(1)	0.036(1)	0.065(1)	–0.0042(8)	0.0044(9)	–0.0026(9)
O(3)	2*i*	0.3075(3)	0.5596(2)	0.3047(2)	0.044(1)	0.034(1)	0.085(2)	0.0005(8)	–0.000(1)	–0.007(1)
O(4)	2*i*	0.0819(5)	0.1517(2)	0.4479(2)	0.104(2)	0.042(1)	0.086(2)	–0.012(1)	–0.009(2)	0.003(1)
O(5)	2*i*	0.2349(4)	0.7267(3)	0.1273(2)	0.052(1)	0.081(2)	0.063(1)	0.001(1)	–0.007(1)	–0.024(1)
O(6)	2*i*	0.5797(3)	0.7172(2)	0.2023(2)	0.038(1)	0.055(1)	0.070(1)	–0.0040(9)	0.006(1)	–0.010(1)
O(7)	2*i*	0.4150(3)	0.7653(2)	0.3762(2)	0.048(1)	0.050(1)	0.064(1)	–0.0043(9)	–0.005(1)	–0.008(1)
O(8)	2*i*	0.8670(4)	0.8217(3)	0.0820(2)	0.054(2)	0.090(2)	0.084(2)	–0.014(1)	–0.007(1)	0.005(2)
C(1)	2*i*	0.0244(5)	1.1454(3)	0.2089(2)	0.060(2)	0.034(1)	0.047(2)	–0.000(1)	–0.009(1)	–0.009(1)
C(2)	2*i*	–0.1704(6)	1.2167(3)	0.2261(2)	0.069(2)	0.042(2)	0.061(2)	0.005(2)	–0.013(2)	–0.011(1)
C(3)	2*i*	–0.2145(7)	1.3575(4)	0.1955(3)	0.094(3)	0.045(2)	0.076(2)	0.021(2)	–0.023(2)	–0.017(2)
C(4)	2*i*	–0.0696(8)	1.4228(4)	0.1492(3)	0.129(4)	0.035(2)	0.067(2)	0.004(2)	–0.017(2)	–0.004(2)
C(5)	2*i*	0.1216(8)	1.3550(4)	0.1324(3)	0.120(4)	0.044(2)	0.083(3)	–0.022(2)	0.004(2)	–0.001(2)
C(6)	2*i*	0.1695(6)	1.2163(3)	0.1634(3)	0.080(2)	0.041(2)	0.071(2)	–0.007(2)	0.002(2)	–0.007(2)
C(7)	2*i*	0.0783(4)	0.9980(3)	0.2394(2)	0.042(1)	0.036(1)	0.048(2)	–0.002(1)	–0.005(1)	–0.009(1)
C(8)	2*i*	–0.0909(4)	0.7115(3)	0.3413(2)	0.037(1)	0.045(2)	0.047(2)	–0.007(1)	–0.006(1)	–0.009(1)
C(9)	2*i*	–0.0347(4)	0.5689(3)	0.3650(2)	0.046(2)	0.043(1)	0.043(1)	–0.011(1)	–0.009(1)	–0.009(1)
C(10)	2*i*	0.1595(5)	0.4974(3)	0.3483(2)	0.055(2)	0.036(1)	0.046(2)	–0.012(1)	–0.007(1)	–0.008(1)
C(11)	2*i*	0.2051(5)	0.3564(3)	0.3753(2)	0.070(2)	0.040(2)	0.054(2)	–0.006(1)	–0.009(2)	–0.011(1)
C(12)	2*i*	0.0536(6)	0.2891(3)	0.4181(2)	0.102(3)	0.038(2)	0.046(2)	–0.025(2)	–0.014(2)	–0.002(1)
C(13)	2*i*	–0.1384(6)	0.3579(3)	0.4335(2)	0.077(2)	0.052(2)	0.053(2)	–0.025(2)	–0.007(2)	–0.001(1)
C(14)	2*i*	–0.1840(5)	0.4945(3)	0.4089(2)	0.059(2)	0.053(2)	0.049(2)	–0.019(1)	–0.005(1)	–0.005(1)
C(15)	2*i*	0.2735(8)	0.0779(4)	0.4434(4)	0.105(4)	0.058(2)	0.109(4)	–0.002(2)	–0.013(3)	–0.011(2)
C(16)	2*i*	0.3506(7)	0.6833(5)	0.0469(3)	0.089(3)	0.089(3)	0.070(2)	–0.005(2)	0.002(2)	–0.029(2)
C(17)	2*i*	0.7661(8)	0.9556(5)	0.0554(4)	0.088(3)	0.110(4)	0.101(3)	–0.028(3)	–0.022(3)	0.016(3)

Acknowledgments. We thank the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China for financial support.

References

1. Wright, W. R. H.; Batsanov, A. S.; Messinis, A. M.; Howard, J. A. K.; Tooze, R. P.; Hanton, M. J.; Dyer, P. W.: Application of molybdenum bis(imido) complexes in ethylene dimerisation catalysis. Dalton Trans. **41** (2012) 5502-5511.
2. Rayati, S.; Rafiee, N.; Wojtczak, A.: cis-Dioxo-molybdenum(VI) Schiff base complexes: Synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins. Inorg. Chim. Acta **386** (2012) 27-35.
3. Modec, B.; Dolenc, D.: Oxidative cleavage of 3-phenyllactic acid in presence of molybdenum complexes. Inorg. Chem. Commun. **23** (2012) 50-53.
4. Itazaki, M.; Ichimura, A.; Nakazawa, H.: Synthesis of silyl-molybdenum complexes connected by a 1,1'-metallocenylene unit and their electrochemical properties. Eur. J. Inorg. Chem. **36** (2011) 5496-5501.
5. Bernardini, G.; Wedd, A. G.; Zhao, C.; Bond, A. M.: Electrochemical probing of the photoreduction of molybdenum and tungsten Dawson-type polyoxometalates in molecular and ionic liquid media using water as an electron donor. Dalton Trans. **41** (2012) 9944-9954.
6. Pramanik, N. R.; Ghosh, S.; Raychaudhuri, T. K.; Butcher, R. J.; Mandal, S. S.: Synthesis, chemical, electrochemical, and structural characterization of binuclear dioxo-bridged molybdenum(VI) complexes of tridentate ONS donors. J. Coord. Chem. **64** (2011) 1207-1215.
7. Rao, S. N.; Munshi, K. N.; Rao, N. N.; Bhadbhade, M. M.; Suresh, E.: Synthesis, spectral and X-ray structural characterization of [cis-MoO_2(L)(solv)] (L = salicylidene salicyloyl hydrazine) and its use as catalytic oxidant. Polyhedron **18** (1999) 2491-2497.
8. Bagherzadeh, M.; Amini, M.; Parastar, H.; Jalali-Heravi, M.; Ellern, A.; Woo, L. K.: Synthesis, X-ray structure and oxidation catalysis of a oxido-peroxido molybdenum(VI) complex with a tridentate Schiff base ligand. Inorg. Chem. Commun. **20** (2012) 86-89.
9. Ngan, N. K.; Lo, K. M.; Wong, C. S. R.: Synthesis, structure studies and electrochemistry of molybdenum(VI) Schiff base complexes in the presence of different donor solvent molecules. Polyhedron **30** (2011) 2922-2932.
10 Bruker. SADABS (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
11. Bruker. SMART (Version 5.625), SAINT (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
12. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.