Di-μ-oxo-bis[(histidinato-κ³N,N,O)oxo-molybdenum(V)] trihydrate

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In the title dinuclear complex, $[Mo_2(C_6H_8N_3O_2)_2O_4]\cdot 3H_2O$, the Mo atoms, bridged by two μ-oxo atoms, have a distorted octahedral coordination environment. Besides the two bridging O atoms, the coordination of each Mo atom is completed by a terminal oxo atom and a tridentate histidinate ligand. The short Mo$\cdots$Mo distance of 2.5458 (4) Å may indicate the existence of an Mo—Mo metal bond. Intermolecular hydrogen bonding between the uncoordinated carboxylate O atoms and amino groups leads to a layer-like arrangement of the molecules. The uncoordinated water molecules link these layers *via* O—H$\cdots$O hydrogen bonds and help to stabilize the crystal packing.

Comment

Complexes of Mo^V ions with amino acids and polycarboxylic acids, including natural α-amino acids, have been intensively investigated since the 1960s (Spence & Chang, 1963; Spence & Lee, 1965; Kay & Mitchell, 1968; Melby, 1969; Spence, 1969) because such compounds are potential models for understanding the action of Mo-containing enzymes, possible Mo–enzyme interactions and the function of molybdenum in biological systems (Spence, 1969; Hille, 1996). To date, many crystal structures of such compounds have been reported in the literature (Cotton *et al.*, 1964; Knox & Prout, 1968; Drew & Kay, 1971; Delbaere & Prout, 1971). However, only a few examples of α-amino acid molybdenum(V) complexes are known so far (Knox & Prout, 1968; Bray & Knowles, 1968; Liu *et al.*, 2000). In this paper, we report the synthesis and crystal structure of the title histidine molybdenum(V) complex, (I), which was previously obtained by a different synthetic route and confirmed only by elemental analysis, IR and UV spectra, optical rotation, electron paramagnetic resonance, and proton magnetic resonance studies (Spence & Lee, 1965; Melby, 1969).

(I)
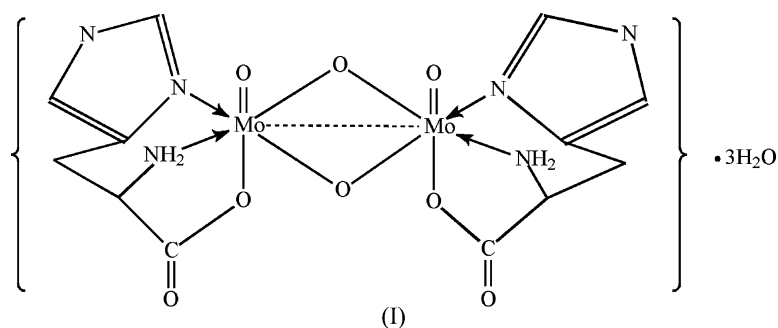
Compound (I) was synthesized from an acidic aqueous solution containing $(NH_4)_6[Mo_7O_{24}]$, L-histidine and $N_2H_4\cdot$-
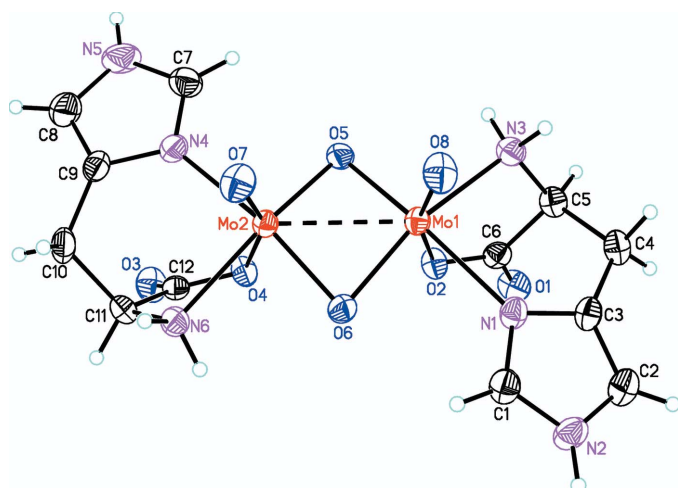
Figure 1
A view of the title histidine molybdenum(V) complex, with the atomic numbering scheme, and with displacement ellipsoids at the 50% probability level. The solvent water molecules have been omitted for clarity.

2HCl. It crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ with three water molecules in the asymmetric unit. The two Mo atoms in (I) have the same distorted octahedral coordination environment (Table 1), and they are bridged by two μ-oxo atoms to form a dinuclear coordination compound (Fig. 1). Besides the bridging O atoms, each Mo atom is coordinated by a terminal oxo atom and a histidinate, which acts as a tridentate chelating ligand through its amino N atom, one imidazolyl N atom and one carboxyl O atom.

The short Mo···Mo distance of 2.5458 (4) Å implies that there is an Mo—Mo bond between the two Mo atoms. According to bond-valence theory (Brown, 1981), the sum of the bond valences around Mo1 is 5.229 and that around Mo2 is 5.262, in good agreement with the valence of Mo^V. However, as observed previously (Spence & Lee, 1965), this compound is silent in electron paramagnetic resonance, which may be attributed to the formation of an Mo—Mo bond (Spence & Lee, 1965; Melby, 1969). In general, the molecular structure of (I) is similar to that of the previously reported dinuclear molybdenum L-cysteinate (Knox & Prout, 1969).

In the solid state, the solvent water molecules are aggregated into trimers via hydrogen bonding. The molecules of (I) form a two-dimensional layer-like arrangement parallel to the c axis via hydrogen-bond interactions between their uncoordinated carboxylic O atoms and the amino groups of neighbouring molecules. These layers are further linked through hydrogen bonding with the trimeric water molecules of crystallization to complete the whole three-dimensional crystal structure.

Experimental

(NH$_4$)$_6$[Mo$_7$O$_{24}$] (1.25 g, 1.0 mmol), L-histidine (0.46 g g, 3.0 mmol) and hydrazine hydrochloride (0.13 g, 1.25 mmol) were added to H$_2$O (20 ml) and stirred to give a mixture of pH = 3–4. Monoclinic block-like yellow crystals of (I) of X-ray quality were deposited within 3 d in about 60% yield. This product is insoluble in common solvents such

as water, ethanol, ethyl acetate, chloroform and acetone, but is readily soluble in N,N-dimethylformamide and dimethylsulfoxide, All chemicals used were of analytical purity and obtained from commercial sources. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3400 (m, OH), 3253, 3135 (m, NH), 1638, 1599 (s, COO), 1437 (m, CH$_2$), 1396 (m), 1381 (m),1107 (s), 947 (vs, MO), 920 (s, MoOMo), 714 (s).

Crystal data

[Mo$_2$(C$_6$H$_8$N$_3$O$_2$)$_2$O$_4$]·3H$_2$O	D_x = 2.017 Mg m^{-3}
M_r = 618.24	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 5483
a = 10.9594 (12) Å	reflections
b = 8.7222 (9) Å	θ = 3.0–28.3°
c = 11.5783 (12) Å	μ = 1.30 mm^{-1}
β = 113.136 (2)°	T = 292 (2) K
V = 1017.76 (19) Å^3	Block, yellow
Z = 2	0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3372 independent reflections
	3343 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.019
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	θ_{max} = 27.0°
	h = −13 → 13
T_{min} = 0.696, T_{max} = 0.781	k = −5 → 11
5964 measured reflections	l = −12 → 14

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.020	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.049	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.13	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
3372 reflections	$\Delta\rho_{min}$ = −0.69 e Å^{-3}
280 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 1006 Friedel pairs
	Flack parameter: 0.03 (3)

Table 1
Selected geometric parameters (Å, °).

Mo1—O8	1.695 (2)	Mo2—O7	1.701 (3)
Mo1—O6	1.9347 (19)	Mo2—O6	1.9286 (19)
Mo1—O5	1.9470 (19)	Mo2—O5	1.932 (2)
Mo1—O2	2.205 (2)	Mo2—O4	2.201 (2)
Mo1—N1	2.210 (2)	Mo2—N6	2.219 (2)
Mo1—N3	2.242 (2)	Mo2—N4	2.228 (2)
Mo1—Mo2	2.5458 (4)		
Mo2—O5—Mo1	82.03 (8)	Mo2—O6—Mo1	82.44 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9A···O1^i	0.85	1.89	2.716 (3)	163
O9—H9B···O10	0.85	2.22	2.885 (4)	136
O10—H10C···O11^{ii}	0.85	2.00	2.844 (4)	170
O10—H10D···O5	0.85	2.34	3.056 (4)	142
O11—H11A···O3^{iii}	0.85	1.91	2.724 (4)	159
O11—H11B···O7	0.85	2.41	3.148 (4)	145
N2—H2···O9^{iv}	0.86	1.88	2.735 (4)	177
N3—H3A···O1^i	0.90	2.21	2.944 (3)	139
N3—H3B···O10^i	0.90	2.18	3.077 (4)	178
N5—H5···O11^v	0.86	2.03	2.869 (3)	165
N6—H6A···O7^{vi}	0.90	2.34	3.091 (4)	141
N6—H6B···O2^{vii}	0.90	2.47	3.150 (3)	133

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

All H atoms were positioned geometrically and refined as riding, with O—H = 0.85 Å, N—H = 0.86–0.90 Å and C—H = 0.93–0.98 Å, and with $U_{iso}(H)$ constrained to be $1.2U_{eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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