

μ -Glycine-O:O'-di- μ -oxo-bis[(glycinate-N,O)oxomolybdenum(V)]

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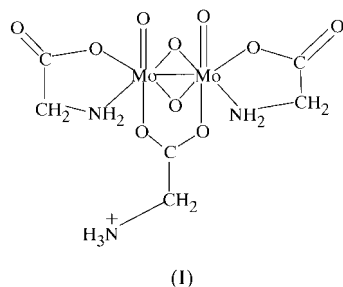
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In the title compound, $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4\text{NO}_2)_2(\text{C}_2\text{H}_5\text{NO}_2)]$, two Mo atoms sit in the same distorted pentagonal bipyramid coordination environment. There are four ligand types: oxo-O, μ_2 -O, μ_2 -glycine and chelate glycine. There is an Mo—Mo bond between the two Mo atoms [2.552 (1) Å]. All amino groups participate in hydrogen bonding with O atoms of other molecules, thus connecting the molecules into a three-dimensional structure.

Comment

Molybdenum is one of the important transition metals in biological systems (Spence, 1969). It is an integral component of the multinuclear M center of nitrogenases and the active sites of a group of oxotransferases (Hille, 1996). Its unique properties appear to be due to its ability to exist in a number of different oxidation states and to coordinate with a variety of ligands. Mo^{V} and Mo^{VI} are generally thought to be the most likely oxidation states involved. The crystal structures of Mo^{V} and Mo^{VI} complexes with amino acids and polycarboxylic acids were reported as possible model compounds as long as 30 years ago (Cotton *et al.*, 1964; Knox & Prout, 1968; Drew & Kay, 1971; Delbaere & Prout, 1971). But so far, the α -amino acid molybdenum(V) complexes have only been known for a



few examples (Knox & Prout, 1968; Bray & Knowles, 1968). In this paper, we report the hydrothermal synthesis and crystal structure of the title glycine molybdenum(V) complex, (I).

The asymmetric unit consists of one $[\text{MoO}(\text{C}_2\text{H}_4\text{O}_2\text{N})]_2\text{O}_2(\text{C}_2\text{H}_5\text{O}_2\text{N})$ molecule. The molecule consists of two Mo

atoms sitting in the same distorted pentagonal bipyramid coordination environment. Each Mo atom is chelated by the N atom and one carboxyl O atom of a glycine molecule. An O atom bonds to each Mo atom as $\text{Mo}=\text{O}$. Two Mo atoms are bridged by two μ_2 -O atoms and by a μ_2 -glycine ligand with each carboxyl-group O atom coordinating to an Mo atom. The amino group of this μ_2 -glycine is protonated and does not take part in coordination. There is an Mo—Mo bond between the two Mo atoms [2.552 (1) Å]. According to bond-valence theory (Brown, 1981), the sum of the bond valences around Mo1 is equal to 4.919 and that around Mo2 is equal to 4.903, which are in good agreement with the valence of Mo^{V} . As shown in Fig. 1, the μ_2 -glycine and two oxo-O atoms are in the same plane. The amino groups of the two chelate glycine molecules are on the same side of this plane and the carboxyl groups are on the other side. The amino group of the μ_2 -glycine is on this plane and is deflected towards Mo1. A comparison with binuclear molybdenum L-cysteinate (Knox & Prout, 1969) shows similar Mo—Mo bond lengths: 2.552 (1) in the title compound and 2.569 (2) Å in Knox's compound. There are three kinds of Mo—O bonds in Knox's compound

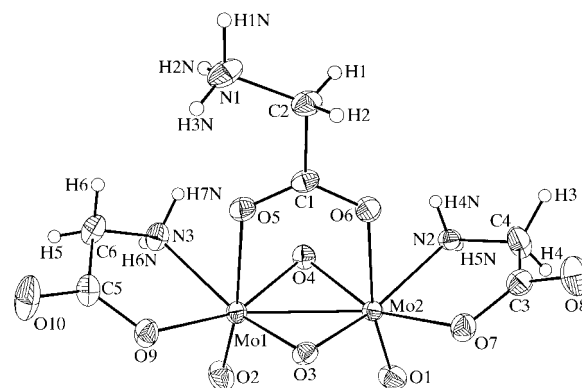


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids.

and the average bond lengths are 1.709 (18) Å for terminal oxo atoms, 1.930 (15) Å for μ_2 -O atoms and 2.295 (16) Å for the O atom of the chelate cysteine. The corresponding distances in the title compound are 1.688 (2), 1.940 (2) and 2.085 (2) Å; only the third is markedly smaller. Since the N—Mo—O angle in the chelate cysteine is 69.9 (6)° and that in the chelate glycine is 77.3 (1)°, the increase of the Mo—O bond length between the Mo and O atoms of the chelate cysteine agrees with Freeman's (1967) observation that N—M—O angles decrease as the average of the M—O distances increases, owing to the constancy of the N...O contact. An interesting aspect of the title compound is the μ_2 -amino acid, which is lacking in Knox's compound. So there are four coordination types of ligand in the title compound: oxo-O, μ_2 -O, μ_2 -glycine and chelate glycine. All amino groups of the title compound participate in hydrogen bonding with O atoms, connecting the molecules into a three-dimensional structure.

Experimental

(NH₄)₆Mo₇O₂₄·4H₂O (0.40 g, 0.32 mmol), NH₂CH₂COOH (2.00 g, 26.6 mmol), KOH (0.30 g, 5.3 mmol) and N₂H₄·H₂SO₄ (0.44 g, 3.4 mmol) were added to H₂O (10 ml, 0.56 mol) and stirred to give a mixture of pH 3–4. The mixture was sealed in a 25 ml digestion bomb and heated at 373 K for 7 d. Red monoclinic block crystals were separated from a red–brown solution and brown precipitate. The chemicals used were all of analytical purity and obtained from commercial sources.

Crystal data

[Mo ₂ O ₄ (C ₂ H ₄ NO ₂) ₂ (C ₂ H ₅ NO ₂) ₂]	Z = 2
M _r = 479.075	D _x = 2.418 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 5.7300 (10) Å	Cell parameters from 21 reflections
b = 10.213 (2) Å	θ = 5–11°
c = 12.232 (2) Å	μ = 1.964 mm ⁻¹
α = 68.15 (3)°	T = 293 (2) K
β = 82.08 (3)°	Block, red
γ = 86.08 (3)°	0.2 × 0.2 × 0.2 mm
V = 657.9 (2) Å ³	

Data collection

AFC-6S diffractometer	θ_{\max} = 30.00°
2 θ scans	h = -8 → 8
Absorption correction: ψ scan (Coppens <i>et al.</i> , 1965)	k = -14 → 0
T _{min} = 0.602, T _{max} = 0.675	l = -17 → 15
4009 measured reflections	3 standard reflections
3811 independent reflections	every 200 reflections
R _{int} = 0.025	intensity decay: 1%

Refinement

Refinement on F ²	w = 1/[$\sigma^2(F_o^2) + (0.0367P)^2 + 0.8169P$]
R[F ² > 2 σ (F ²)] = 0.031	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.086	(Δ/σ) _{max} = 0.001
S = 1.089	$\Delta\rho_{\max}$ = 0.64 e Å ⁻³
3811 reflections	$\Delta\rho_{\min}$ = -2.01 e Å ⁻³
242 parameters	
All H atoms refined	

Table 1

Selected bond lengths (Å) for (I).

Mo1—O2	1.682 (2)	Mo2—O1	1.694 (2)
Mo1—O4	1.941 (2)	Mo2—O4	1.929 (2)
Mo1—O3	1.944 (2)	Mo2—O3	1.945 (2)
Mo1—O9	2.077 (2)	Mo2—O7	2.092 (2)
Mo1—N3	2.212 (3)	Mo2—N2	2.184 (3)
Mo1—O5	2.314 (2)	Mo2—O6	2.273 (2)
Mo1—Mo2	2.5515 (7)		

The refined dimensions involving H atoms include N—H 0.79 (5)–0.93 (5) Å and C—H 0.84 (7)–1.07 (5) Å.

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D...A	D—H...A
N1—H1N...O8 ⁱ	3.143 (4)	137 (4)
N1—H1N...O10 ⁱⁱ	3.092 (4)	140 (4)
N1—H2N...O10 ⁱⁱⁱ	2.816 (4)	164 (6)
N1—H3N...O8 ^{iv}	2.975 (5)	167 (5)
N2—H4N...O3 ⁱⁱⁱ	2.834 (3)	162 (5)
N2—H5N...O1 ^v	2.916 (3)	149 (6)
N3—H6N...O4 ^{vi}	2.847 (4)	165 (5)

Symmetry codes: (i) 2 - x, 1 - y, -1 - z; (ii) 1 - x, -y, -1 - z; (iii) 1 + x, y, z; (iv) 1 - x, 1 - y, -1 - z; (v) 1 - x, 1 - y, -z; (vi) 1 - x, -y, -z.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1994); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: TEXSAN (Molecular Structure Corporation, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL (Siemens, 1990); software used to prepare material for publication: CIFTAB in SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1289). Services for accessing these data are described at the back of the journal.

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