Crystal structure of bis(tetra-*n*-butylammonium) bis(2-sulfidopropionato)-disulfidodioxodimolybdate(V), $[(\text{NC}_4\text{H}_9)_4]_2\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_2\text{H}_4\text{SCOO})_2$

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Abstract

$\text{C}_{38}\text{H}_{80}\text{Mo}_2\text{N}_2\text{O}_6\text{S}_4$, triclinic, $P\bar{1}$ (no. 2), $a = 11.366(9)$ Å, $b = 11.429(8)$ Å, $c = 20.45(1)$ Å, $\alpha = 96.42(4)^\circ$, $\beta = 99.88(5)^\circ$, $\gamma = 101.6(1)^\circ$, $V = 2534.5$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.094$, $wR_{\text{ref}}(F^2) = 0.310$, $T = 293$ K.

Source of material

$[\text{Mo}^{\text{VI}}\text{O}_2(\text{OCOCH}(\text{S})\text{CH}_3)_2]$ is reduced by $\text{CH}_3\text{CH}(\text{SH})\text{CO}_2\text{H}$ to the stable dimeric molybdenum(V) complexes $[\text{Mo}_2^{\text{V}}\text{O}_2\text{S}(\text{OCOCH}(\text{S})\text{CH}_3)_3]$ and $[\text{Mo}_2^{\text{V}}\text{O}_2\text{S}_2(\text{OCOCH}(\text{S})\text{CH}_3)_2]$, and the thiolactic acid is oxidized to disulfide as shown by ^1H and ^{13}C NMR spectroscopy. The ESR spectrum of this reaction shows the presence of an ESR-active monomeric molybdenum(V) species, with an isotropic g value of $\langle g \rangle = 1.976$ and an isotropic 95.97 Mo hyperfine parameter $\langle A \rangle = 36 \times 10^{-4} \text{ cm}^{-1}$, respectively, which rapidly dimerizes forming an ESR-silent molybdenum(V) complexes. In a reaction vessel previously deoxygenated, 50 mmol of thiolactic acid ($\text{CH}_3\text{CH}(\text{SH})\text{CO}_2\text{H}$), 6 mmol of (*n*-C₄H₉)₄NBr and 2 mmol of $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ were placed. Over these 20 ml of methanol (previously deoxygenated by bubbling argon 30 min in an ultrasonic bath) was added under argon stream, which was maintained for an additional 15 min, and then the vessel was flame-sealed. By cooling the resulting solution to 5 °C overnight, clear orange and yellow prismatic crystals were obtained. Elemental analysis: found – C, 46.55 %; H, 8.23 %; N, 2.85 %; S, 13.05 %; calc. for $\text{Mo}_2\text{O}_6\text{S}_4\text{C}_{38}\text{H}_{80}\text{N}_2$ – C, 46.52 %; H, 8.22 %; N, 2.86 %; S, 13.07 %. ^1H , ^{13}C NMR, IR and UV/VIS data are available in the CIF.

Experimental details

Due to the low crystal quality the number of observed reflections was small and geometrical restraints were used when needed. Distance restraints were applied to the N–C–C–C chains on both tetrabutylammonium moieties to keep all distances close to 1.50 Å. The $\text{OCOCH}(\text{S})\text{CH}_3$ ligands were refined keeping similar bond lengths and angles, including the Mo coordination distances, using soft restraints. H atoms were geometrically fixed to their parent ones and their displacement parameters calculated as $1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$. The highest peak in the electron density was 0.80 e Å^{-3} and the deepest hole was -0.82 e Å^{-3} both near Mo2.

Discussion

Thiols may be considered physiological reductants acting as endogenous electron donors in reductase reactions of molybdenum hydroxylases[1] in animals and microorganisms. Previous studies showed [2–5] that reduction of aqueous molybdate by 2-mer-

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capto-acetic acid (thioglycolic acid) yields solutions exhibiting ESR signals which account for about 1 % of the available molybdenum with parameters similar to those for xanthine oxidase. Thereafter these authors demonstrated the capacity of molybdate ions to oxidize thioglycolic acid, cysteine and glutathione giving disulfide derivatives. The proposed mechanism involves the formation of the [Mo^{VI}O₂(OCOCH₂(S))₂] complex which is subsequently reduced by excess of thioglycolic acid to give an ESR-active monomeric molybdenum(V) species which rapidly dimerizes forming an ESR-silent-oxo complex and disulfide. Our investigations [6,7] have demonstrated that the Mo(VI) complexes containing sterically hindered ligands can be quantitatively reduced by the free acid yielding the monomeric molybdenum(V) complexes, the structure of which has been determined by X-ray crystallography.

The structural characterization of the binuclear oxomolybdenum(V) complexes confirms the structural versatility of thiolic ligands, and constitutes another example of the proclivity of molybdenum(V) complexes to be binuclear if the adjacent groups to the ligating sulfur atoms do not provide steric hindrance and prevent dimerization upon reduction. The crystal structure of the title compound is a dimeric molybdenum(V) complex anions with two molecules of tetrabutylammonium as the counter ions. The binuclear complex anion exhibits a cofacial bi-octahedral geometry which appears to be quite common in molybdenum(V) chemistry. The Mo atom is shifted toward the terminal unshared O atom with values of the axial angles ranging from 131.0(2)° to 155.8(3)° and Mo—Mo distance of 2.834(4) Å. The thioglycate ligand are contained in LSQ-planes forming 36.2(1)° and 29.8(1)° angles with the LSQ-plane built for Mo1-Mo2-S1-S2.

Table 1. Data collection and handling.

Crystal:	red, prismatic, size 0.16 × 0.16 × 0.33 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	6.98 cm ⁻¹
Diffractometer, scan mode:	Nonius CAD4, ω/2θ
2θ _{max} :	51.96°
N(hkl) _{measured} , N(hkl) _{unique} :	10209, 9916
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 3653
N(param) _{refined} :	472
Programs:	DIREDF [8], SHELX-97 [9], PLATON [10], WinGX [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(2L)	2i	-0.3663	-0.3421	0.6022	0.145
H(3M)	2i	-0.4055	-0.4160	0.6978	0.335
H(3L)	2i	-0.5170	-0.3693	0.6625	0.335
H(3N)	2i	-0.4282	-0.2913	0.7266	0.335
H(2O)	2i	0.2341	0.2279	0.9567	0.156
H(3P)	2i	0.3969	0.2930	0.9067	0.390
H(3Q)	2i	0.3426	0.4009	0.9328	0.390
H(3O)	2i	0.3130	0.3494	0.8560	0.390
H(19A)	2i	0.8418	0.0176	0.3795	0.116
H(19B)	2i	0.8867	-0.0347	0.4447	0.116
H(35A)	2i	1.1707	0.2514	0.0734	0.174
H(35B)	2i	1.0410	0.1867	0.0303	0.174
H(10A)	2i	0.5234	-0.1395	0.4627	0.104
H(10B)	2i	0.4777	-0.0655	0.4074	0.104
H(18A)	2i	0.6768	0.0595	0.4302	0.092
H(18B)	2i	0.7163	-0.0192	0.4842	0.092
H(38A)	2i	1.1086	0.4306	0.0772	0.134
H(38B)	2i	1.0528	0.5165	0.1217	0.134
H(22A)	2i	0.6984	-0.1095	0.3067	0.134
H(22B)	2i	0.5642	-0.1868	0.2943	0.134
H(14A)	2i	0.6361	-0.2982	0.3714	0.124
H(14B)	2i	0.7670	-0.2134	0.3859	0.124
H(13A)	2i	0.1305	-0.3634	0.4003	0.208
H(13B)	2i	0.2259	-0.4367	0.3818	0.208
H(13C)	2i	0.1728	-0.3573	0.3315	0.208
H(12A)	2i	0.3233	-0.2630	0.4574	0.128
H(12B)	2i	0.2708	-0.1840	0.4070	0.128
H(30A)	2i	0.8599	0.3984	0.0702	0.144
H(30B)	2i	0.9148	0.3062	0.0296	0.144
H(34A)	2i	1.0989	0.2333	0.1710	0.123
H(34B)	2i	0.9715	0.1584	0.1307	0.123

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(24A)	2i	0.6152	-0.0521	0.2031	0.227
H(24B)	2i	0.4730	-0.0880	0.2007	0.227
H(26A)	2i	0.8908	0.2863	0.1977	0.127
H(26B)	2i	1.0220	0.3621	0.2308	0.127
H(15A)	2i	0.6349	-0.2814	0.4847	0.134
H(15B)	2i	0.7628	-0.1896	0.5009	0.134
H(21A)	2i	0.9076	0.3282	0.4534	0.215
H(21B)	2i	0.7785	0.2408	0.4279	0.215
H(21C)	2i	0.8791	0.2442	0.3839	0.215
H(20A)	2i	0.8988	0.1627	0.5090	0.139
H(20B)	2i	0.9971	0.1637	0.4637	0.139
H(11A)	2i	0.4518	-0.3168	0.3835	0.127
H(11B)	2i	0.3978	-0.2398	0.3318	0.127
H(31A)	2i	0.7472	0.2310	0.1106	0.192
H(31B)	2i	0.7889	0.1467	0.0567	0.192
H(28A)	2i	0.9209	0.4384	0.3113	0.216
H(28B)	2i	0.8654	0.5515	0.2990	0.216
H(23A)	2i	0.6314	0.0665	0.3164	0.145
H(23B)	2i	0.4965	-0.0051	0.3138	0.145
H(16A)	2i	0.8186	-0.3725	0.4334	0.236
H(16B)	2i	0.8399	-0.3539	0.5122	0.236
H(32A)	2i	0.6437	0.3230	0.0251	0.482
H(32B)	2i	0.7031	0.2604	-0.0305	0.482
H(25A)	2i	0.5187	0.0859	0.1512	0.460
H(25B)	2i	0.6091	0.1520	0.2178	0.460
H(25C)	2i	0.4679	0.1168	0.2161	0.460
H(27A)	2i	0.8288	0.4618	0.1756	0.187
H(27B)	2i	0.9608	0.5380	0.2091	0.187
H(29A)	2i	0.7120	0.3928	0.3132	0.532
H(29B)	2i	0.7374	0.3109	0.2528	0.532
H(29C)	2i	0.6822	0.4235	0.2402	0.532
H(39A)	2i	1.2437	0.4087	0.1723	0.192
H(39B)	2i	1.1884	0.4970	0.2166	0.192
H(17A)	2i	0.7285	-0.5483	0.4699	0.547
H(17B)	2i	0.6276	-0.4975	0.4271	0.547
H(17C)	2i	0.6467	-0.4774	0.5056	0.547
H(36A)	2i	1.0761	0.0163	0.1008	0.241
H(36B)	2i	1.1241	0.0209	0.0329	0.241
H(33A)	2i	0.5174	0.1275	-0.0285	0.532
H(33B)	2i	0.5551	0.1359	0.0496	0.532
H(33C)	2i	0.6245	0.0702	0.0024	0.532
H(40A)	2i	1.2656	0.5939	0.1056	0.280
H(40B)	2i	1.2870	0.6623	0.1796	0.280
H(37A)	2i	1.2872	0.0207	0.1192	0.563
H(37B)	2i	1.2629	0.1352	0.1597	0.563
H(37C)	2i	1.3105	0.1450	0.0926	0.563
H(41A)	2i	1.4740	0.6305	0.1599	0.699
H(41B)	2i	1.4174	0.4919	0.1379	0.699
H(41C)	2i	1.4342	0.5499	0.2130	0.699

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	2i	-0.1718(4)	0.1269(4)	0.7432(2)	0.086(3)	0.105(3)	0.109(3)	0.040(2)	0.018(2)	0.007(2)
S(2)	2i	0.0394(3)	-0.0640(3)	0.7330(2)	0.079(2)	0.082(2)	0.083(2)	0.023(2)	0.019(2)	0.016(2)
O(1)	2i	-0.1147(8)	-0.0027(9)	0.6013(4)	0.093(7)	0.111(8)	0.081(6)	0.023(6)	0.017(5)	0.026(6)
O(2)	2i	0.1093(9)	0.2188(8)	0.7220(5)	0.129(8)	0.080(7)	0.105(7)	0.001(6)	0.043(6)	0.029(6)
Mo(1)	2i	-0.1447(1)	-0.0372(1)	0.67417(6)	0.0780(9)	0.0829(9)	0.0729(7)	0.0222(7)	0.0144(6)	0.0141(6)
O(3B)	2i	-0.3350(7)	-0.0703(8)	0.6442(5)	0.083(8)	0.115(9)	0.117(8)	0.035(7)	0.014(6)	0.012(7)
C(1B)	2i	-0.402(1)	-0.176(1)	0.6209(7)	0.12(2)	0.11(1)	0.09(1)	0.03(1)	0.01(1)	-0.01(1)
C(2B)	2i	-0.356(1)	-0.284(1)	0.6431(8)	0.11(2)	0.11(1)	0.13(2)	0.00(1)	0.01(1)	0.01(1)
S(2B)	2i	-0.1969(4)	-0.2482(3)	0.6787(2)	0.097(3)	0.082(3)	0.102(3)	0.012(2)	-0.007(2)	0.009(2)
O(4B)	2i	-0.5031(9)	-0.195(1)	0.5830(6)	0.105(9)	0.16(1)	0.115(9)	0.015(9)	-0.017(7)	-0.009(8)
C(3B)	2i	-0.434(1)	-0.346(2)	0.686(1)	0.09(2)	0.23(3)	0.33(4)	-0.01(2)	0.02(2)	0.13(3)
Mo(2)	2i	0.0370(1)	0.1340(1)	0.76931(6)	0.0811(9)	0.0752(8)	0.0792(8)	0.0170(7)	0.0241(7)	0.0173(6)
O(3C)	2i	0.0221(9)	0.2612(8)	0.8482(4)	0.123(9)	0.073(7)	0.076(6)	0.021(6)	-0.013(6)	-0.002(5)
C(1C)	2i	0.106(1)	0.299(1)	0.9014(7)	0.17(2)	0.07(1)	0.12(1)	0.05(1)	0.08(1)	0.03(1)
C(2C)	2i	0.218(1)	0.242(1)	0.9100(7)	0.11(2)	0.12(2)	0.13(1)	0.01(1)	0.02(1)	-0.04(1)
S(2C)	2i	0.1857(4)	0.0990(4)	0.8586(2)	0.093(3)	0.110(3)	0.099(3)	0.036(3)	0.003(2)	0.000(2)
O(4C)	2i	0.103(1)	0.3766(9)	0.9479(5)	0.19(1)	0.096(8)	0.099(8)	0.052(9)	0.016(8)	-0.003(6)
C(3C)	2i	0.327(2)	0.329(2)	0.901(2)	0.12(2)	0.19(3)	0.44(5)	-0.00(2)	0.08(3)	-0.10(3)
N(1)	2i	0.992(1)	0.3393(9)	0.1289(5)	0.11(1)	0.090(9)	0.076(7)	0.031(8)	0.012(7)	0.015(7)
C(19)	2i	0.842(1)	0.023(1)	0.4272(7)	0.07(1)	0.12(1)	0.11(1)	0.03(1)	0.020(8)	0.03(1)
N(2)	2i	0.6332(8)	-0.1205(9)	0.3934(4)	0.071(8)	0.11(1)	0.073(7)	0.025(7)	0.013(6)	0.005(7)
C(35)	2i	1.097(2)	0.191(2)	0.0724(8)	0.20(2)	0.11(2)	0.14(2)	0.03(2)	0.07(2)	0.01(1)
C(10)	2i	0.511(1)	-0.136(1)	0.4149(6)	0.070(9)	0.10(1)	0.081(9)	0.000(8)	0.009(7)	0.000(8)
C(18)	2i	0.7142(9)	-0.008(1)	0.4377(6)	0.055(8)	0.09(1)	0.076(8)	0.007(7)	-0.002(7)	0.010(8)
C(38)	2i	1.089(2)	0.446(1)	0.1211(8)	0.17(2)	0.07(1)	0.11(1)	0.02(1)	0.06(1)	0.021(9)
C(22)	2i	0.619(1)	-0.113(2)	0.3191(5)	0.10(1)	0.16(2)	0.070(9)	0.02(1)	0.021(9)	0.00(1)
C(14)	2i	0.690(1)	-0.229(1)	0.4009(7)	0.10(1)	0.11(1)	0.10(1)	0.04(1)	0.018(9)	-0.008(9)
C(13)	2i	0.198(1)	-0.363(1)	0.3781(9)	0.12(2)	0.11(1)	0.14(2)	-0.02(1)	-0.01(1)	-0.03(1)
C(12)	2i	0.301(1)	-0.257(1)	0.4101(8)	0.10(1)	0.07(1)	0.13(1)	0.002(9)	-0.01(1)	-0.011(9)
C(30)	2i	0.885(1)	0.322(2)	0.0707(7)	0.14(2)	0.09(1)	0.11(1)	0.01(1)	-0.00(1)	0.00(1)
C(34)	2i	1.039(2)	0.225(1)	0.1296(7)	0.13(1)	0.08(1)	0.09(1)	0.02(1)	0.02(1)	0.008(8)
C(24)	2i	0.547(2)	-0.027(2)	0.2193(7)	0.19(2)	0.30(3)	0.16(2)	0.15(2)	0.10(2)	0.10(2)
C(26)	2i	0.952(2)	0.358(1)	0.1954(6)	0.13(1)	0.11(1)	0.09(1)	0.04(1)	0.05(1)	0.040(9)
C(15)	2i	0.712(1)	-0.259(1)	0.4701(7)	0.09(1)	0.09(1)	0.15(2)	0.025(9)	-0.00(1)	0.00(1)
C(21)	2i	0.865(2)	0.250(1)	0.429(1)	0.16(2)	0.10(1)	0.19(2)	0.03(1)	0.06(2)	0.07(1)
C(20)	2i	0.910(1)	0.154(1)	0.4629(7)	0.11(1)	0.12(2)	0.13(1)	0.02(1)	0.06(1)	0.04(1)
C(11)	2i	0.418(1)	-0.246(1)	0.3791(7)	0.07(1)	0.12(1)	0.11(1)	0.02(1)	0.005(9)	-0.03(1)
C(31)	2i	0.774(2)	0.226(2)	0.068(1)	0.15(2)	0.15(2)	0.13(2)	-0.03(2)	-0.01(2)	0.01(2)
C(28)	2i	0.864(2)	0.469(2)	0.281(1)	0.22(3)	0.14(2)	0.22(3)	0.06(2)	0.12(2)	0.04(2)
C(23)	2i	0.572(2)	-0.008(2)	0.2980(7)	0.12(2)	0.17(2)	0.08(1)	0.04(1)	0.03(1)	0.02(1)
C(16)	2i	0.778(2)	-0.367(2)	0.471(2)	0.16(2)	0.09(2)	0.29(3)	0.01(2)	-0.02(2)	-0.03(2)
C(32)	2i	0.675(3)	0.253(3)	0.011(2)	0.32(5)	0.39(6)	0.29(4)	-0.20(4)	-0.20(4)	0.11(4)
C(25)	2i	0.535(4)	0.093(2)	0.199(1)	0.43(6)	0.33(5)	0.13(2)	0.04(4)	0.06(3)	0.01(3)
C(27)	2i	0.900(2)	0.465(2)	0.2099(9)	0.20(2)	0.13(2)	0.18(2)	0.06(2)	0.09(2)	0.05(2)
C(29)	2i	0.738(2)	0.392(4)	0.271(2)	0.21(4)	0.61(8)	0.18(3)	0.05(4)	0.01(3)	-0.09(4)
C(39)	2i	1.205(2)	0.477(2)	0.172(1)	0.14(2)	0.14(2)	0.17(2)	-0.04(2)	0.02(2)	0.03(2)
C(17)	2i	0.687(3)	-0.483(2)	0.468(2)	0.58(7)	0.18(3)	0.46(6)	0.20(4)	0.31(6)	0.08(4)
C(36)	2i	1.130(2)	0.065(2)	0.077(1)	0.21(3)	0.18(3)	0.22(3)	0.07(2)	0.08(2)	-0.03(2)
C(33)	2i	0.585(3)	0.136(3)	0.008(2)	0.31(5)	0.39(6)	0.31(5)	0.13(4)	-0.11(4)	-0.03(5)
C(40)	2i	1.290(2)	0.588(2)	0.153(2)	0.18(3)	0.16(3)	0.32(4)	-0.07(2)	0.06(3)	0.03(2)
C(37)	2i	1.259(2)	0.094(3)	0.116(2)	0.23(4)	0.37(5)	0.65(9)	0.18(4)	0.19(5)	0.28(6)
C(41)	2i	1.415(3)	0.563(4)	0.167(3)	0.32(6)	0.29(5)	0.9(1)	0.05(5)	0.32(8)	0.20(7)

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