Crystal structure of tetraguanidinium dioxo-tetraperoxo-μ-tartrato-dimolybdate(VI) dihydrate, $(CN_3H_6)_4[Mo_2O_2(O_2)_4(C_4H_2O_6)] \cdot 2H_2O$

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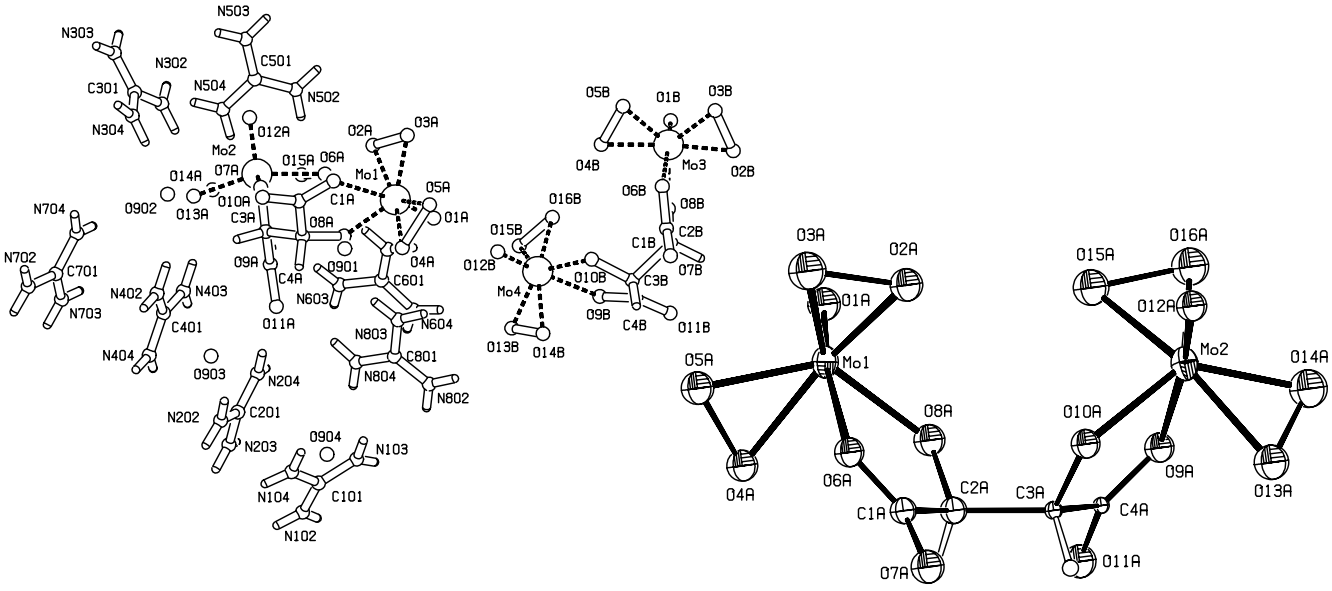

Abstract

$C_{16}H_{60}Mo_4N_{24}O_{36}$, orthorhombic, $Pna2_1$ (No. 33), $a = 29.387(9)$ Å, $b = 9.979(3)$ Å, $c = 19.062(5)$ Å, $V = 5590.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.094$, $wR_{ref}(F^2) = 0.264$, $T = 293$ K.

Source of material

Crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation at 278 K of an aqueous mixture of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, tartaric acid, $C_4H_4O_6$, guanidinium carbonate, $(CN_3H_6)_2CO_3$ and an excess of a 35 wt.% hydrogen peroxide solution.

Experimental details

To keep a reasonable data/parameters ratio, only the Mo atoms were refined with anisotropic temperature factors. The light atoms were refined isotropically. All the H atoms were calculated with AFIX and included in the refinement with a common isotropic temperature factor ($U_{iso} = 0.08$ Å^2). The H atoms of the four water molecules were not localized.

Discussion

In the frame of research aimed at developing new synthetic procedures of oxide materials, the so-called chelate method, which consists in the thermal decomposition of solid metal precursors obtained from a solution of the complexed metals, was shown to be an appropriate way to get multimetallic oxides [1,2]. The title compound was isolated during attempts to synthesize new alkali metal-free precursors for Mo-based oxides, in order to avoid any contamination of the final material after removal of the surrounding ligands during the calcination step leading to the oxide. Guanidinium derivatives are therefore particularly welcome.

The structure of the bridged dinuclear $[Mo_2O_2(O_2)_4(C_4H_2O_6)]^{4-}$ anion is illustrated in the figure (right). As first reported by Dengel et al. in the case of the analogous potassium derivative, $K_4[Mo_2O_2(O_2)_4(C_4H_2O_6)] \cdot 4H_2O$ [3], the tartrato ligand is tetradentate and forms a bridge between two monooxodiperoxo $[MoO(O_2)_2]$ entities. Both molybdenum atoms are sevenfold coordinated by oxygen atoms from the peroxo, oxo, carboxylato and hydroxo groups. The coordination polyhedra correspond to two edge-sharing pentagonal bipyramids. In each bipyramid, the axial positions are occupied by a terminal oxo ligand [$\bar{d}$(Mo—O) = 1.69(2) Å] and an oxygen atom from a deprotonated carboxylato group [$\bar{d}$(Mo—O) = 2.26(2) Å]. The equatorial positions are taken by two slightly asymetrically bound peroxo ligands [$\bar{d}$(Mo—O) = 1.94(3) Å and 1.96(3) Å, $\bar{d}$(O—O) = 1.47(4) Å] and the oxygen atom from the deprotonated hydroxo group of the tartrato ligand [$\bar{d}$(Mo—O) = 1.98(2) Å]. The axial oxygen atom O, *trans* to the double-bonded oxygen atom, lies at a significantly longer mean distance from the molybdenum atom (2.26(2) Å) and is thus less tightly bound than the other oxygen atoms in the anion. This phenomenon was also observed for other seven-coordinated molybdenum(VI) peroxo complexes of the type $[MoO(O_2)_2(L)]^{2-}$ (L = oxalate, glycolate, citrate) [4-6] and $[Mo_2O_2(O_2)_2(OH)_2(L)_2]^{2-}$ (L = oxalate)

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[7] and illustrates the important *trans* influence of the oxo ligand on the structural parameters. The bond distances obtained for the title compound are in good agreement with those observed in the potassium derivative, $K_4[Mo_2O_2(O_2)_4(C_4H_2O_6)] \cdot 4H_2O$ [3]. Moreover, the average $\overline{d}$(O—O) distance in the peroxo groups is 1.47(4) Å, which does not differ significantly from the values found in the peroxide ion (1.49 Å) and in other peroxo molybdate(VI) complexes [4-7]. The crystal structure is held together by ionic attractions between the guanidinium cations and the complexed anions (figure, left), and by hydrogen bonding involving the four water molecules and oxygen atoms from the complexes.

Table 1. Data collection and handling.

Crystal:	yellow, tabular, size 0.05 × 0.28 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	9.92 cm^{-1}
Diffractometer, scan mode:	MAR345, 120 images, $\Delta\phi = 3°$
$2\theta_{max}$:	43.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11153, 3355
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2975
$N(param)_{refined}$:	341
Programs:	SHELX-97 [8], PLATON [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
O(1A)	4*a*	0.3671(8)	0.080(3)	0.062(1)	0.041(7)
O(2A)	4*a*	0.2834(8)	0.211(3)	0.071(1)	0.041(6)
O(3A)	4*a*	0.318(1)	0.316(3)	0.093(2)	0.054(8)
O(4A)	4*a*	0.3901(8)	0.249(3)	–0.053(1)	0.037(6)
O(5A)	4*a*	0.3906(8)	0.334(3)	0.013(1)	0.041(6)
O(6A)	4*a*	0.2997(8)	0.347(3)	–0.051(1)	0.033(6)
C(1A)	4*a*	0.283(1)	0.301(4)	–0.102(2)	0.026(8)
O(7A)	4*a*	0.2590(8)	0.356(3)	–0.147(1)	0.042(7)
C(2A)	4*a*	0.289(1)	0.145(4)	–0.109(2)	0.027(8)
H(2A)	4*a*	0.3079	0.1294	–0.1504	0.080
O(8A)	4*a*	0.3121(8)	0.087(3)	–0.053(1)	0.037(6)
C(3A)	4*a*	0.2461(9)	0.069(3)	–0.119(2)	0.012(6)
H(3A)	4*a*	0.2342	0.0954	–0.1648	0.080
C(4A)	4*a*	0.2526(9)	–0.081(3)	–0.122(1)	0.010(6)
O(9A)	4*a*	0.2289(8)	–0.151(3)	–0.083(1)	0.033(6)
O(10A)	4*a*	0.2129(7)	0.102(2)	–0.070(1)	0.032(5)
O(11A)	4*a*	0.2824(8)	–0.130(3)	–0.164(1)	0.042(7)
O(12A)	4*a*	0.1450(7)	0.066(3)	0.027(1)	0.035(6)
O(13A)	4*a*	0.1423(9)	–0.072(3)	–0.104(1)	0.046(7)
O(14A)	4*a*	0.1373(9)	–0.171(3)	–0.052(2)	0.055(8)
O(15A)	4*a*	0.2312(9)	–0.042(3)	0.049(1)	0.049(7)
O(16A)	4*a*	0.197(1)	–0.158(3)	0.054(2)	0.053(8)
O(1B)	4*a*	0.4416(9)	0.845(3)	0.491(2)	0.051(7)
O(2B)	4*a*	0.5288(9)	0.956(3)	0.482(2)	0.053(7)
O(3B)	4*a*	0.5008(9)	1.071(3)	0.491(2)	0.049(7)
O(4B)	4*a*	0.4226(9)	0.961(3)	0.360(2)	0.053(8)
O(5B)	4*a*	0.4269(9)	1.075(3)	0.406(1)	0.047(7)
O(6B)	4*a*	0.5113(8)	1.026(3)	0.345(1)	0.036(6)
O(7B)	4*a*	0.5648(8)	0.983(3)	0.265(1)	0.040(7)
O(8B)	4*a*	0.4983(7)	0.783(3)	0.380(1)	0.031(6)
C(1B)	4*a*	0.536(1)	0.949(4)	0.309(2)	0.031(9)
C(2B)	4*a*	0.530(1)	0.800(3)	0.329(2)	0.018(7)
H(2B)	4*a*	0.5587	0.7652	0.3459	0.080
C(3B)	4*a*	0.516(1)	0.721(4)	0.259(2)	0.036(9)
H(3B)	4*a*	0.5402	0.7325	0.2247	0.080
C(4B)	4*a*	0.511(1)	0.575(4)	0.276(2)	0.038(9)
O(9B)	4*a*	0.4745(8)	0.524(3)	0.255(1)	0.038(6)
O(10B)	4*a*	0.4776(7)	0.782(3)	0.234(1)	0.029(6)
O(11B)	4*a*	0.5395(9)	0.507(3)	0.305(1)	0.046(7)
O(12B)	4*a*	0.401(1)	0.794(4)	0.149(2)	0.060(9)
O(13B)	4*a*	0.433(1)	0.540(4)	0.120(2)	0.08(1)
O(14B)	4*a*	0.474(1)	0.624(4)	0.121(2)	0.08(1)
O(15B)	4*a*	0.381(1)	0.573(4)	0.234(2)	0.08(1)
O(16B)	4*a*	0.399(1)	0.671(4)	0.283(2)	0.069(9)
C(301)	4*a*	–0.027(1)	1.005(3)	0.468(2)	0.04(1)
N(302)	4*a*	–0.041(1)	1.108(3)	0.503(2)	0.05(1)
H(30A)	4*a*	–0.0270	1.1343	0.5399	0.080
H(30B)	4*a*	–0.0657	1.1489	0.4901	0.080
N(303)	4*a*	0.0101(9)	0.941(3)	0.486(2)	0.039(8)
H(30C)	4*a*	0.0250	0.9659	0.5226	0.080
H(30D)	4*a*	0.0193	0.8736	0.4619	0.080
N(304)	4*a*	–0.051(1)	0.950(3)	0.418(2)	0.043(8)
H(30E)	4*a*	–0.0776	0.9815	0.4079	0.080
H(30F)	4*a*	–0.0407	0.8826	0.3947	0.080
C(401)	4*a*	0.327(1)	0.182(3)	0.264(2)	0.036(9)
N(402)	4*a*	0.328(1)	0.312(3)	0.253(2)	0.07(1)
H(40A)	4*a*	0.3342	0.3658	0.2865	0.080
H(40B)	4*a*	0.3228	0.3428	0.2113	0.080
N(403)	4*a*	0.336(1)	0.134(4)	0.326(2)	0.06(1)
H(40C)	4*a*	0.3416	0.1874	0.3605	0.080
H(40D)	4*a*	0.3351	0.0487	0.3335	0.080
N(404)	4*a*	0.318(1)	0.100(4)	0.211(2)	0.06(1)
H(40E)	4*a*	0.3168	0.015	0.2177	0.080
H(40F)	4*a*	0.3124	0.1325	0.1700	0.080
C(501)	4*a*	0.328(1)	0.929(3)	0.494(2)	0.038(9)
N(502)	4*a*	0.297(1)	0.871(5)	0.533(2)	0.07(1)
H(50A)	4*a*	0.2908	0.902	0.5744	0.080
H(50B)	4*a*	0.2819	0.8024	0.5178	0.080
N(503)	4*a*	0.350(1)	1.032(3)	0.516(2)	0.06(1)
H(50C)	4*a*	0.3448	1.064	0.5566	0.080
H(50D)	4*a*	0.3703	1.0678	0.4891	0.080
N(504)	4*a*	0.339(1)	0.855(4)	0.439(2)	0.06(1)
H(50E)	4*a*	0.3631	0.8742	0.4147	0.080
H(50F)	4*a*	0.3227	0.7869	0.4268	0.080
C(601)	4*a*	0.3156(9)	0.678(3)	0.025(2)	0.036(9)
N(602)	4*a*	0.316(1)	0.806(3)	0.042(2)	0.06(1)
H(60A)	4*a*	0.3398	0.8426	0.0589	0.080
H(60B)	4*a*	0.2917	0.8540	0.0352	0.080
N(603)	4*a*	0.280(1)	0.632(4)	–0.011(2)	0.049(9)
H(60C)	4*a*	0.2586	0.6862	–0.0232	0.080
H(60D)	4*a*	0.2788	0.5493	–0.0230	0.080
N(604)	4*a*	0.3514(9)	0.599(3)	0.034(2)	0.045(8)
H(60E)	4*a*	0.3763	0.6301	0.0509	0.080
H(60F)	4*a*	0.3497	0.5153	0.0224	0.080
C(701)	4*a*	0.439(1)	0.188(4)	0.212(2)	0.05(1)
N(702)	4*a*	0.442(1)	0.251(4)	0.152(2)	0.06(1)
H(70A)	4*a*	0.4407	0.2059	0.1133	0.080
H(70B)	4*a*	0.4457	0.3361	0.1507	0.080
N(703)	4*a*	0.434(2)	0.058(4)	0.214(3)	0.11(2)
H(70C)	4*a*	0.4326	0.0135	0.1757	0.080
H(70D)	4*a*	0.4323	0.0179	0.2538	0.080
N(704)	4*a*	0.446(1)	0.247(5)	0.274(2)	0.07(1)
H(70E)	4*a*	0.4461	0.1999	0.3121	0.080
H(70F)	4*a*	0.4493	0.3327	0.2768	0.080
C(801)	4*a*	0.100(1)	0.288(3)	0.403(2)	0.04(1)
N(802)	4*a*	0.0607(9)	0.227(4)	0.414(2)	0.048(9)
H(80A)	4*a*	0.0395	0.2666	0.4366	0.080
H(80B)	4*a*	0.0563	0.1473	0.3975	0.080
N(803)	4*a*	0.107(1)	0.410(3)	0.427(2)	0.047(8)
H(80C)	4*a*	0.0865	0.4506	0.4501	0.080
H(80D)	4*a*	0.1331	0.448	0.4194	0.080
N(804)	4*a*	0.134(1)	0.221(4)	0.374(2)	0.06(1)
H(80E)	4*a*	0.1607	0.2574	0.3715	0.080
H(80F)	4*a*	0.1299	0.1415	0.3580	0.080
C(201)	4*a*	0.210(2)	0.069(5)	0.225(2)	0.08(2)
N(202)	4*a*	0.203(1)	0.158(5)	0.175(2)	0.09(1)
H(20A)	4*a*	0.1987	0.1321	0.1325	0.080
H(20B)	4*a*	0.2029	0.2424	0.1848	0.080
N(203)	4*a*	0.209(2)	–0.052(5)	0.200(3)	0.12(2)
H(20C)	4*a*	0.2149	–0.1194	0.2269	0.080
H(20D)	4*a*	0.2030	–0.0648	0.1565	0.080
N(204)	4*a*	0.219(1)	0.106(4)	0.290(2)	0.050(9)
H(20E)	4*a*	0.2252	0.0466	0.3212	0.080
H(20F)	4*a*	0.2187	0.1895	0.3008	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
C(101)	4*a*	0.073(2)	0.205(5)	0.171(2)	0.06(1)
N(102)	4*a*	0.081(2)	0.089(5)	0.143(3)	0.13(2)
H(10A)	4*a*	0.0752	0.0170	0.1657	0.080
H(10B)	4*a*	0.0913	0.0844	0.1006	0.080
N(103)	4*a*	0.058(1)	0.239(4)	0.233(2)	0.05(1)
H(10C)	4*a*	0.0502	0.1777	0.2630	0.080
H(10D)	4*a*	0.0545	0.3220	0.2442	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
N(104)	4*a*	0.086(2)	0.312(6)	0.135(3)	0.13(2)
H(10E)	4*a*	0.0991	0.3019	0.0944	0.080
H(10F)	4*a*	0.0821	0.3909	0.1514	0.080
O(901)	4*a*	0.126(1)	0.937(4)	0.341(2)	0.08(1)
O(902)	4*a*	0.320(1)	0.830(5)	0.271(2)	0.11(1)
O(903)	4*a*	0.211(3)	0.50(1)	0.170(6)	0.31(5)
O(904)	4*a*	0.031(2)	0.595(9)	0.122(4)	0.19(3)

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)	4*a*	0.3414(1)	0.2038(3)	0.0191(2)	0.029(2)	0.024(2)	0.039(2)	–0.000(1)	–0.001(2)	–0.002(2)
Mo(2)	4*a*	0.1792(1)	–0.0380(3)	–0.0192(2)	0.029(2)	0.027(2)	0.044(2)	–0.000(1)	0.003(2)	–0.003(2)
Mo(3)	4*a*	0.4718(1)	0.9384(3)	0.4311(2)	0.035(2)	0.023(2)	0.050(2)	–0.001(1)	0.002(2)	–0.005(2)
Mo(4)	4*a*	0.4290(1)	0.6717(3)	0.1923(2)	0.055(2)	0.019(2)	0.057(2)	–0.001(2)	–0.023(2)	–0.003(2)

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