METAL-ORGANIC COMPOUNDS

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Bis(*tert*-butylammonium) Molybdate(VI)

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Abstract

During the course of our extensive studies on the molybdenum-*tert*-butylamine base system, we isolated the title compound, $[C_4H_{12}N]_2[MoO_4]$, by reaction of stoichiometric amounts of MoO_3 and *tert*-butylamine in aqueous media. The asymmetric unit of di-*tert*-butylammonium molybdate(VI) consists of two tetrahedral $[MoO_4]^{2-}$ anions and four *tert*-butylammonium cations. The crystal packing is stabilized by the electrostatic interactions and an extensive network of hydrogen contacts involving the O atoms from the anions, and the N atoms and some C atoms of the cations.

Comment

There are many examples of molybdate salts with inorganic cations which contain the tetrahedral $[MoO_4]^{2-}$ anion, such as α-$MnMoO_4$ (Abrahams & Reddy, 1965), α-$ZnMoO_4$ (Abrahams, 1967), $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968), K_2MoO_4 (Gatehouse & Leverett, 1969), $Gd_2(MoO_4)_3$ (Jeitschko, 1972), Cs_2MoO_4 (Gonschorek & Hahn, 1973), $La_2(MoO_4)_3$ (Jeitschko, 1973), $Na_2MoO_4.2H_2O$ (Matsumoto, Kobayashi & Sasaki, 1975), $Na_5Sc(MoO_4)_4$ (Klevtsova, Kozeeva & Klevtsov, 1976), $MgMoO_4$ (Barakin, Klevtsova & Gaponenko, 1982), $MnMoO_4.H_2O$ (Clearfield, Moini & Rudolf, 1985), $CaMoO_4$, $CdMoO_4$ and $PbMoO_4$ (Hazen, Finger & Mariathasan, 1985), $CsV(MoO_4)_2$ (Lii, Wang, Chiang & Wang, 1989), $K_2Th(MoO_4)_3$ and $K_4Th(MoO_4)_4$ (Huyghe, Lee, Quarton & Robert, 1991). However, only a few structures of molybdates with organic cations have been described in the literature, *e.g.* bis(dicyclohexylammonium) molybdate(VI)–water (1/2) and bis(cyclohexylammonium) molybdate(VI) (Thiele & Fuchs, 1979), bis(guanidinium) molybdate(VI) (Ozeki, Ichida & Sasaki, 1987) and ethylenediammonium molybdate(VI) (Bensch, Hug, Emmenegger, Reller & Oswald, 1987).

This work was undertaken as a part of our research on polyoxometallates of the *tert*-butylammonium cation (Román, San José, Luque & Gutiérrez-Zorrilla, 1993). We are interested in studying the anion influence on the crystal packing and properties. The asymmetric unit of the compound contains two isolated and discrete tetrahedral $[MoO_4]^{2-}$ anions and four *tert*-butylammonium cations (Fig. 1) linked together by electrostatic interactions and an extensive network of hydrogen bonds. The $[MoO_4]^{2-}$ anions consist of fairly regular O-atom tetrahedra, that of Mo(2) being slightly more regular than that of Mo(1). The Mo—O bond lengths are close to the Mo—O average bond length of 1.77 Å, except for the Mo(1)—O(14) distance of

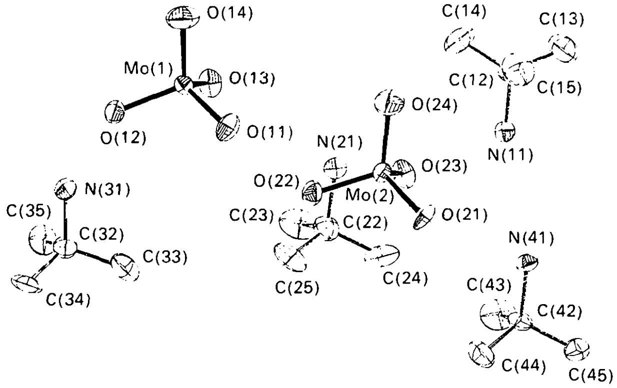

Fig. 1. Displacement ellipsoid plot (*PLATON*; Speck, 1990) of the asymmetric unit of bis(*tert*-butylammonium) molybdate(VI). Ellipsoids are plotted at the 50% probability level; H atoms are omitted.

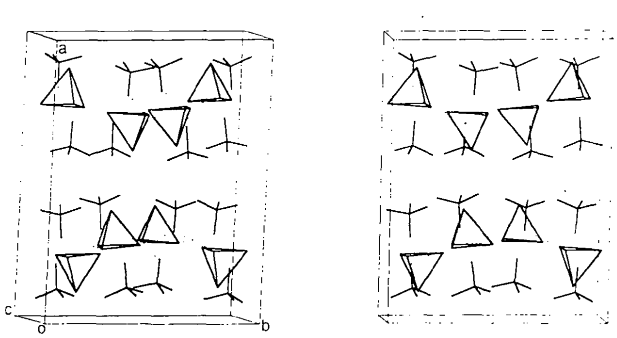

Fig. 2. Stereoview of the unit cell for $[C_4H_{12}N]_2[MoO_4]$ showing the hydrogen bonding.

1.739 (7) Å which is unusually short. The O—Mo—O angles are close to tetrahedral. A stereoview of the unit cell of the title compound is shown in Fig. 2.

The *tert*-butylammonium cations and molybdate anions follow the sequence *cac*, *cac* along the [100] direction, and are connected *via* an extensive network of hydrogen bonds of types N—H···O (N···O = 2.78–2.82 Å) and C—H···O (C···O = 3.41–3.45 Å) (Desiraju, 1991; Taylor & Kennard, 1982; Steiner & Saenger, 1993). The tetrahedral faces formed by atoms O(X1), O(X2) and O(X3) (X = 1, 2 or 3) of the molybdate anions, parallel to the plane *yz*, are located at two different *x* levels, $\frac{1}{4}$ and $\frac{3}{4}$. The C—N bonds are nearly parallel to the [100] direction. The H atoms linked to the N atom are directed towards the O atoms O(X1), O(X2) and O(X3) from different molybdate anions.

Experimental

The title compound was isolated in aqueous solution. Synthesis, chemical characterization and thermogravimetric studies have been reported recently (Román, San José, Aranzabe & Luque, 1992).

Crystal data

$[C_4H_{12}N]_2[MoO_4]$
$M_r = 308.23$
Monoclinic
$P2_1/a$
$a = 18.267$ (1) Å
$b = 13.738$ (1) Å
$c = 11.816$ (1) Å
$\beta = 102.139$ (5)°
$V = 2899.2$ (2) Å^3
$Z = 8$
$D_x = 1.412$ Mg m^{-3}
$D_m = 1.40$ (1) Mg m^{-3}
D_m measured by flotation in acetone/tetrachloromethane mixture

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12$–20°
$\mu = 0.88$ mm^{-1}
$T = 296$ (2) K
Prism
0.60 × 0.35 × 0.15 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.75$, $T_{\max} = 1.24$
8444 measured reflections
8444 independent reflections

4742 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 30°$
$h = -25 \rightarrow 25$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 16$
2 standard reflections monitored every 100 reflections intensity variation: none

Refinement

Refinement on F
$R = 0.070$
$wR = 0.084$

$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 1.10$ e Å^{-3}
$\Delta\rho_{\min} = -0.92$ e Å^{-3}

$S = 1.195$
4742 reflections
271 parameters
H-atom parameters not refined

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo(1)	0.20960 (4)	0.12642 (4)	−0.01196 (6)	0.0220 (2)
Mo(2)	0.28638 (4)	0.36931 (5)	0.51346 (6)	0.0234 (2)
O(11)	0.2390 (4)	0.0725 (5)	−0.1317 (5)	0.034 (2)
O(12)	0.2472 (4)	0.2455 (4)	0.0128 (6)	0.033 (2)
O(13)	0.2394 (4)	0.0543 (4)	0.1133 (5)	0.034 (2)
O(14)	0.1124 (4)	0.1340 (6)	−0.0427 (8)	0.054 (3)
O(21)	0.2536 (4)	0.3174 (5)	0.6309 (5)	0.033 (2)
O(22)	0.2583 (4)	0.4930 (4)	0.4961 (5)	0.034 (2)
O(23)	0.2510 (4)	0.3039 (4)	0.3835 (5)	0.034 (2)
O(24)	0.3857 (4)	0.3615 (6)	0.5428 (8)	0.055 (3)
N(11)	0.2915 (4)	0.1129 (5)	0.3435 (6)	0.024 (2)
C(12)	0.3756 (5)	0.1045 (8)	0.3626 (9)	0.035 (3)
C(13)	0.3932 (7)	0.0022 (9)	0.3233 (9)	0.055 (4)
C(14)	0.4023 (7)	0.1834 (9)	0.2911 (9)	0.057 (4)
C(15)	0.4090 (7)	0.1174 (9)	0.4904 (9)	0.059 (4)
N(21)	0.7084 (4)	0.1153 (6)	0.1637 (7)	0.030 (2)
C(22)	0.6233 (6)	0.1034 (8)	0.1381 (9)	0.039 (3)
C(23)	0.5990 (7)	0.0799 (9)	0.0109 (9)	0.063 (5)
C(24)	0.5893 (6)	0.1997 (9)	0.1638 (9)	0.051 (4)
C(25)	0.6047 (7)	0.0231 (9)	0.2139 (9)	0.058 (4)
N(31)	0.8100 (4)	0.1369 (5)	0.8654 (6)	0.025 (2)
C(32)	0.8959 (5)	0.1425 (7)	0.8993 (9)	0.034 (3)
C(33)	0.9174 (7)	0.2414 (9)	0.8621 (9)	0.058 (4)
C(34)	0.9275 (6)	0.0607 (9)	0.8364 (9)	0.049 (4)
C(35)	0.9171 (6)	0.1285 (8)	1.0294 (9)	0.047 (3)
N(41)	0.1885 (4)	0.1333 (5)	0.6407 (7)	0.026 (2)
C(42)	0.1029 (4)	0.1389 (7)	0.6063 (8)	0.029 (3)
C(43)	0.0809 (7)	0.1531 (9)	0.4759 (9)	0.058 (4)
C(44)	0.0777 (6)	0.2232 (8)	0.6717 (9)	0.048 (4)
C(45)	0.0710 (5)	0.0442 (8)	0.6415 (9)	0.039 (3)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for the* MoO_4^{2-} *anions and hydrogen bonds* (Å)

Mo(1)—O(11)	1.777 (7)	Mo(2)—O(21)	1.773 (7)
Mo(1)—O(12)	1.774 (6)	Mo(2)—O(22)	1.775 (9)
Mo(1)—O(13)	1.769 (6)	Mo(2)—O(23)	1.779 (6)
Mo(1)—O(14)	1.739 (7)	Mo(2)—O(24)	1.777 (7)
O(13)—Mo(1)—O(14)	109.2 (4)	O(23)—Mo(2)—O(24)	108.0 (4)
O(12)—Mo(1)—O(14)	108.8 (4)	O(22)—Mo(2)—O(24)	109.8 (4)
O(12)—Mo(1)—O(13)	109.8 (3)	O(22)—Mo(2)—O(23)	109.9 (3)
O(11)—Mo(1)—O(14)	109.0 (4)	O(21)—Mo(2)—O(24)	108.8 (4)
O(11)—Mo(1)—O(13)	110.0 (3)	O(21)—Mo(2)—O(23)	110.6 (3)
O(11)—Mo(1)—O(12)	110.2 (3)	O(21)—Mo(2)—O(22)	109.8 (3)
N(11)···O(22$^{\rm i}$)	2.80 (1)	N(31)···O(13$^{\rm v}$)	2.81 (1)
N(11)···O(13)	2.81 (1)	N(41)···O(21)	2.81 (1)
N(11)···O(23)	2.79 (1)	N(41)···O(22$^{\rm i}$)	2.82 (1)
N(21)···O(12$^{\rm ii}$)	2.81 (1)	N(41)···O(11$^{\rm vi}$)	2.78 (1)
N(21)···O(11$^{\rm iii}$)	2.81 (1)	C(13)···O(13)	3.41 (1)
N(21)···O(23$^{\rm ii}$)	2.78 (1)	C(15)···O(24)	3.45 (2)
N(31)···O(21$^{\rm ii}$)	2.82 (1)	C(24)···O(14$^{\rm ii}$)	3.43 (2)
N(31)···O(12$^{\rm iv}$)	2.79 (1)		

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

Intensity data were corrected for Lorentz and polarization effects. Only a unique data set was collected. The structure was solved using direct methods (*DIRDIF*; Beurskens *et al.*, 1992). An absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to data refined with isotropic displacement parameters. A weighting scheme of type $w = w_1.w_2$ with $w_1 = k_1/(a + b|F_o|)^2$ and $w_2 = k_2/(c + d\sin\theta/\lambda)$ was used to obtain flat dependence in $\langle w\Delta^2F\rangle$ *versus* $\langle F_o\rangle$ and *versus* $\langle\sin\theta/\lambda\rangle$ (*PESOS*; Martínez-Ripoll & Cano, 1975); the coefficients used are $k_1 = 0.582$; $k_2 = 1.036$; $a = 3.468$, $b = 0.449$ for $|F_o| \le 1.28$; $a = 4.098$, $b = -0.177$ for $1.28 < |F_o| \le 5.47$; $a = 2.551$, $b = 0.092$ for $5.47 < |F_o| \le 10.92$; $a = 5.082$, $b = -0.1374$ for $10.92 < |F_o| \le 21.28$; $a = 2.048$, $b = 0.0094$ for $21.28 < |F_o| \le 66.45$; $a = 1.049$, $b = 0.028$ for $|F_o| > 66.45$; $c = 4.446$, $d = -11.415$ for $\sin\theta/\lambda \le 0.33$; $c = 0.216$, $d = 1.792$ for $0.33 < \sin\theta/\lambda \le 0.44$; $c = 2.253$, $d = -2.904$ for $0.44 < \sin\theta/\lambda \le 0.51$; $c = 0.071$, $d = 1.556$ for $\sin\theta/\lambda > 0.51$. Non-H atoms were refined anisotropically. H atoms were calculated geometrically at their expected positions and included as fixed contributors. Most calculations were carried out using the *XRAY*76 system (Stewart *et al.*, 1976) running on a MicroVAX 3800 computer. Geometric calculations were performed using *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Pyridine-2-thiolato Molybdenum Complex

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Abstract

The coordination polyhedra of the two molybdenum(0) atoms in tetraethylammonium nonacarbonyl-1κ^5C,2κ^4C-μ-(pyridine-2-thiolato-1:2κ^2S,-2κN)-dimolybdate, $(C_8H_{20}N)[Mo_2(\mu\text{-}C_5H_4NS)(CO)_9]$ are distorted octahedra which share an S atom from a pyridine-2-thiolato ligand. The Mo···Mo distance is 4.5609 (7) Å.

Comment

Molybdenum complexes containing Mo—S and Mo—N bonds are of special interest because of their relevance to a variety of molybdenum-containing enzymes (Cramer, Hodgson, Gillum & Mortenson, 1978) and hydrodesulfurization catalysts (Anzenhofer & de Boer, 1969). To our knowledge,