ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2008. Том 49, № 6 *Ноябрь – декабрь* *С. 1187 – 1190*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73

ELECTROSTATIC Mo—O (METHANOL) BOND IN BENZYLTRIPHENYLPHOSPHONIUM *trans*-TETRACHLORO(METHANOL)OXOMOLYBDATE(V)

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Received June, 28, 2008

Benzyltriphenylphosphonium *trans*-tetrachloro(methanol)oxomolybdate(V) has been obtained from methanol suspension of benzyltriphenylphosphonium molybdate(VI) saturated with hydrogen chloride. The crystal structure comprises discrete *trans*-tetrachloro(methanol)oxomolybdate(V) anions and benzyltriphenylphosphonium cations. The anion has distorted octahedral geometry of central atom with visible *trans* influence imposed by short Mo—O bond (1.659(2) Å). The methanol O atom is bonded to the Mo atom, the bond being mostly electrostatic in character. A comparison with previously reported structures indicates that the methanol methyl moiety can switch between different positions with respect to the chloride ligands.

Keywords: Crystal structure; electrostatic bond; Mo(V) complex; oxomolybdates.

Salts with $[MoOCl_4L]^-$ complex anions have been obtained for L = water [1], tetrahydrofuran [2], N,N-dimethylformamide [3] and methanol [4]. The $[MoOCl_4(CH_3OH)]^-$ anion has been reported as a pyridinium salt [4]. The salts with $[MoOCl_4L]^-$ anion are usually isolated as by-products in synthetic routes [5] or as products of reduction of molybdates(VI) in acidic media with the aid of such reducing agents as hydrazinium chloride [6]. In this study molybdates(VI) with organic cations have been used as starting compounds; they were suspended in various solvents and their reaction with gaseous hydrogen chloride has been investigated. When methanol was used as the reaction medium, the title salt was obtained in a crystalline form.

Experimental $[PPh_3CH_2Ph][MoOCl_4(CH_3OH)]$. All chemicals were purchased from Aldrich and used as such. Benzyltriphenylphosphonium molybdate(VI) was obtained in a reaction of benzyltriphenylphosphonium chloride with ammonium molybdate(VI) in aqueous solution. Benzyltriphenylphosphonium molybdate(VI) (0.1 g) was suspended in methanol (2.5 ml). A stream of gaseous hydrogen chloride was bubbled through the suspension. The solid phase dissolved entirely with release of much heat. The mixture turned yellow and subsequently green. The green solution was moved to a separate open vessel and left for crystallization. After a few days crystals in form of green blocks appeared in the vessel.

X-Ray Diffraction Study. The X-ray diffraction data were collected at 100(2) K using a Kuma KM-4 diffractometer equipped with MoK_α radiation source and a CCD detector. For crystal structure solution and refinement, SHELXS-97 (direct methods) and SHELXL-97 (full-matrix least-squares refinement) were used [7]. Crystal data for $C_{26}H_{26}Cl_4MoO_2P$: triclinic, space group *P*-1, $a = 11.760(3)$ Å, $b = 11.938(3)$ Å, $c = 12.106(3)$ Å, $\alpha = 119.53(3)°$, $\beta = 102.97(3)°$, $\gamma = 101.86(3)°$, $Z = 2$, $V = 1337.1(6)$ Å^3, μ(MoK$_\alpha$ = 0.97 mm^{-1}, 23381 reflections measured, 10115 independent reflections ($R_{int} = 0.028$). Absorption correction: analytical [8], transmission factors: $T_{min} = 0.542$, $T_{max} = 0.742$. The H2 atom from the hydroxyl group in the methanol molecule was found on difference Fourier map. A distance restraint of 0.82 Å was imposed on the O—H bond length. All remaining H

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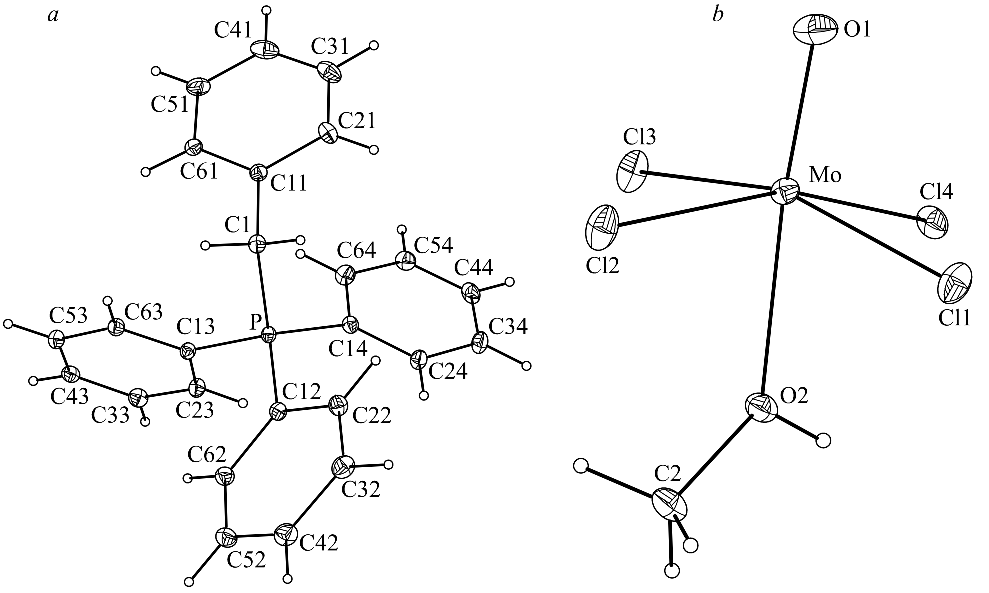

Fig. 1. Molecular structures of the cation (*a*) and anion (*b*) with atom labeling scheme

atoms were generated geometrically and during refinement the riding model with C—H bond length of 0.95 Å for H atoms from the methyl group, 0.99 Å for H atoms from the methylene group and 0.98 Å for H atoms from the phenyl groups was used. The final R1 and wR2 values: 0.027 and 0.071. CCDC No. 656263.

Results and discussion. The title crystal comprises *trans*-tetrachloro(methanol)oxomolybdate(V) anions (charge –1) and benzyltriphenylphosphonium cations (charge +1) (Fig. 1). In each anion the Mo atom is bonded to the *oxo* ligand, with the Mo—O distance of 1.659(2) Å indicative of a multiple bond [4] (Table 1). In *trans* position to the *oxo* ligand the molecule of methanol is coordinated through the O2 atom; the corresponding Mo—O distance is 2.317(2) Å. The anion geometry seems to be affected by the *trans* influence of the short Mo—O bond (compare with [9] and references therein). The coordination sphere of the Mo atom is completed with four chloride ligands forming equatorial plane of a distorted octahedron (the Mo atom deviates from thus defined plane by approximately 0.34 Å towards the *oxo* ligand).

Assuming that the methanol ligand could be bonded to the central metal ion *via* the bisector of the O2 atom electron lone pairs or *via* the O2 atom electron lone pair (see [10] for similar considerations

Table 1

Selected bond lengths (Å) *and angles* (deg.) *in the structure studied*

Bond / Angle	Bond length / angle	Bond / Angle	Bond length / Angle	Bond / Angle	Bond length / Angle
Mo—O1	1.659 (2)	O1—Mo—O2	175.5 (1)	O2—Mo—Cl1	81.4 (1)
Mo—Cl1	2.411 (2)	O1—Mo—Cl1	96.2 (1)	O2—Mo—Cl2	84.8 (1)
Mo—Cl2	2.351 (1)	O1—Mo—Cl2	99.0 (1)	O2—Mo—Cl3	82.8 (1)
Mo—O2	2.317 (2)	O1—Mo—Cl3	99.7 (1)	O2—Mo—Cl4	78.0 (1)
Mo—Cl3	2.370 (2)	O1—Mo—Cl4	98.2 (1)	Cl3—Mo—Cl1	164.1 (1)
Mo—Cl4	2.398 (1)	Cl2—Mo—Cl1	89.1 (1)	Cl3—Mo—Cl4	89.7 (1)
		Cl2—Mo—Cl3	87.7 (1)	Cl4—Mo—Cl1	88.7 (1)
		Cl2—Mo—Cl4	162.8 (1)	Cl3—Mo—O2—C2	–84.4 (2)
		Cl1—Mo—O2—C2	93.8 (2)	Cl4—Mo—O2—C2	–175.6 (2)
		Cl2—Mo—O2—C2	3.9 (2)		

Table 2

Hydrogen bonding geometry (Å, deg.)

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2...Cl1^{i}	0.82	2.42	3.211(2)	164
C21—H21...Cl4	0.95	2.83	3.728(2)	158
C31—H31...Cl2^{i}	0.95	2.72	3.647(2)	165
C1—H1B...Cl4^{ii}	0.99	2.64	3.591(2)	162

Symmetry codes: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $-x+2, -y+1, -z+1$.

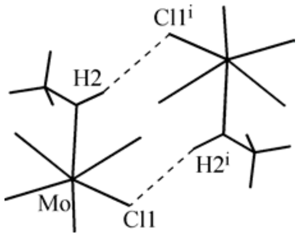

Fig. 2. View of the anion hydrogen-bonded dimeric motif formed in the crystal structure. Hydrogen bonds are depicted with dashed lines. Symmetry code: [i] $-x+1, -y+1, -z+1$

regarding the M—O (water) bond), the Mo—O2 bond could be mostly of ion-dipole character (sum of the bond angles around the O2 atom close to 360°) or mostly of covalent character (sum of the bond angles around the O2 atom close to 327°), respectively. Among the crystal structures of *trans*-aquatetrachlorooxomolybdates(V) deposited in the CSD database [11] for which the Mo atom is bonded to a water molecule instead of the methanol ligand, examples of both posibilities could be observed (see e.g. [4], [12] for the ion-dipole interaction case, or [13] for the covalent case). The sum of the bond angles around the methanol O atom for the title compound (approximately 357°, see Table 2) leads to the conclusion that the Mo—O2 coordination bond is mostly electrostatic [10]. Similar electrostatic bond could be observed for the analogous anion reported by Modec & Brenčič [4]. However, the orientation of the methanol methyl moiety with respect to the chloride ligands differs in the two cases. The methyl moiety orientation in the compound of the present study may be shown by the Cl—Mo—O2—C2 torsion angles listed in Table 2. Thus defined orientation implies repulsive steric interaction between the methyl moiety and the Cl2 ligand. As a result, among the O2—Mo—Cl bond angles the O2—Mo—Cl2 bond angle has the largest value (Table 2). Another consequence is the formation of a C2—H2B...Cl intramolecular contact which does not seem to be a stabilizing interaction. On the other hand, the methanol moiety orientation in the analogous anion reported by Modec & Brenčič [4] is different (the Cl—Mo—O—C torsion angles are –50, –140, 129 and 38°). This arrangement does not create any significant steric interaction between the methyl moiety and the chloride ligands. As a result, no such anionic angular distortion as in the case of our study could be observed. However, a similar intramolecular C—H...Cl contact is present (C...Cl distance of 3.43 Å, C—H...Cl bond angle of 118°).

The geometrical parameters of the cation are typical [14]. The crystal structure is stabilized by O—H(methanol)...Cl and weak C—H...Cl hydrogen bonds (Table 2). The O—H(methanol)...Cl hydrogen bonds allow to distinguish dimeric motifs consisting of two symmetry-related anions (Fig. 2). The hydrogen bonding seems to be a cause of each anion deformation in this particular case. The strongest hydrogen bond, O2—H2...Cl1* ([*] $-x+1, -y+1, -z+1$; Table 2), apparently affects the Mo—Cl1 bond length (Table 1). The methyltriphenylphosphonium cations are arranged in layers which are parallel to the *ac* plane and not stabilized by any phenyl ring stacking interactions (Fig. 3). The anions

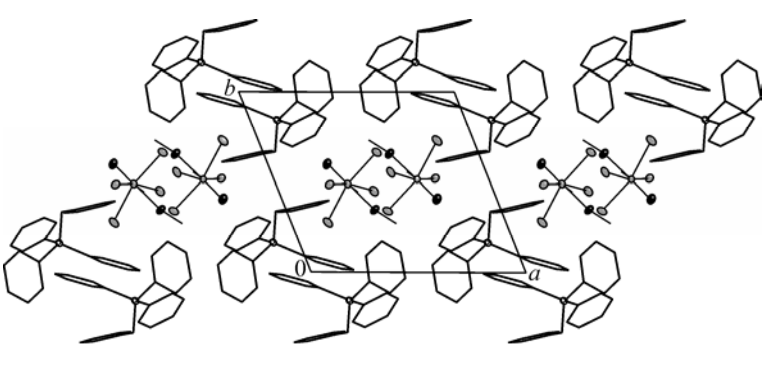

Fig. 3. Cation layers parallel to the *ac* plane. Hydrogen atoms are omitted for clarity

are situated in canals formed between the cation layers and are stabilized by weak C—H…Cl hydrogen bonds, the strongest of which involves the methylene moiety from the symmetry-related cation benzyl group (Table 2).

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