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Two Tetrahalooxomolybdate(V) Structures, [Ph₃PNPPH₃][MoOBr₄] and [PPh₄][MoOL₄(H₂O)]

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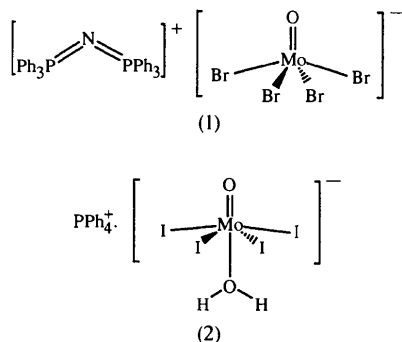
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Abstract

Both title compounds, bis(triphenylphosphine)iminium tetrabromooxomolybdate(V), (C₃₆H₃₀NP₂)[MoOBr₄], and tetraphenylphosphonium aquatetraiodooxomolybdate(V), (C₂₄H₂₀P)[MoOL₄(H₂O)], form by air oxidation of solutions containing the [Mo₃X₁₂]³⁻ anion, *i.e.* the bis(triphenylphosphine)iminium salt for X = Br and the tetraphenylphosphonium salt for X = I. Both anions have been reported previously in different salts. The geometry of the tetrabromooxomolybdate(V) anion is square pyramidal with the oxo ligand occupying the apical position, whereas the aquatetraiodooxomolybdate(V) anion can be described as a pseudo-octahedron with the aqua and oxo ligands occupying *trans* positions.

Comment

The bis(triphenylphosphine)iminium tetrabromooxomolybdate(V) salt, (1), crystallizes in the monoclinic space group *C2/c* with the central N atom of the [Ph₃PNPPH₃]⁺ cation located on a twofold axis. The



[MoOBr₄]⁻ anion is composed of a half-occupancy central Mo atom, two Br atoms and a single half-occupancy O atom located in close proximity to an inversion center. The inversion center generates two half-occupancy [MoOBr₄] molecules. This molecule may be described as a central Mo atom with five terminal lig-

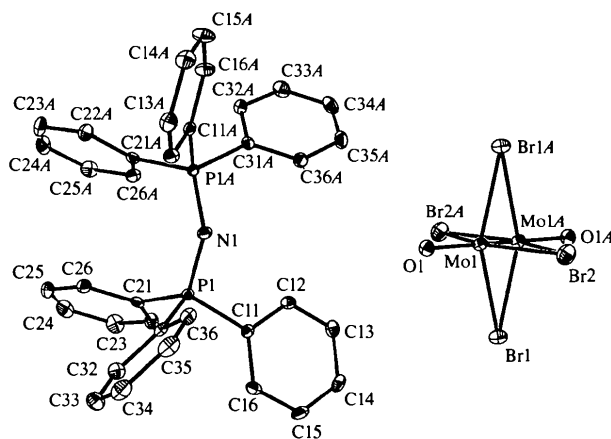


Fig. 1. The molecular configuration and labeling scheme for [Ph₃PNPPH₃][MoOBr₄], indicating the ordered cation and the 50:50 disorder of the anion around the inversion center. Ellipsoids are drawn at the 30% probability level.

ands, namely an oxo and four Br atoms, as shown in Fig. 1.

The tetraphenylphosphonium aquatetraiodooxomolybdate(V) salt, (2), crystallizes in the tetragonal space group *P4/n* with the cation occupying a 4 position. The anion is located on a fourfold axis with a major and a minor orientation in such a way that, as for the [MoOBr₄]⁻ anion, full-occupancy halogen atoms result from the overlapping of the two moieties. Two sets of Mo, O(oxo) and O(aqua) atoms are axially located on either side of the plane described by the four I atoms in a refined ratio of 0.71:0.29 (Fig. 2).

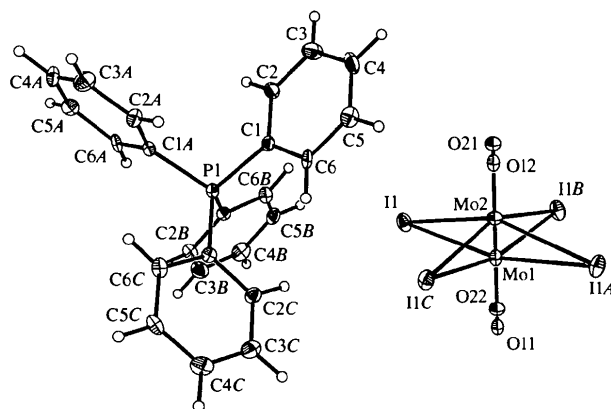


Fig. 2. The molecular configuration and labeling scheme for the disordered [PPh₄][MoOL₄(H₂O)] complex, showing the ordered cation and emphasizing the relative placement of the two orientations of the anion (major:minor = 0.71:0.29). Ellipsoids are drawn at the 30% probability level.

The most interesting feature of each of these structures is the Mo—O(oxo) distance. In a recent contribution, where we reported the structure of base-free tetra-

iodomolybdate(V) (Gordon *et al.*, 1995) with an Mo—O distance of 1.61 (2) Å, we pointed out that the corresponding distance in a previously reported [MoOBr₄][−] salt, *i.e.* with the [PPh₄]⁺ counterion (Schumaker *et al.*, 1982), was too long [1.73 (1) Å], a possible reason being compositional disorder with other unknown species. For compound (1), this distance is 1.636 (4) Å, in agreement with previous results. The corresponding tetrachlorooxomolybdate(V) also shows a shorter Mo—O(oxo) distance, *e.g.* 1.61 (1) Å in the tetraphenylarsonium salt (Garner *et al.*, 1977) and 1.646 (6) Å in the bis(triphenylphosphine)iminium salt (Blake *et al.*, 1995); this latter compound and the tetrabromooxomolybdate(V) salt reported here are not isomorphous.

The Mo—O(oxo) distance in compound (2) is less reliable, given the partial overlap of electron densities between the oxo and aqua O atoms from the two disordered fragments (Fig. 2). In a previously reported structure containing the same anion, [(C₂H₅)₄N]⁺[MoOL₄(H₂O)], such a distance was found to be 1.65 (1) Å (Bino & Cotton, 1979).

The average Mo—Br distance of 2.4802 (6) Å in compound (1) compares well with the distance of 2.469 (1) Å found for the same bond in the corresponding tetraphenylphosphonium salt (Schumaker *et al.*, 1982). The average Mo—I distance of 2.735 (3) Å in compound (2) compares well with the distance of 2.76 (1) Å found for the same bond in the corresponding tetraethylammonium salt (Bino & Cotton, 1979).

As has been discussed previously (Gordon *et al.*, 1995), coordination of an axial ligand to the tetrahalooxomolybdate(V) moiety reduces the O(oxo)—Mo—X angle. Accordingly, the O(oxo)—Mo—I angle in compound (2) [97.75 (6)° for the major orientation] is significantly less than the average O—Mo—Br angle in compound (1) [102.9 (6)°], and the *trans*-X—Mo—X bond angle is greater in compound (2) [164.49 (12)°] than in compound (1) [average 154.17 (5)°]. Similar values are found for the other base-free and base adducts of the same class (Gordon *et al.*, 1995).

Experimental

[Ph₃PNPPPh₃]₃[Mo₃Br₁₂] was prepared by dissolution of [Ph₃PNPPPh₃]₃[MoBr₄(thf)₂] (thf is tetrahydrofuran) in dichloromethane. Crystallization of this solution by cooling to 253 K afforded crystals of [Ph₃PNPPPh₃]₃[MoOBr₄]. [PPh₄]₃[Mo₃I₁₂] was prepared as described previously (Gordon *et al.*, 1995). Crystallization of a dilute dichloromethane solution by diffusion of a heptane layer afforded crystals of [PPh₄]₃[MoOL₄(H₂O)].

Compound (1)

Crystal data

(C₃₆H₃₀NP₂)₃[MoOBr₄]
M_r = 970.13

Mo Kα radiation
λ = 0.71073 Å

Monoclinic
C2/c
a = 27.960 (3) Å
b = 9.1643 (8) Å
c = 18.488 (2) Å
β = 131.137 (8)°
V = 3567.8 (6) Å³
Z = 4
D_x = 1.806 Mg m^{−3}

Cell parameters from 25 reflections
θ = 10.7–18.1°
μ = 4.967 mm^{−1}
T = 153 (2) K
Block
0.55 × 0.45 × 0.45 mm
Brown–yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.085, T_{max} = 0.107
3211 measured reflections
3142 independent reflections

2624 reflections with I > 2σ(I)
R_{int} = 0.020
θ_{max} = 24.98°
h = 0 → 33
k = 0 → 10
l = −21 → 16
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.029
wR(F²) = 0.070
S = 1.115
3142 reflections
274 parameters
All H atoms refined
w = 1/[σ²(F_o²) + (0.0316P)² + 8.5059P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.563 e Å^{−3}
Δρ_{min} = −0.523 e Å^{−3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.00013 (6)
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Mol†	0.27240 (3)	0.28171 (6)	0.02523 (4)	0.01996 (15)
Br1	0.23420 (2)	0.26375 (5)	0.11388 (3)	0.03889 (14)
Br2	0.29523 (2)	0.00942 (4)	0.05741 (3)	0.03816 (14)
O1†	0.3426 (2)	0.3561 (5)	0.1034 (3)	0.0252 (10)
P1	0.50172 (4)	0.87067 (8)	0.33347 (6)	0.0146 (2)
N1	1/2	0.8224 (4)	1/4	0.0202 (8)
C11	0.44031 (14)	0.7738 (3)	0.3196 (2)	0.0163 (6)
C12	0.38655 (15)	0.7294 (4)	0.2286 (2)	0.0214 (7)
C13	0.3394 (2)	0.6520 (4)	0.2163 (3)	0.0248 (8)
C14	0.3457 (2)	0.6181 (4)	0.2948 (3)	0.0284 (8)
C15	0.3982 (2)	0.6620 (4)	0.3847 (3)	0.0304 (8)
C16	0.4457 (2)	0.7401 (4)	0.3983 (2)	0.0250 (8)
C21	0.49200 (14)	1.0628 (3)	0.3395 (2)	0.0169 (6)
C22	0.4365 (2)	1.1180 (4)	0.3133 (2)	0.0232 (7)
C23	0.4295 (2)	1.2676 (4)	0.3148 (3)	0.0309 (8)
C24	0.4770 (2)	1.3601 (4)	0.3420 (3)	0.0313 (9)
C25	0.5328 (2)	1.3054 (4)	0.3682 (3)	0.0281 (8)
C26	0.5407 (2)	1.1567 (4)	0.3675 (2)	0.0217 (7)
C31	0.57546 (14)	0.8177 (3)	0.4480 (2)	0.0166 (6)
C32	0.6061 (2)	0.9001 (4)	0.5312 (2)	0.0237 (7)
C33	0.6617 (2)	0.8513 (4)	0.6167 (3)	0.0306 (8)
C34	0.6869 (2)	0.7202 (4)	0.6207 (3)	0.0313 (9)
C35	0.6576 (2)	0.6368 (4)	0.5405 (3)	0.0292 (8)
C36	0.6017 (2)	0.6839 (4)	0.4535 (3)	0.0230 (7)

† Site occupancy = 0.5.

Table 2. Selected geometric parameters (Å, °) for (2)

Mo1—O1	1.636 (4)	Mo1—Br1'	2.4896 (7)
Mo1—Br2'	2.4026 (7)	Mo1—Br2	2.5473 (7)
Mo1—Br1	2.4814 (7)		
O1—Mo1—Br2'	102.4 (2)	Br1—Mo1—Br1'	154.12 (3)
O1—Mo1—Br1	103.4 (2)	O1—Mo1—Br2	103.4 (2)
Br2'—Mo1—Br1	88.41 (2)	Br2'—Mo1—Br2	154.22 (3)
O1—Mo1—Br1'	102.2 (2)	Br1—Mo1—Br2	86.06 (2)
Br2'—Mo1—Br1'	89.08 (2)	Br1'—Mo1—Br2	85.08 (2)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Compound (2)

Crystal data

(C₂₄H₂₀P)[MoOL₄(H₂O)]M_r = 976.93

Tetragonal

P4/n

a = 13.258 (2) Å

c = 7.8926 (15) Å

V = 1387.3 (4) Å³

Z = 2

D_x = 2.339 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 9.3–18.4°

μ = 5.000 mm⁻¹

T = 153 (2) K

Block

0.325 × 0.150 × 0.125 mm

Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

by integration

T_{min} = 0.477, T_{max} = 0.562

1335 measured reflections

1225 independent reflections

1031 reflections with

I > 2σ(I)

R_{int} = 0.040θ_{max} = 24.96°

h = -15 → 0

k = 0 → 15

l = -9 → 0

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.055wR(F²) = 0.127

S = 1.195

1225 reflections

77 parameters

H atoms not refined

w = 1/[σ²(F_o²) + (0.0482P)² + 17.3173P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 1.548 e Å⁻³Δρ_{min} = -1.458 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0002 (3)

Scattering factors from

International Tables for Crystallography (Vol. C)

C4	0.0128 (8)	0.2418 (8)	0.1305 (15)	0.034 (3)
C5	0.0109 (8)	0.3135 (7)	0.2570 (14)	0.028 (2)
C6	-0.0668 (6)	0.3150 (7)	0.3766 (13)	0.022 (2)

† Site occupancy = 0.71. § Site occupancy = 0.29.

Table 4. Selected geometric parameters (Å, °) for (2)

I1—Mo1	2.7107 (8)	Mo1—O12	2.33 (2)
I1—Mo2	2.758 (2)	Mo2—O21	1.80 (3)
Mo1—O11	1.80 (2)	Mo2—O22	2.32 (3)
O11—Mo1—I1	97.75 (6)	O22—Mo2—I1	76.88 (13)
O12—Mo1—I1	82.25 (6)	I1'—Mo2—I1	153.8 (3)
I1—Mo1—I1'	164.49 (12)	I1—Mo2—I1'''	87.04 (6)
I1—Mo1—I1''	88.96 (2)	I1''—Mo2—I1'''	153.8 (3)
O21—Mo2—I1	103.12 (13)		

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

Normal data collection procedures were used for both compounds. For compound (1), refinement of the heavy-atom model with SHELXL93 (Sheldrick, 1993) converged well and all H atoms were located directly from two subsequent difference Fourier maps and allowed to refine freely. The C—H distances were found to range from 0.78 (4) to 0.95 (4) Å (average 0.890 Å), while the U_{eq} values ranged from 0.012 (8) to 0.041 (11) Å² (average 0.028 Å²), clearly supporting refinement of these atoms. For compound (2), after the initial location of the Mo and I atoms, it soon became apparent that disorder was present because of the appearance of a relatively large peak, 15 e Å⁻³, approximately 1 Å from the initially found Mo atom on the opposite side of the I₄ plane. The occupancies of these two atoms were initially refined resulting in an Mo1:Mo2 ratio of 0.71:0.29. Additional difference Fourier maps also revealed the presence of two large peaks, 9.2 and 7.9 e Å⁻³, which were input as O atoms for an oxo and an aqua species. Other peaks also appeared along the Mo1—Mo2 vector and eventually two sets of atoms were chosen such that the ensemble was fully occupied by both an oxo and an aqua species. The atoms of the (Mo1, O11, O12):(Mo2, O21, O22) ensemble had their overall occupancies optimized, resulting in a ratio of 0.709 (3):0.291 (3), nearly identical to the initial ratio. The occupancies were fixed at 0.71:0.29. Attempts were made to refine all of the anisotropic displacement parameters independently but the O atoms were uncooperative. Therefore, the final refinement included two EADP (Sheldrick, 1993) constraints, with all displacement parameters set identical, for the two sets of atoms, Mo1 = O11 = O12 and Mo2 = O21 = O22. A SAME (Sheldrick, 1993) restraint was also added to force the major and minor contributors to be nearly identical. Refinement of the structure converged smoothly. H atoms bonded to C atoms were placed in calculated positions; these were dependent on both the type of bonding at the C atom and the temperature (153 K in this case), with the aromatic H atoms calculated with C—H = 0.93 Å and U(H) set equal to 1.2U(parent). The two aqua H atoms were not calculated. A final difference Fourier map possessed three large peaks, 1.55, 1.05 and 1.03 e Å⁻³, within 1.2 Å of the I atom; the next two highest peaks, 0.95 and 0.86 e Å⁻³, were within 0.5 Å of Mo1, while the remainder of the map was featureless with |Δρ| < 0.62 e Å⁻³.

For both compounds, data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD-4 (Harms, 1997) and SHELXTL (Siemens, 1994); program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
I1	0.08406 (5)	0.13377 (5)	0.68544 (9)	0.0290 (3)
Mo1†	1/4	1/4	0.7318 (3)	0.0180 (5)
O11†	1/4	1/4	0.960 (2)	0.0180 (5)
O12†	1/4	1/4	0.436 (2)	0.0180 (5)
Mo2§	1/4	1/4	0.6061 (8)	0.0208 (12)
O21§	1/4	1/4	0.378 (3)	0.0208 (12)
O22§	1/4	1/4	0.900 (3)	0.0208 (12)
P1	-1/4	1/4	1/2	0.0164 (10)
C1	-0.1435 (7)	0.2447 (7)	0.3622 (12)	0.019 (2)
C2	-0.1413 (7)	0.1727 (8)	0.2332 (13)	0.025 (2)
C3	-0.0634 (9)	0.1706 (9)	0.1193 (14)	0.036 (3)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1139). Services for accessing these data are described at the back of the journal.

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Aqua(2,3-dimethylpyridine-*N*)(*N*-salicylidene-glycinato-*O,N,O'*)copper(II)

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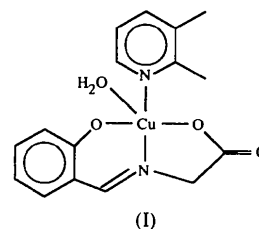
Abstract

In the title compound, [Cu(C₉H₇NO₃)(C₇H₉N)(H₂O)], the Cu^{II} centre has a square-pyramidal environment with a tridentate *N*-salicylidene-glycinato Schiff base dianion and a 2,3-dimethylpyridine ligand coordinated in the basal plane. The apex of the pyramid is occupied by the O atom of the coordinated water molecule at a distance of 2.384(3) Å. The monomers are associated through hydrogen bonds, forming infinite chains. The copper(II) polyhedra are arranged in a single magnetic orientation.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneamino-carboxylato type

(TSB²⁻) represent relatively simple models for the study of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes, which are of the general type [Cu(TSB)(L)]_n (Warda, 1994), three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand L (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the copper coordination geometry can be square planar or square pyramidal when a neutral donor ligand is located at the apical site (*n* = 1) (Ueki *et al.*, 1969). If a phenolic O atom from an adjacent molecule is apically coordinated, dimeric structures are formed (*n* = 2) (Warda, 1994). A tetrameric structure (*n* = 4) is found in the case of (4-ethylpyridine)(*N*-salicylidene-glycinato)copper(II) (Warda, 1997a). Polymeric structures (*n* = ∞) are generally achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule, thus forming infinite zigzag chains (Ueki *et al.*, 1967), or when a bidentate ligand connects the apical sites to form one-dimensional chains (Warda, 1994). In this communication, a complex, (I), with *n* = 1, but with chain character arising from hydrogen bonding, is reported.



The Cu^{II} ion has square-pyramidal [4+1] coordination geometry, with the tridentate Schiff base *N*-salicylidene-glycinato dianion and the monodentate 2,3-dimethylpyridine ligand in the basal plane. The apical position is occupied by a water O atom at a distance of 2.384(3) Å. The pyridine ring is inclined with respect to the basal plane (through O1, O2, N1 and N2) at an angle of 70.0(1)° and the Cu atom lies 0.155(1) Å out of this plane, displaced towards the O4 atom (PLATON; Spek, 1997).

The monomers are associated through hydrogen bonding, forming chains *via* O4—H41···O3 interactions that are connected by O4—H42···O3 hydrogen bonds to a second, inverted chain. These chains run parallel to the crystallographic *x* axis (Fig. 2).

In the case of the polymeric structure of (3,5-dimethylpyridine)(*N*-salicylidene-glycinato)copper(II) reported recently (Warda, 1997b), the apical distance is 2.386(2) Å to a carboxylic O atom of an adjacent molecule. In that structure, the copper(II) polyhedra are tilted with an angle 2γ of 85° (2γ is the angle describing the orientation of the main axes of the polyhedra with respect to one another and should therefore