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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(triphenylphosphine)iminium Tetrachlorooxomolybdenum(V) at 150 K

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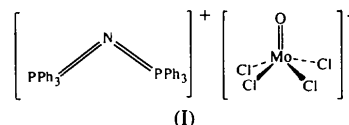
Abstract

In the title compound $[\text{C}_{36}\text{H}_{30}\text{NP}_2]^+ \cdot [\text{MoOCl}_4]^-$, the anions reside in hydrophobic channels formed by the cations and, unlike other salts of this anion, the compound is stable with respect to atmospheric hydrolysis.

Comment

In order to obtain mixed Mo–Bi oxo complexes to serve as models for catalytic activity during the

Sohio process for the oxidation of propene to acrolein (Grasselli & Burrington, 1981), the compound $\text{PPN}^+ \cdot \text{Et}_3\text{NH}^+ \cdot [\text{Cl}_2(\text{O})\text{Mo}(\mu_2\text{-O})_2(\text{O})\text{MoCl}_2]^{2-}$ (Blake, Limberg, Parsons & Downs, 1995), where PPN^+ is $[\text{N}(\text{PPh}_3)_2]^+$, was treated with BiCl_3 in CH_2Cl_2 . Green crystals, obtained as a by-product of this reaction, were shown to be $\text{PPN}^+ \cdot [\text{MoOCl}_4]^-$, (I), by chemical analysis and IR and NMR spectroscopy.



All known salts of the $[\text{MoOCl}_4]^-$ anion are unstable, both in non-aqueous solution and in the solid state, to the action of moist air and they readily take up one water molecule to give $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ (*Gmelin Handbook of Inorganic Chemistry*, 1990). However, solid (I) proved to be completely stable in air, a fact which led us to investigate its structure in order to seek an explanation for this characteristic.

The structure of the $[\text{MoOCl}_4]^-$ anion in compound (I) (Fig. 1) is similar to those determined previously (*Gmelin Handbook of Inorganic Chemistry*, 1990) and most closely resembles that in $[\text{AsPh}_4]_2[\text{MoOCl}_4][\text{MoOCl}_4(\text{CH}_3\text{CN})]$ (Weller, Müller, Weiher & Dehnicke, 1980). The strong $\text{Mo}=\text{O}$ bond [1.646(6) Å, bond order 2.5 (Schröder, 1975)] exerts a powerful *trans* influence which makes the formation of a trigonal-bipyramidal structure unfavourable and the $[\text{MoOCl}_4]^-$ anion universally adopts a square-pyramidal geometry. Repulsions between the closely bound O atom and the chloro ligands increase the $\text{O}-\text{Mo}-\text{Cl}$ angles [109.6(3), 108.4(3), 101.8(3) and 101.2(3)° in compound (I)], which vary somewhat beyond the range (101–105°) defined as typical for oxo and nitrido complexes of the type XMCl_4^- ($X = \text{N}, \text{O}; M = \text{Mo}, \text{Re}, \text{Ru}, \text{Os}$) (Dehnicke & Strähle, 1981). The metal atom lies 0.614(2) Å from the mean plane of the four Cl atoms.

The distortion of the $[\text{MoOCl}_4]^-$ anion in (I) from C_{4v} symmetry is in contrast to the undistorted (though

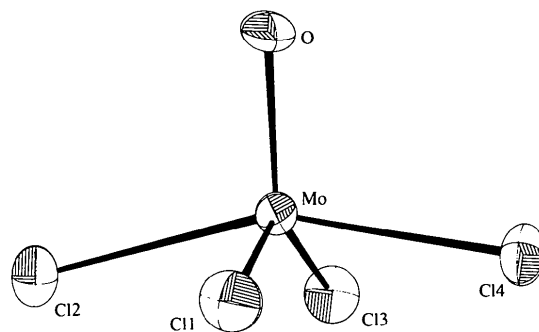


Fig. 1. The structure of the $[\text{MoOCl}_4]^-$ anion in compound (I). Displacement ellipsoids enclose 50% probability surfaces.

non-crystallographic) point symmetry of the anion in $[AsPh_4][MoOCl_4]$ (Knopp, Lörcher & Strähle, 1977). A more pronounced distortion of this type has been observed in the isostructural salt $PPN^+[TcOCl_4]^-$ (Cotton, Davison, Day, Gage & Trop, 1979) and has been ascribed to the bulk of the PPN^+ cation (Baldas, Boas, Bonnyman & Williams, 1984).

The $[MoOCl_4]^-$ anion resides in channels of PPN^+ cations in which it is efficiently enclosed by the hydrophobic phenyl groups (Fig. 2). In this environment, reaction with atmospheric water is effectively prevented leading to the unusual stability of this salt to aerial hydrolysis. It is also possible that these conditions additionally prevent dimerization of the anions such as has been observed in the presence of the $[(CH_3)_2C=NH_2]^+$ counteranion (Klinzing, El-Kholi, Müller, Dehnicke & Findeisen, 1989).

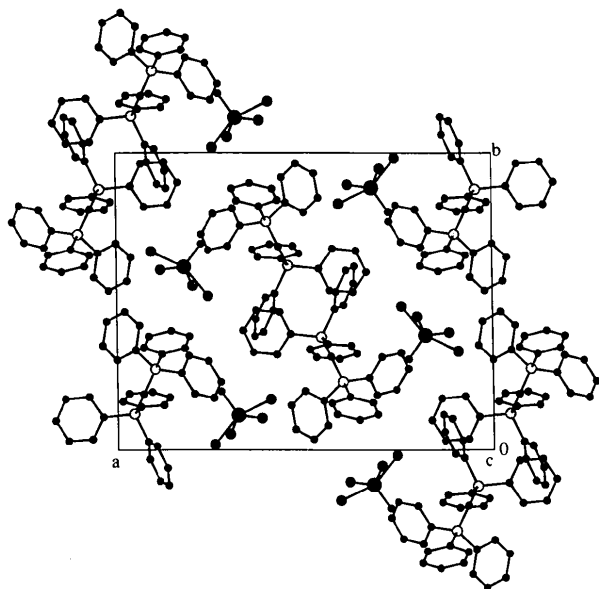


Fig. 2. A packing diagram of the structure along the c axis illustrating the incorporation of the $[MoOCl_4]^-$ anions into hydrophobic channels formed by phenyl groups.

Experimental

$PPN^+.Et_3NH^+[Mo_2O_4Cl_4]^{2-}$ (0.5 g, 0.48 mmol) and $BiCl_3$ (0.3 g, 0.95 mmol) were mixed in a flamed-out Schlenk tube under an N_2 atmosphere. The suspension formed by the addition of CH_2Cl_2 (50 ml) was stirred for 24 h after which all the $BiCl_3$ had been consumed with the formation of a green solution over a very viscous red-brown oil. The supernatant solution was recovered by filtration and overlaid with Et_2O (100 ml) causing green crystals of compound (I) (0.110 g, 29% yield) to precipitate after one week. These were isolated by filtration [IR: $\nu(Mo=O)$ 999 cm^{-1} ; 1H NMR: 7.7 (*s*, *br*), 7.5 (*s*, *br*)]. A single crystal of compound (I) was mounted under N_2 in a Lindemann capillary and data collection performed at 150 K (Cosier & Glazer, 1986).

Crystal data

$(C_{36}H_{30}NP_2)[MoOCl_4]$
 $M_r = 792.29$
 Orthorhombic
 $Pna2_1$
 $a = 21.470$ (6) Å
 $b = 16.765$ (2) Å
 $c = 9.6155$ (14) Å
 $V = 3461.0$ (12) Å³
 $Z = 4$
 $D_x = 1.521$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 44 reflections
 $\theta = 15-16^\circ$
 $\mu = 0.811$ mm⁻¹
 $T = 150.0$ (2) K
 Lath
 $0.80 \times 0.31 \times 0.19$ mm
 Green

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω - θ scans with on-line profile analysis (Clegg, 1981)
 Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
 $T_{min} = 0.547$, $T_{max} = 0.621$
 3137 measured reflections
 2743 independent reflections

2416 observed reflections [$F > 4\sigma(F)$]
 $R_{int} = 0.0306$
 $\theta_{max} = 22.52^\circ$
 $h = -1 \rightarrow 23$
 $k = -18 \rightarrow 1$
 $l = -1 \rightarrow 10$
 3 standard reflections
 frequency: 60 min
 intensity decay: not significant

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0422$
 $wR(F^2) = 0.0872$
 $S = 1.082$
 2739 reflections
 407 parameters
 $w = 1/[\sigma^2(F_o^2) + 16.8557P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = -0.001$
 $\Delta\rho_{max} = 0.487$ e Å⁻³
 $\Delta\rho_{min} = -0.607$ e Å⁻³

Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.00059 (13)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983) parameter = -0.06 (7)

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

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

	x	y	z	U_{eq}
Mo	0.32011 (3)	0.88378 (5)	0.75802 (10)	0.0268 (2)
O	0.2755 (3)	0.8043 (4)	0.7710 (10)	0.044 (2)
Cl1	0.29822 (13)	0.9470 (2)	0.5466 (4)	0.0485 (8)
Cl2	0.25780 (12)	0.9821 (2)	0.8632 (4)	0.0493 (8)
Cl3	0.38362 (11)	0.8934 (2)	0.9531 (3)	0.0384 (7)
Cl4	0.40793 (11)	0.8305 (2)	0.6450 (3)	0.0409 (7)
N	0.0690 (3)	0.8135 (4)	1.0281 (9)	0.024 (2)
P1	0.04379 (10)	0.87878 (14)	0.9243 (3)	0.0188 (6)
P2	0.10041 (10)	0.72870 (15)	1.0434 (3)	0.0221 (6)
C1	-0.0386 (4)	0.8890 (5)	0.9480 (10)	0.021 (2)
C2	-0.0747 (4)	0.8207 (5)	0.9599 (11)	0.026 (2)
C3	-0.1377 (4)	0.8277 (6)	0.9917 (11)	0.031 (3)
C4	-0.1651 (4)	0.9008 (6)	1.0092 (11)	0.032 (3)
C5	-0.1298 (4)	0.9687 (6)	0.9949 (11)	0.029 (3)
C6	-0.0669 (4)	0.9635 (5)	0.9653 (11)	0.024 (2)
C7	0.0795 (4)	0.9733 (5)	0.9599 (10)	0.021 (2)
C8	0.1033 (4)	0.9872 (6)	1.0935 (11)	0.029 (3)
C9	0.1308 (4)	1.0605 (6)	1.1219 (12)	0.028 (2)

C10	0.1337 (4)	1.1185 (6)	1.0201 (12)	0.029 (3)
C11	0.1102 (4)	1.1046 (6)	0.8895 (11)	0.029 (2)
C12	0.0830 (4)	1.0317 (6)	0.8594 (11)	0.031 (3)
C13	0.0611 (4)	0.8551 (5)	0.7448 (12)	0.025 (2)
C14	0.0140 (4)	0.8375 (5)	0.6520 (11)	0.025 (2)
C15	0.0309 (4)	0.8116 (5)	0.5183 (11)	0.027 (3)
C16	0.0914 (5)	0.8060 (6)	0.4809 (12)	0.036 (3)
C17	0.1385 (4)	0.8239 (6)	0.5752 (11)	0.030 (3)
C18	0.1234 (4)	0.8497 (6)	0.7080 (10)	0.025 (2)
C19	0.0492 (4)	0.6651 (5)	1.1388 (11)	0.021 (2)
C20	0.0005 (4)	0.6971 (6)	1.2127 (10)	0.027 (2)
C21	-0.0386 (4)	0.6497 (6)	1.2901 (12)	0.035 (3)
C22	-0.0276 (5)	0.5687 (7)	1.2997 (12)	0.042 (3)
C23	0.0213 (4)	0.5357 (5)	1.2269 (13)	0.039 (3)
C24	0.0595 (4)	0.5821 (5)	1.1448 (12)	0.028 (2)
C25	0.1192 (4)	0.6778 (5)	0.8821 (12)	0.021 (2)
C26	0.0708 (4)	0.6572 (5)	0.7913 (11)	0.027 (3)
C27	0.0841 (5)	0.6198 (5)	0.6681 (12)	0.033 (3)
C28	0.1443 (5)	0.6012 (6)	0.6354 (13)	0.040 (3)
C29	0.1921 (4)	0.6192 (6)	0.7249 (12)	0.040 (3)
C30	0.1798 (5)	0.6592 (6)	0.8485 (12)	0.032 (3)
C31	0.1706 (4)	0.7421 (5)	1.1409 (11)	0.026 (2)
C32	0.1904 (4)	0.6840 (6)	1.2373 (12)	0.032 (3)
C33	0.2422 (4)	0.7015 (7)	1.3168 (11)	0.037 (3)
C34	0.2749 (4)	0.7719 (6)	1.3040 (12)	0.037 (3)
C35	0.2560 (4)	0.8259 (6)	1.2077 (12)	0.032 (3)
C36	0.2041 (4)	0.8124 (6)	1.1254 (11)	0.029 (2)

Table 2. Selected geometric parameters (Å, °)

Mo—O	1.646 (6)	Mo—Cl3	2.324 (3)
Mo—Cl1	2.340 (3)	Mo—Cl4	2.353 (3)
Mo—Cl2	2.351 (3)		
O—Mo—Cl1	108.4 (3)	Cl1—Mo—Cl3	141.94 (10)
O—Mo—Cl2	101.8 (3)	Cl1—Mo—Cl4	86.08 (11)
O—Mo—Cl3	109.6 (3)	Cl2—Mo—Cl3	86.45 (11)
O—Mo—Cl4	101.2 (3)	Cl2—Mo—Cl4	157.06 (10)
Cl1—Mo—Cl2	86.67 (12)	Cl3—Mo—Cl4	85.93 (11)

H atoms were placed in calculated positions (C—H = 0.95 Å) and allowed to ride on the C atoms to which they are attached with $U_{iso}(H) = 1.2U_{eq}(C)$ in subsequent cycles of refinement.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CAMERON* (Pearce & Watkin, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octacarbonyl-1 κ^4 C,2 κ^4 C- μ_3 -[cyclohexylphosphanido(2-)]- μ -hydrido-1:2 κ^2 H-tricyclohexylphosphine-3 κ P-gold-dimanganese(Mn—Mn)

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Abstract

The title compound, [AuMn₂H(C₆H₁₁P)(C₁₃H₃₃P)(CO)₈], has an Mn—Mn bond length of 2.933 (1) Å which is symmetrically bridged by an H and a P atom. The 'coordination' of the P atom is completed by one cyclohexyl and one (tricyclohexylphosphine)gold 'ligand'.

Comment

[Mn₂(μ -H){ μ_3 -PCy(AuPCy₃)}(CO)₈], (I), where Cy is cyclohexyl, constitutes the first example of a μ -H and μ_3 -P bridged transition metal–gold complex. It may be derived formally from the family of [M₂(μ -H)(μ -PR₂)(CO)₈] compounds (Haupt, Heinekamp, Flörke & Jüptner, 1992) by substitution of one R ligand by an AuPR₃ group.