

Fig. 2. Stereoview of the packing in the cell of $\text{RuCl}_2(\text{CO})(\text{CN}-p\text{-ClC}_6\text{H}_4)(\text{PPh}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$.

trans to CO was 2.428 (6) Å and Ru—Cl *trans* to CSe was 2.477 (7) Å. The longer values are at the upper end of the range found for Ru—Cl bonds in similar complexes (Clark & James, 1977).

The isocyanide coordination is characterized by Ru—C 1.94 (2), C—N 1.14 (3) and N—PhCl 1.34 (3) Å; Ru—C—N 176 (2) and C—N—PhCl 165 (2)°. Unfortunately, the uncertainties in these bond lengths and angles are too high to permit detailed interpretation. However, the geometry can be compared with that in $\text{RuI}_2\{\text{CHN}(\text{CH}_3)(p\text{-CH}_3\text{C}_6\text{H}_4)\}(\text{CO})(\text{CN}-p\text{-CH}_3\text{C}_6\text{H}_4)(\text{PPh}_3)$ (Clark, 1977) with Ru—C 1.998 (16), C—N 1.15 (2), N—PhCH₃ 1.42 (2) Å; Ru—C—N 177.1 (7), C—N—PhCH₃ 170.9 (10)°. It is noted that the secondary carbene situated *trans* to CNR in the latter complex exerts a not insignificant *trans* influence in comparison with the chloride ligand in the present complex. Both isocyanides are very significantly bent from linearity, as has been observed in many other isocyanide complexes, with the larger bend occurring

at N. The angle C—N—Ph in the present complex (165°) gives a slightly greater deviation from linearity than has been found hitherto (Badley, 1969). As has been commented previously (Clark, 1977), there is no suggestion that the isocyanide coordination should be described as anything other than linear in the electronic sense. The influence of packing forces becomes particularly evident in the present complex when intermolecular distances are calculated. It is found that there are ten such contacts shorter than 3.6 Å [shortest 3.35 Å, O(1)⋯C(24)']. However, in a trial calculation in which the isocyanide group as a whole was rotated so that Ru—C—N—Ph—Cl was made collinear a large number of catastrophically close contacts resulted (shortest approximately 0.8 Å). It is clear that forces due to crystal-packing requirements can easily dominate in determining the particular geometry adopted by such elongated ligands as *p*-substituted aromatic isocyanides.

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Acta Cryst. (1982). **B38**, 2258–2261

Bis(tetraphenylarsonium) Di- μ -oxo-bis[dichloro(oxo)molybdate(V)] Dichloromethane Hydrogen Chloride Solvate

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(Received 30 November 1981; accepted 22 March 1982)

Abstract. $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Mo}_2\text{Cl}_4\text{O}_4] \cdot \text{CH}_2\text{Cl}_2 \cdot \frac{1}{2}\text{HCl}$, $M_r = 1267.5$, triclinic, $P\bar{1}$, $a = 12.280$ (7), $b = 13.632$ (6), $c = 18.532$ (6) Å, $\alpha = 71.85$ (3), $\beta = 74.12$ (4), $\gamma = 62.45$ (4)°; reduced-cell parameters: $a' = 12.280$ (7), $b' = 13.482$ (6), $c' = 18.532$ (6) Å, $\alpha' = 93.77$ (3),

$\beta' = 105.88$ (4), $\gamma' = 116.31$ (4)°, transformation matrix (100)/(110)/(001); $U = 2582.3$ Å³, $Z = 2$, $D_m = 1.64$ (1), $D_x = 1.630$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 2.20$ mm⁻¹, $F(000) = 1258$; final $R = 0.087$ for 4799 observed reflections. The structure of the title compound consists of discrete anions, cations and solvent molecules. In the dinuclear anion, the two

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Mo atoms are bridged by two O atoms, and the coordination sphere about each metal is completed by a terminal O atom and two terminal Cl atoms. The terminal O atoms are *cis* with respect to the Mo(μ -O)₂-Mo unit, and the geometry around the Mo atoms in the [Mo₂Cl₄O₄]²⁻ anion is distorted square-pyramidal. There is a weak metal-metal interaction in the anion [Mo...Mo = 2.591 (2) Å].

Introduction. In an attempt to prepare molybdenum analogues of the dinuclear tungsten(IV) complexes XCl₂W(μ -S)(μ -SR)₂WCl₂X [X = (CH₃)₂S, Cl⁻; R = CH₃, C₂H₅] (Boorman, Coddling, Kerr, Moynihan & Patel, 1982; Patel & Boorman, 1982), a hydrolysis reaction involving an oxomolybdenum impurity, MoCl₃O.S(CH₃)₂, in a wet CH₂Cl₂ solution containing [As(C₆H₅)₄]₂Cl resulted in the formation of the dimeric Mo^V complex [As(C₆H₅)₄]₂[Mo₂Cl₄O₄].CH₂Cl₂.½HCl.* The orange-red crystals were obtained at 250 K from dichloromethane-diethyl ether solutions.

A preliminary photographic examination of a large crystal of the title complex indicated a triclinic cell since, regardless of the crystal orientation, no symmetry higher than $\bar{1}$ was observed in any of the photographs. A crystal with approximate dimensions 0.3 × 0.3 × 0.4 mm was then mounted in an arbitrary orientation on an Enraf-Nonius CAD-4 computer-controlled diffractometer, and the cell parameters were obtained from a least-squares fit of the angular settings of 25 accurately centred reflections with $8.8^\circ \leq \theta \leq 16.4^\circ$. Intensities were collected with graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å) at 298 K using an $\omega/2\theta$ scan mode with a scan width of $\Delta\omega = 1.5(0.54 + 0.35 \tan \theta)^\circ$. Of the 9049 independent reflections measured in the range $2^\circ \leq \theta \leq 25^\circ$, 4815 had intensities greater than $3\sigma(I)$ and were considered to be observed. Standard Lorentz and polarization factors were applied and data were corrected for absorption using the program *CADABS*. This is a local modification of a Gaussian integration program (Coppens, Leiserowitz & Rabinovich, 1965) and the maximum and minimum transmission factors were 0.659 and 0.584 respectively. The centrosymmetric space group $P\bar{1}$ was chosen on the basis of the E statistics and the measured density – successful refinement of the structure in this space group confirmed this selection. The positions of the Mo and

As atoms were located from the Patterson map, and those of all the other atoms in the structure except the H atoms were obtained from subsequent difference Fourier syntheses. All the atoms of the anion and the As atoms of the cations were refined anisotropically. The atoms of the solvent species (whose presence in the crystal lattice was verified mass spectroscopically) were refined with isotropic thermal parameters. The CH₂Cl₂ solvent molecule in the structure appears to be somewhat disordered. Refinement of the occupancy factors for the atoms in this group did not produce converged values (variation of 0.60–0.98). Since the configuration of the anion is the most important aspect of this structure, the disorder in the dichloromethane molecule was not considered serious enough to justify refining a model to account for it; hence the occupancy parameters for the atoms in this group were set to unity, and the disorder is reflected in the high thermal parameters for these atoms. The occupancy factor for the Cl atom of the HCl solvent molecule refined successfully to a value of 0.48 (5). The occupancy factor for the Cl atom of the HCl solvent species was fixed at a value of 0.5 in the final stages of the refinement in accord with the measured density. The cationic phenyl rings were refined as rigid bodies, and the H atoms of the phenyl rings were placed in calculated positions, but were not refined. In the final stages of the full-matrix least-squares refinement, 16 low-angle reflections with abnormally high $w(\Delta F)$ values were excluded from the refinement. These reflections are tabulated in the structure-factor table.* No peaks of chemical significance could be located in the final difference map, which showed maximum fluctuations of $\pm 0.38 e \text{ \AA}^{-3}$. The final R factors were $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.087$, and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.012$. The weighting scheme

* See previous footnote.

Table 1. Fractional coordinates and U_{eq} ($\times 10^2$) for the atoms in the [Mo₂Cl₄O₄]²⁻ anion

E.s.d.'s are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^* (Å ²)
Mo(1)	0.1144 (1)	0.3219 (1)	0.7810 (1)	3.7 (1)
Mo(2)	0.3146 (1)	0.1546 (1)	0.7394 (1)	3.5 (1)
Cl(11)	0.0908 (5)	0.4878 (4)	0.8142 (3)	6.1 (4)
Cl(12)	-0.0609 (4)	0.4475 (4)	0.7164 (3)	7.2 (4)
Cl(21)	0.5280 (4)	0.1274 (5)	0.7189 (3)	5.6 (4)
Cl(22)	0.3736 (5)	0.0775 (5)	0.6274 (3)	5.3 (4)
O(1)	0.1612 (9)	0.2446 (9)	0.7004 (6)	3.8 (7)
O(2)	0.2887 (9)	0.2754 (8)	0.7837 (6)	4.0 (7)
O(3)	0.0506 (11)	0.2558 (10)	0.8609 (7)	6.1 (8)
O(4)	0.3036 (12)	0.0444 (9)	0.8110 (7)	6.8 (9)

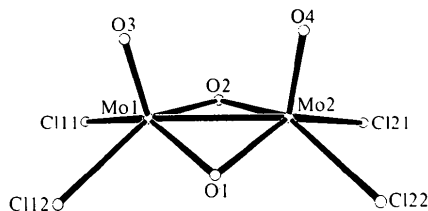
* $U_{eq} = \frac{1}{3} \text{trace } \bar{U}$, where \bar{U} is the diagonalized U_{ij} matrix.

* Synthetic details and lists of structure factors, fractional coordinates and thermal parameters for the non-H atoms of the cations and solvent molecules, anionic anisotropic thermal parameters, calculated positions for the phenyl-ring H atoms, intra-anionic non-bonded contacts, selected bond distances and angles in the cations and CH₂Cl₂ solvent molecule, and least-squares-planes' calculations for the anion have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36826 (69 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances (Å) and angles (°) in the [Mo₂Cl₄O₄]²⁻ anion

E.s.d.'s are in parentheses.

	Mo(1)—Mo(2)	2.591 (2)	
Mo(1)—Cl(11)	2.395 (7)	Mo(2)—Cl(21)	2.407 (6)
Mo(1)—Cl(12)	2.392 (6)	Mo(2)—Cl(22)	2.401 (7)
Mo(1)—O(1)	1.90 (1)	Mo(2)—O(1)	1.91 (1)
Mo(1)—O(2)	1.94 (1)	Mo(2)—O(2)	1.92 (1)
Mo(1)—O(3)	1.68 (1)	Mo(2)—O(4)	1.70 (1)
	Mo(1)—O(1)—Mo(2)	85.7 (6)	
	Mo(1)—O(2)—Mo(2)	84.2 (6)	
Cl(11)—Mo(1)—Cl(12)	85.0 (2)	Cl(21)—Mo(2)—Cl(22)	85.3 (2)
Cl(11)—Mo(1)—O(1)	145.6 (4)	Cl(21)—Mo(2)—O(1)	143.6 (4)
Cl(11)—Mo(1)—O(2)	83.0 (4)	Cl(21)—Mo(2)—O(2)	82.2 (4)
Cl(11)—Mo(1)—O(3)	104.1 (5)	Cl(21)—Mo(2)—O(4)	105.7 (5)
Cl(12)—Mo(1)—O(1)	83.2 (3)	Cl(22)—Mo(2)—O(1)	83.2 (4)
Cl(12)—Mo(1)—O(2)	147.0 (3)	Cl(22)—Mo(2)—O(2)	148.7 (3)
Cl(12)—Mo(1)—O(3)	102.1 (4)	Cl(22)—Mo(2)—O(4)	101.8 (5)
O(1)—Mo(1)—O(2)	89.6 (5)	O(1)—Mo(2)—O(2)	90.1 (5)
O(1)—Mo(1)—O(3)	109.9 (6)	O(1)—Mo(2)—O(4)	110.4 (6)
O(2)—Mo(1)—O(3)	110.6 (5)	O(2)—Mo(2)—O(4)	109.1 (6)

Fig. 1. An ORTEP (Johnson, 1965) view of the [Mo₂Cl₄O₄]²⁻ anion showing the atomic-numbering scheme. The atoms are represented by arbitrary-sized spheroids, and the Mo...Mo interaction has been indicated.

was $w = [1.5\sigma^2(F) + 0.001F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight was 0.97, and the maximum shift-to-error in the final refinement cycle was 0.009. All calculations were performed using the XRAY 76 programs (Stewart, 1976), unless otherwise noted. Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positions for the [Mo₂Cl₄O₄]²⁻ anion are given in Table 1, and selected bond lengths and angles in the anion are given in Table 2.* A view of the [Mo₂Cl₄O₄]²⁻ anion is given in Fig. 1.

Discussion. The structure of the title compound consists of discrete anions, cations, and CH₂Cl₂ and HCl solvent molecules. The [Mo₂Cl₄O₄]²⁻ anion belongs to a well known and characterized group of compounds containing the unit YMo(μ -X)(μ -X')MoY where Y = O or S; X = X' = O; X = X' = S; X = O,

X' = S (Spivak & Dori, 1975). Each Mo atom in the anion exhibits approximate square-pyramidal coordination (if the Mo...Mo interaction is ignored), with a closely bound terminal O atom at the apex, and two bridging O atoms and two terminal Cl atoms forming the base. The [Mo₂Cl₄O₄]²⁻ species consists of two such square pyramids fused along a basal-plane edge, with the dihedral angle between the two Cl₂(O_b)₂ ($b =$ bridging) planes being 161.1 (5)°. The Mo atoms are displaced 0.61 (1) and 0.62 (5) Å above their respective basal planes. In addition, the Mo₂(O_t)₂ ($t =$ terminal) plane is within 2° of being perpendicular to the Cl₂(O_b)₂ planes. The terminal O atoms are *cis* with respect to the central Mo(μ -O)₂Mo unit, as is most often the case in complexes possessing the Mo₂O₄ moiety (Spivak & Dori, 1975). The [Mo₂Cl₄O₄]²⁻ anion possesses approximate C_{2v} (2mm) symmetry, with the pseudo-twofold rotation axis passing through the mid-points of the O_t-O_t, O_b-O_b, and Mo-Mo vectors. The length of the Mo-Mo vector, 2.591 (2) Å, indicates that a weak interaction (\approx Mo-Mo single bond) exists between the two metal atoms in the dimeric anion (Chisholm, Huffman, Kirkpatrick, Leonelli & Folting, 1981). The structure of the [Mo₂Cl₄O₄]²⁻ anion has been reported previously, as the trihydrated pyridinium salt (Mattes, Altmeyen & Fetzer, 1976). In their structure ($R = 0.164$) the Mo atoms were found to be pseudo six-coordinate due to short Mo=O...Mo interactions [O...Mo = 2.42 (8) Å] between anions stacked along the short *c* axis [4.11 (1) Å] of the orthorhombic cell. The present report provides a more precise determination of the structural parameters of the [Mo₂Cl₄O₄]²⁻ anion, as a solvated tetraphenylarsonium salt. The bulkiness of the [As(C₆H₅)₄]⁺ cations in this compound prevented any interanionic Mo=O...Mo interactions and consequently the Mo atoms in the dimeric anion are truly five-coordinate. In the pyridinium salt of [Mo₂Cl₄O₄]²⁻, the Cl-Mo-Cl angle was found to be 92.3 (1)°, and it was hypothesized that in the absence of interanionic Mo=O...Mo interactions, this angle would be less than 92.3 (1)° (Dance, Wedd & Boyd, 1978). This was verified in the structure of [As(C₆H₅)₄]₂[Mo₂Cl₄O₄]·CH₂Cl₂·½HCl, since the Cl-Mo-Cl angles were found to be 85.0 (2) and 85.3 (2)°.

The bond distances and angles in the two crystallographically independent [As(C₆H₅)₄]⁺ cations are in agreement with those found in other structures in which this cation acts as counter ion for transition-metal-containing anions (Patel, Boorman, Kerr & Moynihan, 1982; Cotton & Murillo, 1975). The orientations of the phenyl rings differ in each cation because of different cation-packing arrangements. The CH₂Cl₂ and HCl molecules occupy the remaining lattice voids in the title compound. A short contact of length 2.86 (4) Å exists between the C atom of the dichloromethane solvate molecule and one of the bridging O atoms [O(2)] of the

* See deposition footnote.

[Mo₂Cl₄O₄]²⁻ anion. The only non-bonding interactions involving the hydrogen chloride solvate species are those indicative of hydrogen bonding between symmetry-related HCl molecules [Cl...Cl' = 2.87 (1) Å]. This situation is different from that in other HCl solvates of transition-metal complexes; recent structural studies (Endres & Schlicksupp, 1979, 1980) have revealed that HCl in a crystal lattice is usually hydrogen-bonded to O and/or N atoms of the metal-containing moiety.

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support (to PMB and KAK) and a postgraduate scholarship to KJM. The mass spectra were recorded by Dr R. Yamdagni, and helpful discussions with Drs P. W. Coddling, J. F. Richardson and R. T. Oakley are gratefully acknowledged.

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Acta Cryst. (1982). **B38**, 2261–2264

1,1,1,2,2,2,3,3-Octacarbonyl-2,3;3,1-di-μ-hydrido-μ₃-phenylphosphido-3-triphenylphosphine-triangulo-triruthenium

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(Received 25 January 1982; accepted 25 March 1982)

Abstract. C₃₂H₂₂O₈P₂Ru₃, [H₂Ru₃(CO)₈(PPh₃)₂(μ₃-PPh)], *M_r* = 899.68, monoclinic, *P*2₁/*c*, *a* = 12.094 (3), *b* = 15.044 (4), *c* = 18.727 (4) Å, β = 94.00 (3)°, *U* = 3398.9 Å³, *D_c* = 1.758 Mg m⁻³, *Z* = 4, μ(Mo *K*α) = 1.31 mm⁻¹, *F*(000) = 1760. Final *R* and *R_w* are 0.027 and 0.030 respectively for 4964 unique observed reflections [*I* ≥ 3σ(*I*); 3 ≤ θ ≤ 25°]. The three Ru atoms define an isosceles triangle with the triphenylphosphine group bonded *trans* to the μ₃-PPh group onto the Ru atom associated with two μ-H bridges, P–Ru–P = 164.8 (1)°.

Introduction. Hydrido clusters involving μ₃-PR bridging units are of interest because of the presence of reactive H atoms attached to an intact metal triangle and many clusters of this type have been prepared (*e.g.* Natarajan, Scheidsteger & Huttner, 1981; Natarajan, Zsolnai & Huttner, 1981; Huttner, Schneider, Mohr & von Seyerl, 1980; Iwasaki, Mays, Raithby, Taylor & Wheatley, 1981). However, relatively little attention has been given to the effect of substitution on this type of cluster and the influence of such a substitution on the metal–metal bonding and the cluster geometry.