Tetrachlorobis(tetrahydrofuran)molybdate(III), a New Intermediate for the Synthesis of Molybdenum(III) Complexes: Preparation and Crystal Structure *

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The preparation and structure are described of a new molybdenum(III) species, $[MoCl_4(thf)_2]^-$ (thf = tetrahydrofuran) which promises to be of value as a starting material for other molybdenum(III) complexes.

There is a lack of molybdenum(III) species soluble in non-aqueous solvents and suitable as starting materials for the preparation of molybdenum(III) complexes. The most widely used is $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran). Its preparation[1,2] from $MoCl_5$ is generally as shown in equation (1). An improved

$$MoCl_5 \longrightarrow [MoCl_4(MeCN)_2] \longrightarrow [MoCl_4(thf)_2] \longrightarrow [MoCl_3(thf)_3] \quad (1)$$

method of synthesis[3] has made it more easily attainable, but it is stable in solution only in thf, and in other solvents, such as benzene, it rapidly loses thf and polymerises. We have now prepared salts of $[MoCl_4(thf)_2]^-$, which do not have this disadvantage.

Results and Discussion

The salt $[NEt_3H][MoCl_4(thf)_2]$ was initially isolated by chance from the attempted reaction of $[MoCl_4(thf)_2]$ with $(HSCH_2CH_2)_2S$ in alcohol in the presence of NEt_3. The expected $[Mo\{(SCH_2CH_2)_2S\}_2]$[4] was not obtained, but the above pink triethylammonium salt was formed. Its identity was finally confirmed by *X*-ray structure analysis (see below). The solid is air-stable for several months, is soluble in solvents such as chloroform, thf, and alcohols, and we have now also prepared the tetraphenylphosphonium and tetraethylammonium salts from solutions obtained by the rapid reduction of $[MoCl_4(thf)_2]$ by zinc metal in alcohol in the presence of base. We have used these salts to prepare three further species, $[MoCl_4(C_5H_5N)_2]^-$,[5] $[MoCl_4(Ph_2PCH_2CH_2PPh_2)]^-$, and $[MoCl_4(PMe_2Ph)_2]^-$. It may clearly be an alternative to $[MoCl_3(thf)_3]$ as a reagent for the preparation of further molybdenum(III) species. Analogous species could not be obtained from parallel reactions with $[MoCl_4(MeCN)_2]$ or $[MoCl_4(PPh_3)_2]$.

The geometry of the anion $[MoCl_4(thf)_2]^-$ in its crystalline tetraphenylphosphonium salt is shown in the Figure, and atomic co-ordinates for the non-hydrogen atoms are shown in Table 1. Table 2 lists relevant bond lengths and angles. Other data have been deposited. The molybdenum atom displays pseudo-octahedral co-ordination, with a square-planar $MoCl_4$ unit and axial co-ordination of the thf. The idealised local symmetry of the molybdenum atom in the $MoCl_4O_2$ co-ordination is D_{4h}, with the C_4 axis passing through the O(1)–Mo–O(2) bond vector.

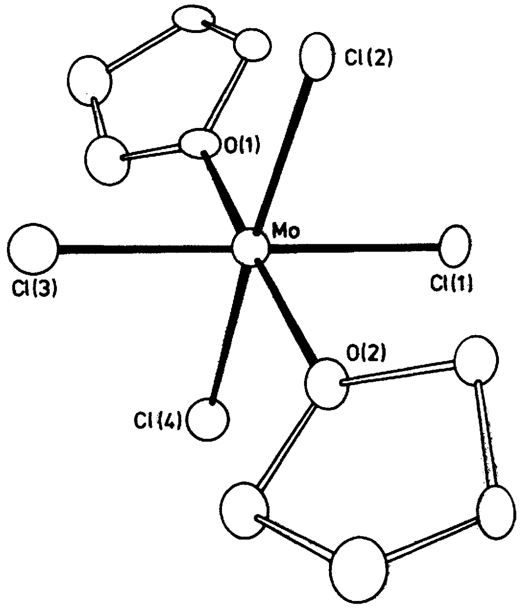

Figure. Perspective view of the $[MoCl_4(thf)_2]^-$ ion. Hydrogen atoms have been omitted

Table 1. Atom co-ordinates (× 10^4) for the ion $[MoCl_4(thf)_2]^-$

Atom	*x*	*y*	*z*
Mo	2 500	−8(5)	2 500
Cl(1)	3 879(9)	−158(12)	3 457(4)
Cl(2)	3 939(9)	−2 393(11)	2 266(3)
Cl(3)	1 162(9)	121(12)	1 536(4)
Cl(4)	1 088(9)	2 420(11)	2 738(4)
O(1)	787(12)	−1 529(15)	2 797(5)
C(1)	−873(14)	−1 310(18)	2 627(6)
C(2)	−1 567(29)	−2 638(37)	2 824(11)
C(3)	−456(17)	−3 634(24)	3 235(8)
C(4)	1 024(14)	−3 118(16)	3 092(6)
O(2)	4 290(13)	1 696(15)	2 365(5)
C(5)	5 934(25)	1 335(30)	2 561(10)
C(6)	6 638(21)	2 916(25)	2 391(8)
C(7)	5 684(15)	3 659(19)	1 962(6)
C(8)	4 038(20)	3 152(23)	2 045(8)

The maximum displacement of chlorine from the ideal plane containing the $MoCl_4$ unit is 0.02 Å for Cl(2). The average Mo–Cl distance, 2.43(1) Å, is identical to that observed for the molybdenum(III) complexes $K_3[MoCl_6]$[6] and $[MoCl_3(C_5H_5N)_3]$.[7] Unfortunately, data for $[MoCl_3(thf)_3]$ are not available. The average Mo–O distance, 2.15(1) Å, is consistent

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* *Supplementary data available* (No. SUP 56172, 9 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 2. Bond lengths (Å) and angles (°) in the ion $[MoCl_4(thf)_2]^-$ with estimated standard deviations in parentheses

Mo–Cl(1)	2.441(8)	Mo–Cl(2)	2.421(9)
Mo–Cl(3)	2.442(8)	Mo–Cl(4)	2.439(9)
Mo–O(1)	2.154(12)	Mo–O(2)	2.155(12)
O(1)–C(1)	1.466(16)	O(1)–C(4)	1.467(18)
O(2)–C(8)	1.406(23)	O(2)–C(5)	1.480(24)
Cl(1)–Mo–Cl(2)	88.9(3)	Cl(1)–Mo–Cl(3)	178.9(3)
Cl(2)–Mo–Cl(3)	90.2(3)	Cl(1)–Mo–Cl(4)	90.7(3)
Cl(2)–Mo–Cl(4)	179.1(3)	Cl(3)–Mo–Cl(4)	90.2(3)
Cl(1)–Mo–O(1)	85.8(4)	Cl(2)–Mo–O(1)	92.6(4)
Cl(3)–Mo–O(1)	94.8(4)	Cl(4)–Mo–O(1)	88.3(4)
Cl(1)–Mo–O(2)	84.7(4)	Cl(2)–Mo–O(2)	92.9(4)
Cl(3)–Mo–O(2)	94.8(4)	Cl(4)–Mo–O(2)	86.2(4)
O(1)–Mo–O(2)	168.9(4)	C(1)–O(1)–C(4)	107.5(10)
Mo–O(1)–C(4)	127.4(8)	O(1)–C(4)–C(3)	107.5(11)
O(1)–C(1)–C(2)	106.9(15)	Mo–O(2)–C(8)	124.1(10)
Mo–O(2)–C(5)	121.9(12)	O(2)–C(5)–C(6)	99.8(16)
C(5)–O(2)–C(8)	113.7(14)		
O(2)–C(8)–C(7)	102.9(13)		

Table 3. Summary of crystal data and experimental details for the structural study of $[PPh_4][MoCl_4(thf)_2]$

Crystal parameters* at 23 °C

$a = 8.809(2)$, $b = 8.074(2)$, $c = 24.168(4)$ Å
$\alpha = 90.00$, $\beta = 99.04(1)$, $\gamma = 90.00°$
$U = 1\,697.4(9)$ Å^3, space group $P2_1$, $Z = 2$
$M = 721.36$, $D_c = 1.411$ g cm^{-3}, $F(000) = 738$

Measurement of intensity data

Crystal dimensions/mm:	0.09 × 0.21 × 0.13
Instrument:	Nicolet *R3m*
Radiation:	Mo-K_α ($\lambda = 0.710\,73$ Å)
Scan mode:	Coupled θ (crystal)—2θ (counter)
Scan rate/° min^{-1}:	Variable 7—30°
Scan range/°:	$0 < 2\theta < 45$
Scan length:	$[2\theta(K_{\alpha_1}) - 1.0]$ to $[2\theta(K_{\alpha_2}) + 1.0]$
Background measurement:	Stationary counter—stationary crystal at beginning and end of each 2θ scan; each for 0.5 of time taken for the 2θ scan
Standards:	3 measured every 197 reflections; no significant deviations
Reflections:	collected 2 514 independent $[I_o > 3\sigma(I_o)]$ 1 345

Reduction of intensity data and summary of structure solution and refinement†

Absorption coefficient (cm^{-1}):	7.83
Structure solution:	Molybdenum located on a three-dimensional Patterson synthesis. Successful Fourier maps yielded all non-hydrogen atoms
Atomic scattering factors‡:	for neutral atoms
Anomalous dispersion§:	real and imaginary components for all atoms
$R[=\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$	0.046
$R'\{=[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.046
Weighting scheme ($g = 0.0005$)	$w = 1/\sigma_{Fo}^2 + g(F_o)^2$
Goodness of fit¶	1.62

* From a least-squares fitting of the setting angle of 25 reflections. † All calculations were performed on a Data General Nova 3 computer with 32 K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package (G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual,' Nicolet XRD Corp., Cupertino, 1979). Data were corrected for background, attenuators, Lorentz, and polarisation effects (but not for absorption) in the usual fashion. ‡ D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321. § 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3. ¶ $[\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o is the number of observations and N_v the number of variables.

with Mo–O single bonds. The bond angles about molybdenum are as expected. The major distortion from idealised octahedral geometry is in O(1)–Mo–O(2) which is 168.9(4)°. The tetrahydrofuran frameworks are mutually eclipsed, and lie between the ClMoCl vectors of the $MoCl_4$ plane, consistent with the absence of π bonding between the Mo^{III} and thf.

The new anionic species are all paramagnetic, with $\mu_{eff.}$ *ca.* 3.8. This compares with the spin-only value of 3.9, and is apparently independent of whether measurements were made in the solid state or in solution (Evans method),[8] and of whether the compounds are *trans*, or *cis*, as is the diphosphine complex. The e.s.r. spectra in frozen solution in methanol are generally broad and without significant structure apart from that of the PMe_2Ph complex. However, neither of the phosphine complexes shows ^{31}P coupling in its e.s.r. spectrum. The compounds are 1 : 1 electrolytes in solution in CH_2Cl_2.

Experimental

Reactions were generally carried out under dinitrogen using conventional Schlenk apparatus. E.s.r. spectra were obtained on a Varian E9 spectrometer, measurements being made in frozen methanol solutions at −196 °C. Analyses were by Mr. C. Macdonald, A.F.R.C. Unit of Nitrogen Fixation. Solid-state magnetic moments were determined by the Faraday method. U.v. and i.r. spectra were obtained using Perkin-Elmer Lambda 5 and Pye-Unicam SP3-200 spectrometers respectively.

Tetraphenylphosphonium Tetrachlorobis(tetrahydrofuran)-molybdate(III).—Tetrachlorobis(tetrahydrofuran)molybdenum(IV)[1] (1.2 g, 3.9 mmol) was suspended in dry, dioxygen-free methanol (50 cm^3) to which triethylamine (0.5 cm^3) had previously been added. To this was added zinc powder (0.7 g, 10.7 mg atom) and the mixture stirred for 15 min, when the purple solution was filtered. The deep brown filtrate was treated with a saturated methanolic solution containing $[PPh_4]Br$ (1.4 g, 3.3 mmol) and on standing large salmon-pink *crystals* separated. These were filtered off, washed well with diethyl ether, and dried *in vacuo*. Yield *ca.* 2 g, 75% (Found: C, 53.2; H, 5.00; Cl, 19.6. $C_{32}H_{36}Cl_4MoO_2P$ requires C, 53.3; H, 5.05; Cl, 19.7%), m.p. 127 °C (decomp.).

The i.r. spectrum in Nujol shows the expected bands due to $[PPh_4]^+$ and to thf. The u.v.–visible spectrum in solution in methanol has maxima at 400 and 496 nm ($\varepsilon = 49.2$ and 30.0 dm^3 mol^{-1} cm^{-1}, respectively). We could obtain no reasonable n.m.r. spectrum; $\mu_{eff.}$ (Evans method,[8] methanol) = 3.90; Λ_M = 41.0 ohm^{-1} cm^2 mol^{-1}; e.s.r., $g = 5.1$.

Tetraphenylphosphonium Tetrachlorobis(dimethylphenylphosphine)molybdate(III).—To a solution of $[PPh_4][MoCl_4(thf)_2]$ (1.0 g, 1.39 mmol) in dichloromethane (50 cm^3) was added PMe_2Ph (3.3 g, 23.9 mmol) and the mixture heated under reflux for 2.5 h, giving a yellow solution. The volume was reduced *in vacuo* to *ca.* 20 cm^3 and diethyl ether added, causing separation of a bright yellow microcrystalline *solid*. This was filtered off, washed well with ether, and dried *in vacuo*. Yield 0.94 g, 79% (Found: C, 55.0; H, 4.75; Cl, 15.8; P, 10.3. $C_{40}H_{42}Cl_4MoP_3$ requires C, 56.3; H, 4.90; Cl, 16.6; P, 10.9%), m.p. 90—93 °C (decomp.); e.s.r., $g = 4.4$ and 3.3.

Tetraphenylphosphonium [1,2-*Bis(diphenylphosphino)ethane*]-*tetrachloromolybdate*(III).—To a solution of $[PPh_4][MoCl_4$-

(thf)$_2$] (1.0 g, 1.39 mmol) in dichloromethane (50 cm^3) was added 1,2-bis(diphenylphosphino)ethane (1.1 g, 2.76 mmol). The pink solution was heated under reflux for 1 h, during which time it became orange-yellow. The mixture was filtered hot, and addition of a few drops of diethyl ether to the filtrate yielded a yellow *precipitate*. This was filtered off, washed with methanol and ether, and dried *in vacuo*. Yield 1.1 g, 82% (Found: C, 59.6; H, 4.70; Cl, 12.8; P, 9.1. $C_{50}H_{44}Cl_4MoP_3$ requires C, 61.5; H, 4.50; Cl, 14.6; P, 9.5%), m.p. 119—122 °C (decomp.); $\mu_{eff.} = 3.79$; $\Lambda_M = 29.1$ ohm^{-1} cm^2 mol^{-1}; e.s.r., $g = 5.1$ (very broad).

Bis(triphenylphosphine)iminium Tetrachlorobis(pyridine)-molybdate(III).—To a suspension of $[N(PPh_3)_2][MoCl_4(thf)_2]$ (1.0 g, 1.09 mmol) in dichloromethane (50 cm^3) was added dry pyridine (1.0 cm^3, 12.7 mmol) and the mixture heated under reflux for 1 h. The resulting yellow solution was filtered, and addition of diethyl ether to the filtrate yielded a bright yellow microcrystalline *solid*. This was filtered off, washed with ether, and dried *in vacuo*. Yield 0.75 g, 74% (Found: C, 57.4; H, 4.40; Cl, 15.0; N, 4.05; P, 6.5. $C_{46}H_{40}Cl_4MoN_3P_2$ requires C, 59.1; H, 4.30; Cl, 15.2; N, 4.50; P, 6.6%), m.p. 228—232 °C (decomp.); $\mu_{eff.} = 3.79$, $\Lambda_M = 42.9$ ohm^{-1} cm^2 mol^{-1}; e.s.r., $g = 4.6$.

Crystallography.—The crystal data and experimental details of the structure determination are given in Table 3. A full description of the experimental details and the methods of structure solution and refinement may be found in ref. 9.

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