Crystal and Molecular Structure, Electron Spin Resonance, and Electronic Spectrum of Tetraphenylarsonium Aquatetrachloro-oxomolybdate(V)

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Crystals of the title complex are tetragonal, space group $P4/n$, with a = 13.090(7), c = 7.440(5) Å, Z = 2. The crystal structure has been solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.054 over 750 statistically significant reflections from diffractometer measurements (Mo-K_α radiation). The distorted octahedral $[\mathrm{MoCl_4O(OH_2)}]^-$ anion has $4mm$ (C_{4v}) symmetry with Mo–O 1.672(15), Mo–O(OH$_2$) 2.393(15), and Mo–Cl 2.359(3) Å, and O–Mo–Cl 99.0(9)°. The $[\mathrm{AsPh_4}]^+$ cation has crystallographic $\bar{4}$ (S_4) symmetry, As–C 1.900(9) Å, and C–As–C angles of 105.5(4) and 111.5(4)°. The polarized single-crystal electronic spectra at room temperature and 5 K show that the first two bands at 13 200 and 22 800 cm^{-1} are xy polarized; these absorptions are assigned to the transitions $b_2^*(4d_{xy},\mathrm{Mo{-}Cl}\ \pi^*)\rightarrow e^*(4d_{xz,yz},\ \mathrm{Mo{-}O}\ \pi^*)$ and $e(4d_{xz,yz},\mathrm{Mo{-}O}\ \pi)\rightarrow b_2^*(4d_{xy},\mathrm{Mo{-}Cl}\ \pi^*)$, or $a_1^*(4d_{z^2},\mathrm{Mo{-}O}\ \sigma^*)$ respectively. The single-crystal e.s.r. parameters, $g_\parallel$ 1.970 ± 0.002 and $g_\perp$ 1.935 ± 0.002, and the Mo hyperfine parameters measured for solutions in concentrated HCl and for polycrystalline $[\mathrm{AsPh_4}][\mathrm{NbCl_4O(OH_2)}]$, $\bar{A}$ 45.5 × 10^{-4} and $A_\parallel$ 72.8 × 10^{-4} cm^{-1}, have been used in conjunction with the electronic spectrum to estimate the metal d-orbital contributions to the metal–ligand antibonding molecular orbitals.

As part of a study of the relation between molecular geometry, electronic structure, and reactivity of molybdenum complexes, we recently reported the e.s.r. behaviour of the species $[\mathrm{MoCl_4O}]^-$, $[\mathrm{MoCl_4O(OH_2)}]^-$, and $[\mathrm{MoCl_5O}]^{2-}$ in dichloromethane solution[1] and single-crystal data for $[\mathrm{AsPh_4}][\mathrm{MoCl_4O}]$.[2] There was good agreement between $\bar{g}$ measured for $[\mathrm{MoCl_4O}]^-$ in solution (1.951 ± 0.002) and in single-crystal phases (1.956 ± 0.002). The e.s.r. spectra of dichloromethane solutions of $[\mathrm{MoCl_4O}]^-$ showed that the $\bar{g}$ value decreased when water (1.947 ± 0.002) and chloride (1.940 ± 0.002) are co-ordinated. It has often been assumed[3] that co-ordination of a ligand *trans* to the Mo–O group which defines the molecular z axis will have little effect on the electronic spectra and e.s.r. parameters of these species since this site is remote from the unpaired electron essentially located in the $4d_{xy}$ orbital of the metal. However, the solution e.s.r. measurements indicate that some changes in the electronic structure do occur when water is co-ordinated to $[\mathrm{MoCl_4O}]^-$. Here we report the details concerning the crystal structure, electronic spectrum, and e.s.r. parameters of $[\mathrm{AsPh_4}][\mathrm{MoCl_4O(OH_2)}]$. This information allows a direct comparison to be made between the geometry and electronic and e.s.r. spectra of the $[\mathrm{MoCl_4O}]^-$ and $[\mathrm{MoCl_4O(OH_2)}]^-$ anions.

EXPERIMENTAL

Preparation.—The salt $[\mathrm{AsPh_4}][\mathrm{MoCl_4O(OH_2)}]$ was prepared as reported previously[1] and single crystals were grown from dry $\mathrm{CH_2Cl_2}$ under dry nitrogen. Microcrystalline samples of $[\mathrm{AsPh_4}][\mathrm{(Mo,Nb)Cl_4O(OH_2)}]$ were also prepared as reported previously.[2]

Crystal Data.—$[\mathrm{AsPh_4}][\mathrm{MoCl_4O(OH_2)}]$, M = 655.1, Tetragonal, a = 13.090(7), c = 7.440(5) Å, U = 1 275 Å^3, D_m (flotation) = 1.72, Z = 2, D_c = 1.706 g cm^{-3}, F(000) = 650. Mo-K_α radiation [λ = 0.710 7 Å, μ(Mo-K_α) = 23.0 cm^{-1}]. Space group $P4/n$ from Laue symmetry and systematic absences: $hk0$ when $h + k \neq 2n$.

Crystallographic Measurements.—A crystal of dimensions *ca.* 0.35 × 0.35 × 0.35 mm, coated with lacquer to prevent decomposition, was orientated on a glass fibre to rotate about the c axis. Preliminary unit-cell dimensions and space-group data having been obtained from oscillation and Weissenberg photographs (Cu-$K_{\bar{\alpha}}$ radiation, λ = 1.541 8 Å) and from precession photographs (Mo-$K_{\bar{\alpha}}$ radiation), the crystal was transferred to an Enraf–Nonium CAD 3 diffractometer (zirconium-filtered Mo-$K_{\bar{\alpha}}$ radiation; 3° take-off angle) and more accurate unit-cell dimensions were calculated by least-squares treatment of the θ, χ, and ϕ angles for 40 high-order reflections widely separated in reciprocal space. Three-dimensional intensity data to θ —25° were recorded by the θ—2θ scanning procedure with scanwidths of $(1.10 + 0.50\tan\theta)°$; background measurements were made at each end of the scan range for a period equal to half the scan duration. Instrument and crystal stability were monitored throughout by remeasuring the intensity of a strong reference reflection after each batch of 99 measurements; no significant variation was noted. Corrections for the usual Lorentz and polarization effects were applied to 750 reflections with $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = scan + total background count. Absorption corrections, established from the ϕ dependence of the intensity of the 005 reflection measured at χ 90°, were also applied to these data.

Structure Analysis.—The structure was solved by the heavy-atom method. The arsenic atom was placed at $\frac{1}{4},\frac{3}{4},0$ [Wyckoff position (2a),[4] space-group origin at $\bar{1}$] and the variable z co-ordinate of the molybdenum atom [Wyckoff position (2c); $\frac{1}{4},\frac{1}{4},z$] was determined from the three-dimensional Patterson map. Positions for the other non-hydrogen atoms were obtained from a three-dimensional F_o Fourier synthesis phased by the arsenic and molybdenum atoms (R 0.35). Refinement of the positional and thermal

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[1] P. M. Boorman, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 1299.

[2] C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J.C.S. Dalton*, 1977, 853.

[3] See, for example, I. N. Marov, V. K. Belyaeva, Yu. N. Dubrov, and A. N. Ermakov, *Russ. J. Inorg. Chem.*, 1971, **16**, 81; D. I. Ryabchikov, I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **169**, 1107.

[4] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1969, vol. 1.

parameters by full-matrix least-squares calculations reduced R to 0.079. Calculated positions for the phenyl-ring hydrogen atoms were confirmed to coincide with regions of positive electron density in a difference-Fourier map and their fixed contributions were included in all the subsequent structure-factor calculations. No allowance was made for the water hydrogen atoms as these must be disordered since they cannot conform to the C_4 site symmetry. Following several more least-squares calculations the refinement converged at R 0.054. Final atomic co-ordinates are in Table 1. Anisotropic thermal parameters and a list of observed and calculated structure amplitudes are in Supplementary Publication No. SUP 22008 (7 pp.).*

TABLE 1

Fractional atomic co-ordinates * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Mo	2 500(—)	2 500(—)	1 980(2)
As	7 500(—)	2 500(—)	0(—)
O	2 500(—)	2 500(—)	4 227(21)
O(OH_2)	2 500(—)	2 500(—)	−1 236(21)
Cl	4 178(2)	1 908(2)	1 483(5)
C(1)	7 924(7)	1 425(6)	1 546(12)
C(2)	8 929(7)	1 012(7)	1 482(13)
C(3)	9 181(8)	260(8)	2 653(15)
C(4)	8 510(9)	−100(9)	3 887(16)
C(5)	7 537(9)	326(9)	3 977(14)
C(6)	7 254(7)	1 079(8)	2 850(12)
H(2)	948	130	51
H(3)	991	−9	254
H(4)	872	−66	480
H(5)	697	8	497
H(6)	649	141	293

* Hydrogen-atom co-ordinates ($\times 10^3$) were not refined and an isotropic temperature factor U 0.063 Å^2 was assumed.

TABLE 2

Electronic-spectral data for $[AsPh_4][MoCl_4O(OH_2)]$. Transition energies are in 10^3 cm^{-1}

Single crystal			Solution in concentrated HCl	
	Liquid-helium			
Room temperature	z polarized	xy polarized	Band position	f
13.4 ($xy > z$)		12.42	14.1	2.1×10^{-4}
		13.20		
		($xy > z$)		
	ca. 14.3vw	13.90		
		14.70		
22.8 ($xy > z$)	23.2	23.2 ($xy > z$)	22.5	1.1×10^{-4}
		24.3		
		26.7		
	27.3		28.1 (sh)	*ca.* 10^{-2}
			32.5	0.7×10^{-1}
			42.4 (sh)	*ca.* 10^{-1}
			47.7	*ca.* 0.5

For all the structure-factor calculations, neutral-atom scattering factors for arsenic, molybdenum, carbon, chlorine, and oxygen were from ref. 5 and for hydrogen from ref. 6, with those of arsenic, chlorine, and molybdenum corrected for the real part of the anomalous dispersion.[7] In the least-squares calculations $\Sigma w\Delta^2$ was minimized with weights w given by the scheme $w^{\frac{1}{2}} = 1$ for $|F_o| < 20.0$ and $w^{\frac{1}{2}} = 20.0/|F_o|$ for $|F_o| > 20.0$.

Electronic-absorption Spectra.—Absorption spectra (10 000—30 000 cm^{-1}) were recorded for concentrated hydrochloric acid solutions of $[NEt_4][MoCl_4O(OH_2)]$ at room temperature and suitably thinned single-crystals of $[AsPh_4]$-$[MoCl_4O(OH_2)]$ at room temperature and 77 and 5 K using equipment and procedures previously described.[8] The orientations of the crystals were such that the electric vector of the incident beam could be polarized parallel and perpendicular to the crystallographic c axis. The data obtained are shown in Figure 1 and summarized in Table 2.

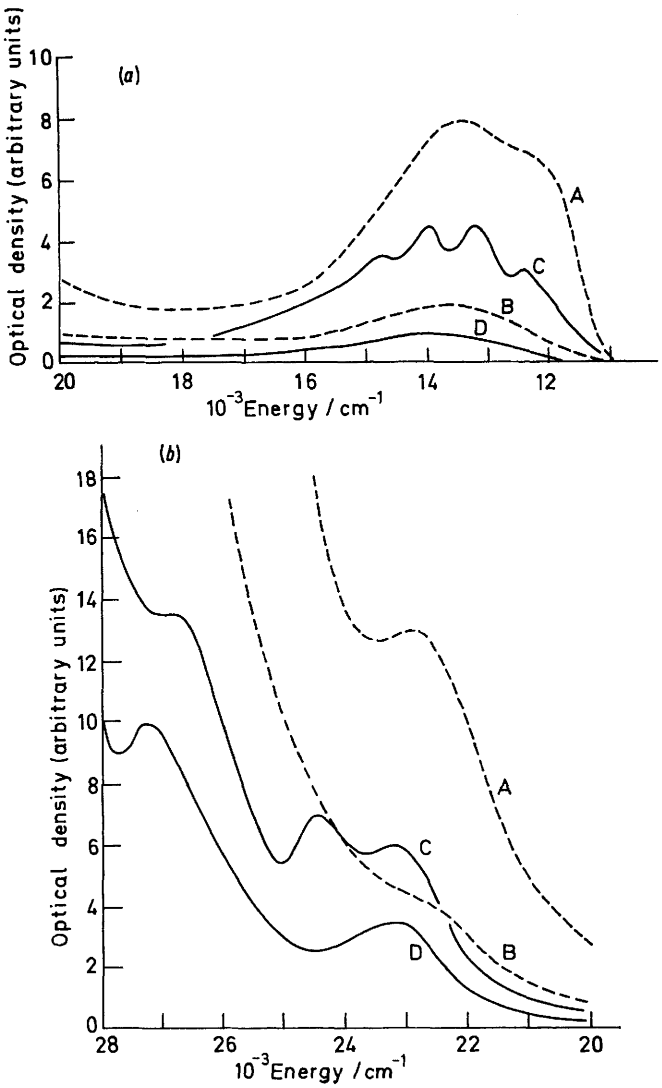

FIGURE 1 Polarized single-crystal electronic spectrum of $[AsPh_4][MoCl_4O(OH_2)]$ in the ranges (a) 11 000—20 000, (b) 20 000—28 000 cm^{-1}; (– – – –) at room temperature, (——) at 5 K. Curves A and C, xy polarization; B and D, z polarization

E.S.R. Spectra.—E.s.r. spectra were recorded at room temperature and Q-band frequencies, as previously des-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

[8] D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 263.

cribed,[9] on single crystals mounted such that the magnetic field could be orientated in a plane perpendicular to the c axis and also in a plane containing the c axis. No molybdenum hyperfine structure was observed at any orientation in either of these planes. The results of these measurements on two different crystals gave $g_{\parallel}$ 1.970 ± 0.002 and $g_{\perp}$ 1.935 ± 0.002. Powder e.s.r. spectra were also recorded for $[\mathrm{AsPh_4}][(\mathrm{Mo,Nb})\mathrm{Cl_4O(OH_2)}]$ at room temperature and *ca.* 150 K. The observed g values were identical, within experimental error, to those obtained for the single crystals. It was possible to determine only $A_{\parallel}$ from the Mo hyperfine splitting in the powder spectra. The value for $A_{\perp}$ was calculated from this value and that for $\bar{A}$ found for $[\mathrm{AsPh_4}][\mathrm{MoCl_4O(OH_2)}]$ in HCl solution. The experimental values were $\bar{A} = 45.5 \times 10^{-4}$ cm^{-1} and $A_{\parallel} = 72.8 \times 10^{-4}$ cm^{-1}.

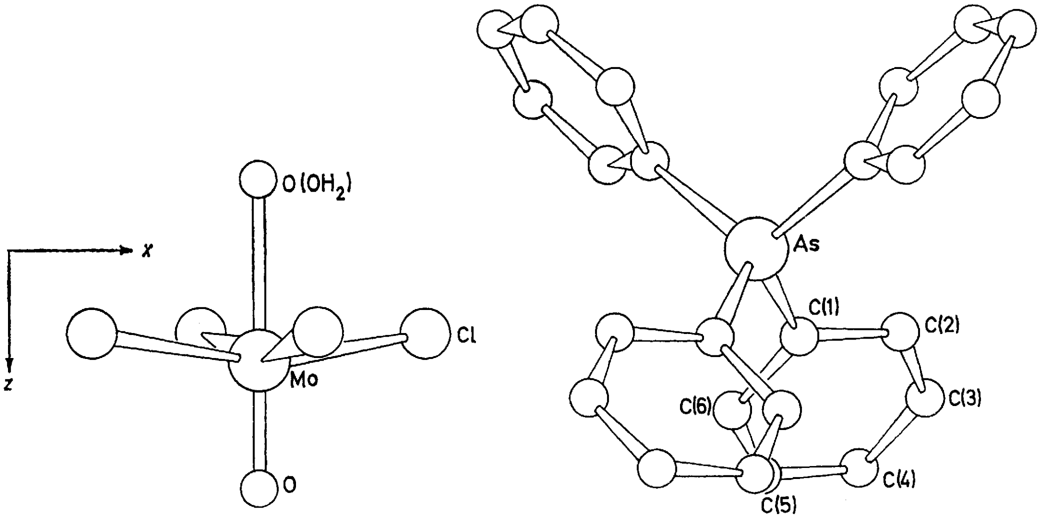

FIGURE 2 Atom numbering and mutual relation between the anion and cation, viewed in projection along the b axis

DISCUSSION

The crystal structure comprises discrete complex distorted octahedral $[\mathrm{MoCl_4O(OH_2)}]^-$ anions with $4mm$ (C_{4v}) point symmetry and distorted tetrahedral $[\mathrm{AsPh_4}]^+$ cations with crystallographic $\bar{4}$ (S_4) point symmetry; the mutal arrangement of an ion pair is shown in Figure 2. Interatomic distances and angles are in Table 3.

The Mo–Cl distance [2.359(3) Å] accords well with that [2.35(3) Å] found[10] in $\mathrm{K[MoCl_4O(OH_2)]}$ and with the mean of the equatorial bonds at six-co-ordinate molybdenum in $[\mathrm{MoCl_5O}]^{2-}$ [2.372(6) Å],[11] in $[\mathrm{Mo_2ClO_2(SPh)_2(S_2CNEt_2)_2}][\mathrm{MoCl_4O(OH_2)}]\cdot\mathrm{CHCl_3}$ [2.375(4) Å],[12] and $[\mathrm{MoCl_4O\{PO(OMe)_2\}}]^{n-}$ [2.368(12) Å].[13] As expected with the increase in co-ordination number, this length is slightly longer than the corresponding distance in similar five-co-ordinate complexes, *e.g.* 2.333(3) in $[\mathrm{MoCl_4O}]^-$ (ref. 2) and 2.305(1)—2.342(1) Å in $[\mathrm{MoCl_3O(PPh_3S)}]$.[14]

The short Mo–O bond [1.672(15) Å] is in good agreement with those determined with similar precision for several other six-co-ordinate oxomolybdenum complexes, *e.g.* 1.641(7) in the anion in $[\mathrm{Mo_2Cl(O_2SPh)_2(S_2CNEt_2)_2}][\mathrm{MoCl_4O(OH_2)}]\cdot\mathrm{CHCl_3}$,[12] 1.668(5) in $[\mathrm{Mo(CN)_4O(OH_2)}]^{2-}$,[15] and 1.677(5) and 1.683(6) Å for the terminal Mo–O bonds in the $[\mathrm{Mo_6O_{19}}]^{2-}$ (ref. 16) and $[\mathrm{Mo_2O_2(edta)S_2}]^{2-}$ anions (edta = ethylenediaminetetra-acetate).[17] Thus the presence of a *trans* ligand appears to diminish the extent of d_{π}–p_{π} Mo–O bonding in these complexes compared with that in the five-co-ordinate $[\mathrm{MoCl_4O}]^-$ anion where the Mo–O bond length is 1.610(10) Å. This Mo–O bond weakening is reflected in ν(Mo–O) which decreases from 1 015 cm^{-1} in $[\mathrm{MoCl_4O}]^-$ (refs. 1 and 18) to 985 cm^{-1} in $[\mathrm{MoCl_4O(OH_2)}]^-$.[18] Another consequence of this effect is that the stronger the π-donor ability of the *trans* ligand, the weaker, and therefore longer, should be the multiple Mo–O bond. Evidence in support of this is to be found in the structural studies on the series of *trans* complexes $[\mathrm{Mo(CN)_4O(OH_2)}]^{2-}$, $[\mathrm{Mo(CN)_4O(OH)}]^{3-}$,[15] and $[\mathrm{Mo(CN)_4O_2}]^{4-}$,[19] where the corresponding distances are 1.668(5), 1.698(7), and 1.834(9) Å. In contrast to these very short multiple Mo–O bonds are the exceptionally long bonds to the *trans* ligand, *e.g.* Mo–O(OH$_2$) of 2.348(8) in $[\mathrm{Mo_2ClO_2(SPh)_2(S_2CNEt_2)_2}][\mathrm{MoCl_4O(OH_2)}]\cdot\mathrm{CHCl_3}$,[12] 2.39(3) in $[\mathrm{MoBr_4O(OH_2)}]^-$, 2.27(5) in $\mathrm{K[MoCl_4O(OH_2)]}$,[10] 2.271(4) in $[\mathrm{Mo(CN)_4O(OH_2)}]^{2-}$,[15] and Mo–O (central) of 2.319(4) Å in $[\mathrm{Mo_6O_{19}}]^{2-}$,[16] the corresponding bond at 2.393(15) Å determined in the present study is no exception. The temperature factors of the O and O(OH$_2$) atoms [$\bar{U}$ 0.057(5) and 0.065(5) Å^2] in the

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[9] C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

[10] T. Gloviak, Dissertation, Wrozlaw, 1967, cited in L. O. Atovmyan, O. A. D'yachenko, and E. B. Lobkoviskki, *Zhur. Strukt. Khim.*, 1970, **11**, 469.

[11] D. L. McFadden and A. T. McPhail, unpublished work.

[12] G. Bunrey, J. H. Enemark, J. I. Gelder, K. Yamanonchi, and W. E. Newton, *Proc. Conf. Chem. and Uses of Molybdenum*, University of Oxford, 1976.

[13] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1975, 1984.

[14] P. M. Boorman, C. D. Garner, F. E. Mabbs, and T. J. King, *J.C.S. Chem. Comm.*, 1974, 663.

[15] P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, 1975, **14**, 2035.

[16] H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, 1973, **12**, 2963.

[17] B. Spivack and Z. Dori, *J.C.S. Dalton*, 1973, 1173.

[18] Present work and J. G. Scane and R. M. Stephens, *Proc. Phys. Soc.*, 1967, **92**, 833.

[19] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1968, **90**, 3374.

$[MoCl_4O(OH_2)]^-$ anion are not significantly different and so there is no indication of any similar, unusually large, thermal motion of the type noted for the $MoBr_4O$ group in $[MoBr_4O(OH_2)]^-$.[20]

The resulting overall anion geometry is that of a distorted octahedron in which the metal atom is displaced by 0.37 Å from the equatorial halogen-atom plane towards the multiply bonded oxygen atom to give supplementary O–Mo–Cl and $O(OH_2)$–Mo–Cl angles of 99.0(9) and 81.0(9)°, and approximately equal O · · · Cl and $O(OH_2)$ · · · Cl distances of 3.098 and 3.085 Å. Therefore, although the metal–ligand bonding interactions control the size of the complex, ligand–ligand repulsions appear to determine the shape. This leads to an arrangement of ligand donor atoms which closely approximates to that of an octahedron compressed down the *z* axis, with the metal ion displaced from the centre along this axis.

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Lengths			
Mo–Cl	2.359 (3)	C(1)–C(6)	1.386 (13)
Mo–O	1.672 (15)	C(2)–C(3)	1.355 (14)
Mo–$O(OH_2)$	2.393 (15)	C(3)–C(4)	1.355 (16)
As–C(1)	1.900 (9)	C(4)–C(5)	1.392 (17)
C(1)–C(2)	1.423 (13)	C(5)–C(6)	1.347 (15)
(*b*) Angles			
Cl–Mo–O	99.0(9)	As–C(1)–C(6)	118.7(7)
Cl–Mo–$O(OH_2)$	81.0(9)	C(1)–C(2)–C(3)	118.7(8)
Cl–Mo–Cl^{V}	88.6(1)	C(2)–C(3)–C(4)	122.0(10)
Cl–Mo–Cl^{VI}	162.0(1)	C(3)–C(4)–C(5)	119.2(11)
C(1)–As–$C(1^{I})$	111.5(4)	C(4)–C(5)–C(6)	121.1(10)
C(1)–As–$C(1^{III})$	105.5(4)	C(1)–C(6)–C(5)	120.0(9)
As–C(1)–C(2)	122.1(7)		
(*c*) Interionic distances <3.70 Å			
O · · · $O(OH_2{}^{IV})$	3.37	Cl · · · $C(3^{I})$	3.78
Cl · · · $C(2^{I})$	3.44	Cl · · · $C(2^{III})$	3.68
Cl · · · $C(4^{II})$	3.62		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I $\frac{1}{2} + y, 1 - x, -z$ IV $x, y, 1 + z$
II $\frac{1}{2} + y, 1 - x, 1 - z$ V $y, \frac{1}{2} - x, z$
III $\frac{3}{2} - x, \frac{1}{2} - y, z$ VI $\frac{1}{2} - x, \frac{1}{2} - y, z$

In order to minimize cation–anion interactions in the isomorphous crystals of salts of $[CrCl_4O]^-$,[21] $[MoCl_4O]^-$,[2] $[RuCl_4N]^-$,[22] and $[OsCl_4N]^-$,[23] the C–As–C valency angles in the $[AsPh_4]^+$ cation depart from ideal tetrahedral values such that one pair of angles is decreased [range 104.9(2)—105.5(3)°], four angles are correspondingly increased [111.8(2)—111.5(3)°], and the arsenic atom is displaced by a significant amount from the least-squares plane through the phenyl-ring atoms (Δ 0.116—0.128 Å). The As–C distances in the same salts range from 1.902(7) to 1.912(5) Å. In the $[MoCl_4O(OH_2)]^-$ salt the As–C bond length [1.900(9) Å] and C–As–C valency angles [105.5(4) and 111.5(4) Å] clearly lie within the same ranges, but the arsenic atom (Δ 0.022 Å) lies close to the phenyl-ring plane (root-mean-square deviation 0.011 Å). Thus, the interionic interactions are relieved in the present study almost exclusively by valency-angle deformation. Although the co-ordinated water molecule does not participate in any hydrogen bonding, it is of note that the *c* axis for the $[MoCl_4O(OH_2)]^-$ salt at 7.440(5) Å is shorter than the *c* axes in the other four salts discussed [7.785(5)—7.842(2) Å] and so the presence of this water molecule appears to reduce anion–anion repulsions in this direction.

Electronic Spectrum.—The electronic spectrum of $[NEt_4][MoCl_4O(OH_2)]$ in concentrated HCl, where e.s.r. measurements[1] indicate that the dominant species is $[MoCl_4O(OH_2)]^-$, has absorption maxima at *ca.* 14 100, 22 500, 28 100, 32 500, 42 400, and 47 700 cm^{-1}. The oscillator strength, *f*, of the first band is approximately twice that of the second band, as found for $[MoCl_4O]^-$ in CH_2Cl_2 solution, and thereafter *f* increases markedly with increasing transition energy (see Table 2). As found for $[MoCl_4O]^-$, the position of the first band in the spectrum is at a slighly different energy in the solid state compared with the solution. This again suggests that there may be some differences in the detailed geometry of the anions in these two phases.

The room-temperature polarized spectra of $[AsPh_4]$-$[MoCl_4O(OH_2)]$ show clearly that the two lowest-energy transitions are *xy* polarized. The general features of these spectra are reproduced at liquid-nitrogen and liquid-helium temperatures. At liquid-helium temperatures some further splittings were observed for the first band in *xy* polarization, but in contrast to $[AsPh_4]$-$[MoCl_4O]$ no fine structure was observed for the second band.[2]

The sense of the polarizations of the first two electronic-spectral absorptions for the $[MoCl_4O(OH_2)]^-$ chromophore of C_{4v} symmetry show that each of the bands arises from a transition of $E \longrightarrow B(A)$ character. By analogy with $[CrCl_4O]^-$,[24] $[MoCl_4O]^-$,[2] and in agreement with previous assignments,[25-34] the first band is attributed to the $b_2{}^*(4d_{xy}$, Mo–Cl $\pi^*) \rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$ excitation. The spatial degeneracy of the ^2E excited state occurs within the orbitals which are predominantly molybdenum 4*d* in character, and it is expected that the orbital degeneracy would be raised by spin–orbit coupling at this metal centre. This would split the ^2E state into two levels, Γ_6 and Γ_7, separated by approximately the value

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[20] J. G. Scane, *Acta Cryst.*, 1967, **23**, 85.

[21] K. D. Hargrave and A. T. McPhail, unpublished work.

[22] F. L. Phillips and A. C. Skapski, *Acta Cryst.*, 1975, **B31**, 2667.

[23] F. L. Phillips and A. C. Skapski, *J. Cryst. Mol. Structure*, 1975, **5**, 83.

[24] C. D. Garner, J. Kendrick, P. Lambert, F. E. Mabbs, and I. H. Hillier, *Inorg. Chem.*, 1976, **15**, 1287.

[25] C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 831.

[26] H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363.

[27] R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, 1964, **41**, 3884.

[28] K. de Armond, B. B. Garrett, and H. G. Gutousky, *J. Chem. Phys.*, 1965, **42**, 1019.

[29] H. Kon and N. N. Sharpless, *J. Phys. Chem.*, 1966, **70**, 105.

[30] P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 1968, **49**, 5510.

[31] D. P. Rilema and C. H. Brubaher, jun., *Inorg. Chem.*, 1970, **9**, 397.

[32] P. Spacu, C. Gheorghiu, M. Constantinescu, and L. Antonescu, *J. Less-Common Metals*, 1976, **44**, 161.

[33] I. N. Marov, *Proc. Conf. Chem. and Uses of Molybdenum*, ed. P. C. H. Mitchell, University of Reading, 1973, p. 63.

[34] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103 and refs. therein.

of the spin–orbit coupling constant, ζ, with Γ_6 lying lower than Γ_7. The selection rules [2] indicate that the higher-energy component should appear in z polarization whereas both components may appear in xy polarization. The spectral resolution obtained is, however, insufficient to allow such an assignment of the electronic origins. The observed fine structure may be assigned to coupling of the electronic excitation with a vibrational mode at *ca.* 760 cm^{-1}. This mode is attributed to the Mo–O stretching mode of the first electronic excited state. (In the ground state this mode is at 985 cm^{-1}.) Such a reduction in the frequency is expected, since the excitation $b_2^*(4d_{xy}$, Mo–Cl $\pi^*)\rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$ would weaken the Mo–O bonding interaction.

The absorption at 22 800 cm^{-1} cannot be assigned unambiguously. The equivalent band in $[\text{MoCl}_4\text{O}]^-$ was previously [2] assigned to the excitation $e(4d_{xz,yz}$, Mo–O $\pi)$ $\rightarrow a_1^*(4d_{z^2}$, Mo–O $\sigma^*)$. However, for the complexes $[\text{AsPh}_4][\text{MoCl}_4\text{O}]$,[2] $[\text{AsPh}_4][\text{MoCl}_4\text{O}(\text{OH}_2)]$, $[\text{AsPh}_4]_2[\text{MoCl}_5\text{O}]\cdot\text{CH}_2\text{Cl}_2$,[35] $[\text{MoCl}_3\text{O}\{\text{P}(\text{NMe}_2)_3\text{O}\}_2]$,[36] and $[\text{MoCl}_3\text{O}(\text{PPh}_3\text{S})]$,[35] this band varies very little in energy and there is no correlation with the changes in the Mo–O bond length. However, the energy of the first band in the spectra of these systems shows a decrease in energy with increasing Mo–O bond length. A similar correlation is expected for the energy of the second band in the spectrum if the transition is as suggested above. Thus the alternative assignment suggested for $[\text{MoCl}_3\text{O}\{\text{P}(\text{NMe}_2)_3\text{O}\}_2]$,[36] namely $e(4d_{xz,yz}$, Mo–O $\pi)\rightarrow b_2^*(4d_{xy}$, Mo–Cl $\pi^*)$, seems to be more reasonable based on the present evidence. This contrasts with earlier interpretations [25-34] which assigned this band in the $[\text{MoO}]^{3+}$ system to the $b_2^*(4d_{xy}$, Mo–Cl $\pi^*)\rightarrow b_2^*(4d_{x^2-y^2}$, Mo–Cl $\sigma^*)$ excitation.

TABLE 4

Molecular-orbital parameters for $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$

Formal charge on Mo	$\xi_{\text{Mo}}(4d)$ [a] / cm^{-1}	$-P_{\text{Mo}}$ [b] / $10^4\ \text{cm}^{-1}$	% Cl($3p$) assumed in e^*	Calc.[c] % $4d$ character in b_2	Calc.[c] % $4d$ character in e^* a	Calc.[c] % $4d$ character in e^* b
5+	1 030	67.5	4	70	66	44
			0	70	71	62
3+	820	55.0	4	86	72	53
			0	86	73	61
2+	695	48.2	4	98	81	65
			0	98	77	65

ξ_{Cl} ($3p$) 587 cm^{-1}; A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance,' Harper and Row, London, 1967, p. 138.

[a] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441. [b] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51. [c] Estimated range of values from fitting process are $<\pm 1\%$ for b_2^* and $<\pm 2\%$ for e^*. Absorption at 22 800 cm^{-1} assigned as $e(4d_{xz,yz}$,Mo–O $\pi)\rightarrow b_2(4d_{xy}$, Mo–Cl $\pi^*)$ in a and $e(4d_{xz,yz}$, Mo–O $\pi)\rightarrow a_1^*(4d_{z^2}$, Mo–O $\sigma^*)$ in b.

The absorptions at $>$23 500 cm^{-1} observed in the single-crystal electronic spectrum of $[\text{AsPh}_4][\text{MoCl}_4\text{O}(\text{OH}_2)]$ in general may be tentatively assigned on a similar basis to corresponding absorptions of $[\text{MoCl}_4\text{O}]^-$. Thus the xy-polarized band at 26 700 cm^{-1} (*cf.* the band at 26 400 cm^{-1} for $[\text{MoCl}_4\text{O}]^-$) may contain one or more of the excitations $e(4d_{xz,yz}$, Mo–O $\pi)\rightarrow a_1^*(4d_{z^2}$, Mo–O $\sigma^*)$, $a_1(4d_{z^2}$, Mo–O $\sigma)\rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$, and $b_1(4d_{x^2-y^2}$, Mo–Cl $\sigma)\rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$. The z-polarized band at 27 300 cm^{-1} (*cf.* the band at 26 800 cm^{-1} for $[\text{MoCl}_4\text{O}]^-$) may be due to one or more of the transitions $a_1(4d_{z^2}$, Mo–O $\sigma)\rightarrow a_1^*(4d_{z^2}$, Mo–O $\sigma^*)$, $e(4d_{xz,yz}$, Mo–O $\pi)\rightarrow e(4d_{xz,yz}$, Mo–O $\pi^*)$, and $b_1(4d_{x^2-y^2}$, Mo–Cl $\sigma)\rightarrow b_1^*(4d_{x^2-y^2}$, Mo–Cl $\sigma^*)$.

The major difference between the low-temperature single-crystal spectra of the $[\text{AsPh}_4]^+$ salts of $[\text{MoCl}_4\text{O}]^-$ and $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$ is the presence of an xy-polarized absorption at 24 300 cm^{-1} for the latter complex. The origin of the band is uncertain; however, it is possible that it corresponds to a transition which is at an energy $>$24 300 cm^{-1} in $[\text{MoCl}_4\text{O}]^-$. If this is so the absorption at 24 300 cm^{-1} may be suggested to occur within the Mo–O part of the chromophore, within which the bonding appears to be weakened by the addended water molecules. Possible assignments which are compatible with this assumption include $a_1(4d_{z^2}$, Mo–O $\sigma)\rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$ and $e(4d_{xz,yz}$, Mo–O $\pi)\rightarrow a_1^*(4d_{z^2}$, Mo–O $\sigma^*)$.

The absorptions observed at $>$28 000 cm^{-1} for $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$ dissolved in concentrated HCl solution are probably best assigned as chlorine to molybdenum charge-transfer transitions on the basis of their high oscillator strengths. As discussed for $[\text{CrCl}_4\text{O}]^-$ (ref. 2) and $[\text{MoCl}_4\text{O}]^-$,[2] we do not consider that the $b_2^*(4d_{xy}$, Mo–Cl $\pi^*)\rightarrow b_1^*(4d_{x^2-y^2}$, Mo–Cl $\sigma^*)$ transition has been observed for $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$. This transition, because of its expected low intensity, may be obscured by the more intense bands in the spectrum at energies $>$22 000 cm^{-1}.

E.S.R. Parameters.—The change in $\bar{g}$ observed between $[\text{MoCl}_4\text{O}]^-$ and $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$ has its origin almost entirely in the large difference in the $g_\perp$ values for these two systems. Expressions relating the principal molecular e.s.r. parameters, the electronic-transition energies, and the molecular-orbital (m.o.) coefficients, assuming square-pyramidal geometry and neglecting metal–ligand overlap terms, have been given previously.[37] These expressions show that the reduction in $g_\perp$ from 2.0023 is inversely proportional to the energy of the excitation $b_2^*(4d_{xy}$, Mo–Cl $\pi^*)\rightarrow e^*(4d_{xz,yz}$, Mo–O $\pi^*)$. Thus the smaller value of $g_\perp$ in $[\text{MoCl}_4\text{O}(\text{OH}_2)]^-$ (1.935) compared

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[35] C. D. Garner and F. E. Mabbs, unpublished work.

[36] C. D. Garner, T. J. King, P. Lambert, and F. E. Mabbs, *J.C.S. Dalton*, 1977, 1191.

[37] C. D. Garner, I. H. Hillier, F. E. Mabbs, C. Taylor, and M. F. Guest, *J.C.S. Dalton*, 1976, 2258.

with $[MoCl_4O]^-$ (1.950) is in part attributable to the lower $b_2^* \rightarrow e^*$ transition energy in the former complex (13 200 cm^{-1}) compared with that in the latter (15 400 cm^{-1}). Similarly, the reduction of $g_{\parallel}$ from 2.0023 is inversely proportional to the $b_2^*(4d_{xy}$, Mo–Cl $\pi^*) \rightarrow b_1^*(4d_{x^2-y^2}$, Mo–Cl σ^*) excitation energy. Both these systems give $g_{\parallel}$ values which are very similar and, since it is likely that the appropriate m.o. coefficients will not be very different it appears that the above $b_2^* \rightarrow b_1^*$ transition energies are very similar in the two systems.

Because we were unable to locate the $b_2^*(4d_{xy}$, Mo–Cl $\pi^*) \rightarrow b_1^*(4d_{x^2-y^2}$, Mo–Cl σ^*) transition we have, as previously,[2] used the experimental data to estimate the percentage 4*d*-orbital contribution to only the b_2^* and e^* m.o.s. The resulting values are summarized in Table 4. The general pattern of the dependence of the m.o. coefficients on the charge assumed on the molybdenum in the complex, noted [2] for $[MoCl_4O]^-$, is also found for $[MoCl_4O(OH_2)]^-$. The amount of $Cl(3p_{\pi})$ character assumed in the $e^*(4d_{xz,yz}$, Mo–O π^*) m.o. generally makes less difference to the metal *d*-orbital character of this orbital on assignment *a* than it does on assignment *b*. However, what is most important in determining the metal contribution to e^* is the assignment of the second band in the electronic spectrum. If the assignment proposed here, namely $e \rightarrow b_2^*$, is correct then the metal 4*d*-orbital contribution to e^* is *ca.* 10—20% greater than would have been estimated from previous assignments,[2,25-34] where the particular excited states proposed did not contribute to $g_{\perp}$. Assuming that a charge of 2+ on the molybdenum is reasonable, then the metal *d*-orbital contribution to e^* is similar to that calculated [24] for $[CrCl_4O]^-$. Reassignment of the second band in the electronic spectrum of $[MoCl_4O]^-$, as above, also results in the *d*-orbital contribution to the e^* m.o. of this species being increased to 82%, a value insignificantly different from that found here. Thus our technique of interpreting the e.s.r. data is not sufficiently sensitive to detect the anticipated increase in the metal character in e^* as the Mo–O bond length increases from $[MoCl_4O]^-$ to $[MoCl_4O(OH_2)]^-$.

On the other hand, the present results, for any assumed charge on the molybdenum, do indicate that there is more metal character in the $b_2^*(4d_{xy}$, Mo–Cl π^*) m.o. of $[MoCl_4O(OH_2)]^-$ than in the corresponding orbital of $[MoCl_4O]^-$. This correlates qualitatively with the expected weakening in the π-bonding between the metal $4d_{xy}$ and $Cl(3p_{\pi})$ orbitals as the Mo–Cl bond length increases from 2.333(3) Å in $[MoCl_4O]^-$ to 2.359(3) Å in $[MoCl_4O(OH_2)]^-$.

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