Crystal Structure of, and Solution Adduct Equilibria involving, Tetraphenylarsonium Tetrachloro-oxochromate(V)

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Crystals of the title complex are tetragonal, space group *P4/n*, with a = 12.590(7), c = 7.840(5) Å, and Z = 2. The crystal structure has been solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.059 over 860 statistically significant reflections from diffractometer measurements (Cu-K_α radiation). The square-pyramidal $[CrCl_4O]^-$ anion has crystallographic $4mm(C_{4v})$ symmetry with Cr–O 1.519(12) and Cr–Cl 2.240(3) Å, and O–Cr–Cl 104.5(1)° The $[AsPh_4]^+$ cation has crystallographic $\bar{4}(S_4)$ symmetry [As–C 1.906(6) Å; C–As–C 105.3(3) and 111.5(3)°]. E.s.r. spectroscopy has been used to estimate the equilibrium constants for the reaction $[CrCl_4O]^- + L \overset{K}{\rightleftharpoons} [CrCl_4OL]^{n-}$ in CH_2Cl_2 solution {n = 1 when L = PPh_3O (K = 3 ± 2), $P(NMe_2)_3O$ (K = 463 ± 130), thf (K < 1), or py (K = 160); n = 2 when L = Cl^- (K = 43 ± 10 with $[AsPh_4]Cl$ and 250 ± 33 $dm^3 mol^{-1}$ with $[NEt_4]Cl$)}.

COMPLEXES of the $[CrO]^{3+}$ fragment have been known for a number of years and there has been considerable attention devoted to their electronic structures.[1,2] Despite this interest, none of the complexes has been characterised by a single-crystal *X*-ray structure determination. Here we report the crystal structure of the title complex. The presence of the oxo-group in a number of systems is known to cause a *trans*-weakening effect which is recognisable in structural, kinetic, and equilibrium information.[3,4] In addition to the structural data, we also report an e.s.r. study of the equilibria involved in the addition of other ligands to the $[CrCl_4O]^-$ ion, similar to that already reported[4] for $[MoCl_4O]^-$.

EXPERIMENTAL

The salt $[AsPh_4][CrCl_4O]$ was prepared and single crystals grown as reported earlier.[5]

Crystal Data.—$C_{24}H_{20}AsCl_4CrO$, $M = 593.2$, Tetragonal, $a = 12.590(7)$, $c = 7.840(5)$ Å, $U = 1\,243$ Å^3, D_m(flotation) = 1.57, $Z = 2$, $D_c = 1.585$, $F(000) = 594$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 96.8 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*. 0.24 × 0.26 × 0.60 mm was sealed inside a thin-walled glass capillary under a nitrogen atmosphere and orientated to rotate about the needle *c* axis. Preliminary unit-cell dimensions and space-group information were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation and precession photographs taken with Mo-K_α radiation (λ 0.710 7 Å). The crystal was then transferred to an Enraf–Nonius CAD 3 diffractometer (nickel-filtered Cu-K_α radiation, 3° take-off angle) and more accurate

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

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

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unit-cell parameters were calculated by least-squares treatment of the θ, χ, and ϕ angles for 40 high-order reflections widely separated in reciprocal space. Intensity data to θ 67° were recorded by the θ—2θ scanning procedure with scan widths $(1.10 + 0.55 \tan \theta)^{\circ}$. Instrument and crystal stability were monitored throughout by remeasuring the intensity of a strong standard reflection after each batch of 99 reflections and no significant variation was noted. Background measurements were made at each end of the scan range for a time equal to half the scan period. These measurements produced 860 independent reflections with $I > 2.0\sigma(I)$ [$\sigma^2(I)$ = scan count + total background count] and these were corrected for the usual Lorentz and polarisation effects. Absorption corrections, established from the dependence of ϕ on the intensity of the 005 reflection measured at χ 90°, were also applied to these data.

Structure Analysis.—Comparison of the intensity data with those of $[AsPh_4][MoCl_4O]$ indicated that the crystals were isomorphous. The arsenic atom was placed at $\frac{3}{4},\frac{1}{4},0$ (space group origin at $\bar{1}$)[6] and the variable z co-ordinate of the chromium atom, constrained by symmetry to lie at $\frac{1}{4},\frac{1}{4},z$, was established from the three-dimensional Patterson map. Positions for the other non-hydrogen atoms were determined from a three-dimensional F_o Fourier synthesis phased by the arsenic and chromium (R 0.38). Refinement of the positional and thermal parameters by full-matrix least-squares calculations proceeded smoothly to R 0.095. Calculated hydrogen-atom positions were confirmed to coincide with regions of significant positive electron density in a difference-Fourier synthesis, and their positional and isotropic thermal parameters were then included as variables in the least-squares cycles. The refinement converged at R 0.059. Final atomic-positional and isotropic thermal parameters are in Table 1. Anisotropic thermal parameters for the non-hydrogen atoms and observed and calculated structure amplitudes are in Supplementary Publication No. SUP 22078 (7 pp.).*

TABLE 1

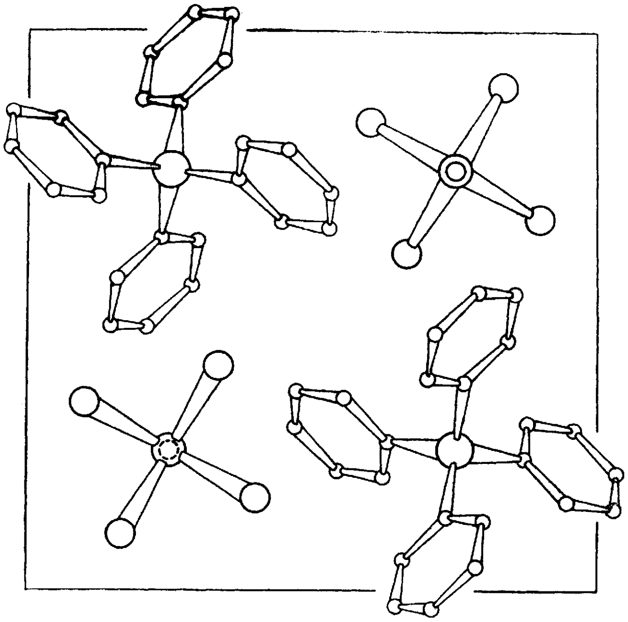
Fractional atomic co-ordinates * ($\times 10^4$) and isotropic thermal parameters (Å $\times 10^3$) for the hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	U
Cr	2 500(—)	2 500(—)	1 219(3)	
As	7 500(—)	2 500(—)	0(—)	
O	2 500(—)	2 500(—)	−718(14)	
Cl	1 648(2)	1 003(2)	1 934(3)	
C(1)	7 348(5)	1 305(5)	1 472(8)	
C(2)	6 578(6)	548(6)	1 135(11)	
C(3)	6 457(8)	−279(6)	2 300(13)	
C(4)	7 092(7)	−318(6)	3 754(12)	
C(5)	7 867(7)	430(6)	4 023(10)	
C(6)	7 984(6)	1 237(6)	2 897(9)	
H(2)	604(6)	61(6)	14(9)	17(19)
H(3)	560(9)	−73(10)	154(13)	77(34)
H(4)	689(7)	−89(7)	436(13)	47(28)
H(5)	831(7)	42(7)	495(10)	39(25)
H(6)	841(7)	163(6)	307(9)	15(20)

* Hydrogen-atom co-ordinates are $\times 10^3$.

For all the structure-factor calculations, neutral-atom scattering factors for arsenic, chromium, carbon, chlorine, and oxygen were from ref. 7 and for hydrogen from ref. 8, with those of As, Cr, and Cl corrected for the real part of anomalous dispersion.[9] In the least-squares calculations $\Sigma w\Delta^2$ was minimised with weights w assigned according to the scheme $w^{\frac{1}{2}} = 1$ for $|F_o| < 17.8$ and $17.8/|F_o|$ for $|F_o| > 17.8$.

E.S.R. Measurements.—These were made on CH_2Cl_2 solutions at room temperature using Q-band frequencies as previously described.[4] All the solutions were prepared in a dry-box under dinitrogen. The relative concentrations of the species in solution were assumed to be proportional[10] to $h(\Delta H)^2$, where h = peak-to-peak height and ΔH = the peak-to-peak width of the first derivative of the Cr ($I = 0$) absorption. Because the relative intensities of the e.s.r. signals changed slowly over a period of several hours, equilibrium data were taken from spectra obtained within 15 min of the preparation of the solutions. Single-crystal e.s.r. spectra were obtained at room temperature and Q-band frequencies as described previously.[11]



Crystal structure, viewed in projection along the c axis

Drying of Reagents.—Dichloromethane was dried as described previously.[4] Pyridine (py) and tetrahydrofuran (thf) were distilled from metallic sodium. Triphenylphosphine oxide, tetraphenylarsonium chloride, and tetraethylammonium chloride were dried *in vacuo* for 48 h, whilst tris(dimethylamino)phosphine oxide was used as supplied (B.D.H., laboratory reagents).

RESULTS AND DISCUSSION

The arrangement of the ions in the crystal, viewed in projection along the c axis, is shown in the Figure. The

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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crystals are isomorphous with those of the corresponding salts of $[MoCl_4O]^-$,[12] $[RuCl_4N]^-$,[13] and $[OsCl_4N]^-$,[14] and contain discrete $[CrCl_4O]^-$ anions with square-pyramidal $4mm(C_{4v})$ point symmetry and distorted tetrahedral $[AsPh_4]^+$ cations with crystallographic $\bar{4}(S_4)$ point symmetry. Interatomic distances and angles are in Table 2.

TABLE 2

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

(*a*) Bond lengths

Cr–Cl	2.240(3)	C(2)–C(3)	1.394(12)
Cr–O	1.519(12)	C(3)–C(4)	1.394(14)
As–C(1)	1.906(6)	C(4)–C(5)	1.375(12)
C(1)–C(2)	1.384(10)	C(5)–C(6)	1.351(11)
C(1)–C(6)	1.377(10)	C–H (mean)	0.99

(*b*) Valency angles

Cl–Cr–O	104.5(1)	As–C(1)–C(6)	118.8(5)
Cl–Cr–Cl′	86.4(1)	C(2)–C(1)–C(6)	121.3(6)
Cl–Cr–Cl″	151.0(2)	C(1)–C(2)–C(3)	117.7(7)
C(1)–As–C(1′)	111.5(3)	C(2)–C(3)–C(4)	120.0(8)
C(1)–As–C(1″)	105.5(3)	C(3)–C(4)–C(5)	120.5(8)
As–C(1)–C(2)	119.9(5)	C(4)–C(5)–C(6)	119.5(8)
C(1)–C(6)–C(5)	120.9(7)		

(*c*) Anion–cation distances <3.70 Å

$O \cdots C(3^I)$	3.33	$O \cdots C(4^I)$	3.67
$C(2) \cdots Cl^{II}$	3.59		

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

I $\frac{1}{2} + y, 1 - x, -z$ II $\frac{1}{2} - y, x, z$

The Cr–Cl distance [2.240(3) Å] agrees well with the mean [2.238(5) Å][15] at five-co-ordinate trigonal-bipyramidal Cr^{III} in $[CrCl_3(NMe_3)_2]$ and is slightly shorter than the mean (2.295 Å)[16] at six-co-ordinate chromium in $[CrCl_2(HOMe)_4]Cl$ and 2.290(5)—2.346(4) Å in $[(\eta\text{-}Ph)CrCl_3Li(thf)_2]_2(C_4H_8O_2)$.[17]

The Cr–O distance [1.519(12) Å] in the $[CrCl_4O]^-$ anion is significantly less than the short lengths usually associated with terminal Cr–O bonds[18] and, like its counterpart in the $[MoCl_4O]^-$ anion recently studied by us,[12] appears to be the shortest distance yet encountered for such a bond. A similar bonding arrangement involving $d_{x^2-y^2}sp$ hybrid orbitals of the metal atoms may be visualised for the $[CrCl_4O]^-$, $[MoCl_4O]^-$, $[RuCl_4N]^-$, and $[OsCl_4N]^-$ anions in each of which p–d π-bonding results from overlap of the oxygen or nitrogen p orbitals with unoccupied metal d_{xz} and d_{yz} orbitals, thereby resulting in multiple bonds which possibly correspond to a bond order of three in each of these species. Despite much smaller $Cl \cdots Cl'$ and $Cl \cdots O$ distances [3.066(4) and 3.004(8) Å] in $[CrCl_4O]^-$ compared with those [3.161(2)—3.183(4) and 3.102(5)—3.164(8) Å] in the other three anions, the valency angles in each of these four anions show very little variation, *e.g.* Cl–M–Cl′ 86.0(1)—86.4(1), Cl–M–Cl″ 149.5(1)—151.0(2), and X–M–Cl 105.2(1)—104.5(1)°, where M is the metal atom and X the axial ligand. This implies that the geometries of the anions are probably determined by a combination of ligand–ligand and bond pair–bond pair electron repulsions. Thus repulsion between the ligands, and also between the π electrons in the M–X multiple bonds and the σ electrons in the M–Cl bonds, are minimised through the increase of the X–M–Cl valency angles from 90°.

In the $[AsPh_4]^+$ cation the valency angles at the arsenic atom show deformations from ideal tetrahedral values similar to those found in the isomorphous crystals of the other three anion salts discussed above. Non-bonded interactions between the phenyl rings and the anions in each of these crystals are minimised by the reduction of a pair of C–As–C valency angles with concomitant increase in the other four angles and out-of-plane displacement of the arsenic atom. In the $[CrCl_4O]^-$ salt these valency angles assume values of 105.5(3) and 111.5(3)°, while in the other salts they range from 104.9(2) to 105.4(3) and 111.8(2) to 111.5(2)°. The arsenic atom is displaced significantly, Δ 0.119 Å, from the least-squares plane through the phenyl ring atoms (root-mean-square deviation 0.008 Å) in the $[CrCl_4O]^-$ salt; corresponding displacements in the other salts are 0.123 $[MoCl_4O]^-$, 0.128 $[RuCl_4N]^-$, and 0.116 Å $[OsCl_4N]^-$. Other dimensions in the cation show no unusual features.

Solution Equilibria.—The addition of $[AsPh_4]Cl$, $[NEt_4]Cl$, $P(NMe_2)_3O$, PPh_3O, or py to dichloromethane solutions of $[AsPh_4][CrCl_4O]$ was monitored by e.s.r. spectroscopy. In each case the original resonance, $\bar{g} = 1.988$, was retained and an additional signal with $\bar{g} = 1.970 \pm 0.001$ was observed. The peak-to-peak linewidths of the first-derivative spectra were 7.5 ± 0.3 and 15.0 ± 1.0 G for $[CrCl_4O]^-$ and $[CrCl_4OL]^{n-}$ respectively.* By analogy with similar observations[4] on $[AsPh_4][MoCl_4O]$, we interpret these observations in terms of equilibrium (1) where $n = 1$ when L =

$$[CrCl_4O]^- + L \overset{K}{\rightleftharpoons} [CrCl_4OL]^{n-} \tag{1}$$

$P(NMe_2)_3O$, PPh_3O, or py and $n = 2$ when $L = Cl^-$ Values of the equilibrium constants, K, for these associative processes are listed in Table 3.

The $\bar{g}$ value for the proposed $[CrCl_5O]^{2-}$ ion here is lower than that (1.9877) reported previously[19] from

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* Throughout this paper: 1 G = 10^{-4} T.

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solution and frozen-glass spectra. A single-crystal study on a system known to contain the $[CrCl_5O]^{2-}$ ion would be valuable to clarify this discrepancy. Addition of chloride ions as $[AsPh_4]Cl$ to a solution of $[AsPh_4][CrCl_4O]$ led to an equilibrium constant for the formation of $[CrCl_5O]^{2-}$ (Table 3) in the range 43 ± 10 dm³ mol⁻¹ which is comparable to that observed in the corresponding molybdenum system.[4] Also, as found in the latter system, the addition of chloride ions as $[NEt_4]Cl$ increased the equilibrium constant substantially (K 250 ± 33 dm³ mol⁻¹). This enhancement in K is again attributed to ion-pair formation between the doubly charged anion and the cation varying as $[NEt_4]^+ \gg [AsPh_4]^+$.

TABLE 3

Equilibrium constants at room temperature for the reaction $[AsPh_4][CrCl_4O] + L^{n-} \rightleftharpoons [AsPh_4]_{(1+n)}[CrCl_4OL]$ (Initial [complex] = 10^{-3} mol dm⁻³)

Added reagent	Initial ratio $[CrCl_4O]$: L	K dm³ mol⁻¹
$[AsPh_4]Cl$	1 : 14.6	33
	1 : 29.2	38
	1 : 43.8	37
	1 : 54.8	53
	1 : 65.7	50
$[NEt_4]Cl$	1 : 20	216
	1 : 40	276
	1 : 50	283
$P(NMe_2)_3O$	1 : 4.8	338
	1 : 9.6	333
	1 : 19.0	593
PPh_3O	1 : 6	1
	1 : 11	2
	1 : 22	3
	1 : 33	5
py	1 : 1.0	160

The equilibrium constants for the formation of monoadducts with PPh_3O and $P(NMe_2)_3O$ were found to be 3 ± 2 and 460 ± 130 dm³ mol⁻¹ respectively. These values are in the same relative order as those found for the corresponding molybdenum systems,[4] but are significantly smaller. The addition of pyridine up to a [py] : [Cr] molar ratio of 1 : 1 gave rise to an e.s.r. signal at $\bar{g} = 1.970$ in addition to that for $[CrCl_4O]^-$. These observations lead to an equilibrium constant of *ca.* 160 dm³ mol⁻¹ for the association of py and $[CrCl_4O]^-$ under these conditions. However, for [py] : [Cr] ratios $> 1 : 1$ no signals due to $[CrCl_4O]^-$ could be detected, the only observable resonance being a very weak signal at $\bar{g} = 1.970$. This behaviour suggests that a redox reaction has occurred, although polymerisation of the chromium(V) species cannot be ruled out. The addition of a large excess of thf ([thf] : Cr > 100 : 1) to a solution of $[AsPh_4][CrCl_4O]$ in CH_2Cl_2 gave an e.s.r. signal at $\bar{g} = 1.980$ in addition to that for $[CrCl_4O]^-$. This additional signal was attributed to $[CrCl_4O(thf)]^-$ with an equilibrium constant of formation which is less than 1 dm³ mol⁻¹.

The small values of the equilibrium constants for the formation of $[CrCl_4OL]^{n-}$ adducts are compatible with the already well established *trans*-weakening effect of the oxo-group in, for example, complexes containing the $[VO]^{2+}$ or $[MoO]^{3+}$ group. In the case of uncharged ligands the equilibrium constants indicate that $[CrCl_4O]^-$ is a poorer acceptor than $[MoCl_4O]^-$. This may represent a general difference between first- and second-transition-series oxometal species since we have so far been unable to detect from e.s.r. measurements any adduct formation in CH_2Cl_2 solution between $[NEt_4]_2[VCl_4O]$ and Cl^-, PPh_3O, or $P(NMe_2)_3O$, or between $[VCl_2O(PPh_3O)_2]$ and PPh_3O.[20]

The attempted isolation of monoadducts of $[AsPh_4][CrCl_4O]$ has so far been unsuccessful. Rapid cooling of solutions or the addition of precipitating solvents simply led to recovery of $[AsPh_4][CrCl_4O]$. Very slow evaporation of the solutions in a dry-box over the course of several days gave purple solids with magnetic moments, based on their chromium content, which indicated that they are chromium(III) complexes. A similar observation has recently been reported by Seddon and Thomas.[2] More rapid concentration at room temperature under dry nitrogen of solutions containing excess of chloride gave orange-brown crystals, the analyses for which correspond closely to $[AsPh_4][CrClO_3]$. Although the magnetic susceptibility of a powdered sample showed it to be diamagnetic, the single crystals gave e.s.r. signals, the overall behaviour being that of a tetragonal system giving $g_{\parallel} = 1.974 \pm 0.001$ and $g_{\perp} = 1.970 \pm 0.001$. Despite the narrow lines (the peak-to-peak width of the first-derivative spectrum was 12 G at $g_{\parallel}$ and 14 G at $g_{\perp}$) no chromium hyperfine lines were resolved. Solutions of these crystals in CH_2Cl_2 gave two e.s.r. signals at $\bar{g} = 1.989$ and 1.972 analogous to the observations on the addition of chloride to a solution of $[AsPh_4][CrCl_4O]$. We therefore tentatively suggest that the orange-brown crystals are $[AsPh_4][CrClO_3]$ containing a small amount of $[CrCl_5O]^{2-}$.

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[7/176 *Received, 2nd February,* 1977]

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