Complexes of Molybdenum and Tungsten Chlorides

By **D. G. Blight, D. L. Kepert, R. Mandyczewsky,*** and **K. R. Trigwell,** The University of Western Australia, Nedlands, Western Australia

Six-co-ordinate complexes of the type $WCl_4(ligand)_2$ and $WCl_4(bidentate)$ and the apparently seven-co-ordinate $[WCl_4(Me_3N)_3]$ have been obtained from $[WCl_4(RCN)_2]$ under mild conditions. Reduction to polymeric tungsten(III) compounds occurs under more vigorous conditions. The bidentate *o*-phenylenebisdimethylarsine forms a number of complexes, including the seven-co-ordinate $[WCl_5(diars)]$ and $[WOCl_4(diars)]$. However no evidence for eight-co-ordinate $[MCl_4(diars)_2]$ or $[MCl_4(diars)_2]^+$ (where M is Mo or W) could be obtained.

FOLLOWING our earlier report[1] that the reaction of pyridine with tungsten(IV) under vigorous conditions yielded the paramagnetic tungsten(III) complex $WCl_3(py)_2$, and the similar work by Boorman, Greenwood, and Hildon[2] who obtained $WCl_3(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)$ and $WCl_3(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2$, we have used this reaction to produce further examples of tungsten(III).

Secondly, the ligand *o*-phenylenebisdimethylarsine, $o\text{-}C_6H_4(AsMe_2)_2$, has proved to be outstandingly successful in stabilising dodecahedral eight-co-ordinate complexes $MCl_4(diars)_2$ (M = Ti, Zr, Hf, V, Nb, Ta, or U)[3-6] or $[MCl_4(diars)_2]^+$ (M = Tc or Re).[7] The properties of the analogous pentavalent (d^1) or tetravalent (d^2) molybdenum and tungsten compounds would be of considerable interest. However, although a number of seven-co-ordinate diarsine compounds are reported in this Paper, we were unsuccessful in obtaining any eight-co-ordinate complexes.

RESULTS AND DISCUSSION

Tungsten(IV).—Simple six-co-ordinate compounds $WCl_4(bipy)$, $WCl_4(Ph_3P)_2$, and $WCl_4(PrCN)(Me_3P)$ were obtained from $WCl_4(PrCN)_2$ or $WCl_4(MeCN)_2$ under mild conditions. These appear completely analogous to other octahedral tungsten(IV) compounds[1,2,8-11] and were not examined in detail.

Under the same conditions trimethylamine formed the tris-adduct $WCl_4(Me_3N)_3$. This compound is significantly conducting in dry nitromethane, but only approaches the value expected for a 1 : 1 electrolyte below 2×10^{-4}M. The compound is therefore apparently seven-co-ordinate in the solid state but dissociates in dilute solution into $[WCl_3(Me_3N)_3]^+$ and Cl^-. The compound has a room-temperature effective magnetic moment of 1·43 B.M., and follows the Curie–Weiss law with $\theta = 6°$. This is in contrast to six-co-ordinate tungsten tetrachloride adducts which have room-temperature effective magnetic moments in the range 1·7—2·1 B.M. but which fall to 1·3—1·5 B.M. at liquid-nitrogen temperatures,[1,2,8-11] and also to the other seven-co-ordinate complex $[WCl_4(PhMe_2P)_3]\frac{1}{2}C_6H_6$ which has an effective magnetic moment of 2·68 B.M. approximately independent of temperature.[2]

Tungsten(III).—The reaction of $WCl_4(MeCN)_2$ with bipyridyl under vigorous conditions forms $WCl_3(bipy)$ which appears completely analogous to $WCl_3(py)_2$ reported earlier.[1]

The analogous reaction with trimethylamine yielded $WCl_3(Me_3N)_2$. The stereochemistries of compounds of the type $[MX_3(Me_3N)_2]$ are of particular interest since the bulky ligands force trigonal bipyramidal stereochemistry, with the organic ligand occupying the two axial sites. This is confirmed by the *X*-ray crystal structures of $AlH_3(Me_3N)_2$,[12] $AlCl_3(Me_3N)_2$,[13] $TiBr_3(Me_3N)_2$,[14] $CrCl_3(Me_3N)_2$,[15] and even $VOCl_2(Me_3N)_2$.[16] On the other hand a polymeric structure for $WCl_3(Me_3N)_2$ with a co-ordination number greater than five is also feasible.

The compound has a room-temperature effective magnetic moment of 0·90 B.M., which increases to 0·98 B.M. at liquid-nitrogen temperatures. This compares with an expected room-temperature value of *ca.* 1·5 B.M., falling to *ca.* 1·2 B.M. at liquid-nitrogen temperatures, for tungsten(III) in a trigonal bipyramidal ligand field,[17] indicating that this is a polymeric compound with a co-ordination number greater than five.

The preparation of analytically pure tungsten(III) compounds with *o*-phenanthroline, triethylamine, trimethylphosphine, triphenylphosphine, triphenylarsine,

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and dimethyl sulphide were unsuccessful despite repeated attempts.[18]

Diarsine Complexes.—Complexes containing one molecule of *o*-phenylenebisdimethylarsine per metal atom which have been characterised here include the seven-co-ordinate tungsten compounds WCl_5(diars) and $WOCl_4$(diars), the molybdenum compounds $MoOCl_3$(diars) and Mo_2OCl_8(diars)$_2$(dioxan) which are probably seven-co-ordinate, and the tetrachloro-adducts $MoCl_4$(diars) and WCl_4(diars) of unknown stereochemistry.

The compound WCl_5(diars) is isomorphous with the previously characterised $NbCl_5$(diars) and $TaCl_5$(diars),[19] and is therefore seven-co-ordinate. The room-temperature effective magnetic moment of 1·19 B.M. is consistent with a single *d* electron.

The diamagnetic non-electrolyte $WOCl_4$(diars) is remarkably stable with respect to air, water, and organic solvents. The crystal structure shows a seven-co-ordinate pentagonal bipyramidal structure.[20] Of all the ligand sites available in the different seven-co-ordinate stereochemistries,[21] the sterically least hindered are the apical sites of the pentagonal bipyramid, which make ligand–metal–ligand angles of 90° to the nearest ligands. The oxygen atom occupies one of these sites, and the bidentate ligand occupies two of the more hindered planar sites as expected, with the chlorine atoms distributed over the remaining apical and three planar sites. A very strong band in the i.r. spectrum at 964 cm^{-1} is assigned to the tungsten–oxygen stretching frequency.

Diarsine was found to reduce $MoOCl_4$ in carbon tetrachloride yielding a yellow-brown mass from which the molybdenum(v) complex $MoOCl_3$(diars) could be isolated. The same compound was also obtained from the reactions of diarsine with: (*a*) $MoCl_5$ in methanol, (*b*) $MoCl_5$ in acetone, (*c*) $MoOCl_3$ in acetone, and (*d*) $MoCl_5$ in concentrated hydrochloric acid.

The compound $MoOCl_3$(diars) is a non-electrolyte in acetonitrile, but differs in properties to other oxomolybdenum(v) complexes which contain a strong, non-bridging, Mo=O group.[22] The magnetic moment of 1·4—1·5 B.M. is low compared with 1·6—1·8 B.M. for other $MoOCl_3$(ligand)$_2$ complexes,[22] but is higher than 1·3—1·4 B.M. observed for molybdenum(v) complexes not containing a molybdenum–oxygen bond.[23,24] The light brown colour of $MoOCl_3$(diars) is in contrast to the usual bright green colours of MoO^{3+} complexes which are associated with the molybdenum–oxygen π-bonds.[22] The molybdenum–oxygen stretching frequencies at 956 and 932 cm^{-1} are lower than usually observed (*ca.* 990 cm^{-1}).[22] The results suggest that the oxygen atom is bridging, but not equidistant between, two metal atoms leading to a seven-co-ordinate structure.

Molybdenum pentachloride and diarsine in dioxan yield a solid analysing as Mo_2OCl_8(diars)$_2$(diox). Oxygen-abstraction reactions between molybdenum pentachloride and dioxan have been described in an earlier paper.[24] The i.r. spectrum confirms the presence of dioxan and diarsine, and also shows a strong molybdenum–oxygen stretching frequency at 988 cm^{-1}. The observed room-temperature effective magnetic moment of 1·54 B.M. confirms the +5 oxidation state. Conductivity measurements indicate a 1 : 1 electrolyte, the most likely formula being the seven-co-ordinate [$MoOCl_2$(diars)$_2$][$MoCl_6$(diox)].

The tetravalent complexes $MoCl_4$(diars) and WCl_4(diars) were readily obtained from acetonitrile. The molybdenum complex was isolated from the reaction of diarsine with molybdenum pentachloride in acetonitrile. Similar reactions with tungsten yielded complexes containing 1·5 molecules of diarsine per tungsten atom (see below). However, WCl_4(diars) could be obtained from the reaction of WCl_5(diars) with acetonitrile. Both complexes are isomorphous with each other, but not with $TiCl_4$(diars).[3,5]

In addition to $WOCl_4$(diars), WCl_5(diars), and WCl_4(diars), routine *X*-ray powder examination of the products formed from tungsten chlorides and diarsine over a wide range of preparative conditions indicate that other compounds were formed. Characterisation of these phases was hampered by their rapid precipitation and insolubility, leading to mixtures which could not be separated into their constituents. It can be certainly stated, however, that none of these products is isomorphous with the known MCl_4(diars)$_2$ or [MCl_4(diars)$_2$]Cl. Analytical results show that these compounds contain *ca.* 1·5 molecules of diarsine for each tungsten atom.[18]

Decomposition of $MoCl_4$(diars), WCl_5(diars), and $WCl_5,1\frac{1}{2}$(diars) with aqueous alkali, extraction of the organic matter and analysis by v.p.c. showed only the presence of diarsine, with no trace of triarsine.[25]

Possibly the most interesting feature of this diarsine chemistry of these Group VI elements is that although seven-co-ordinate complexes are readily prepared, we were unable to prepare the eight-co-ordinate [MCl_4(diars)$_2$]$^+$ or [MCl_4(diars)$_2$]. The former are known for the Group VII elements technetium and rhenium, and the latter for the Group IV elements titanium, zirconium, and hafnium, the Group V elements vanadium, niobium, and tantalum, and uranium (see Introduction). It is difficult to account for this difference in terms of the trends in atomic properties of these elements. The technetium and rhenium compounds were prepared by chlorination of the divalent compounds [MCl_2(diars)$_2$] and it was thought that they may not be

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compounds of diarsine with metal(V), but of chlorinated diarsine with the metal in a lower oxidation state. It is known that the higher metal chlorides chlorinate aromatic compounds,[26,27] and also that free diarsine reacts with chlorine to form (diars.Cl)$^+$Cl$^-$. However decomposition of [ReCl$_4$(diars)$_2$]Cl and extraction of the ligand again showed only the presence of unchanged diarsine.

Magnetic data for trimethylamine complexes

$WCl_4(Me_3N)_3$		$WCl_3(Me_3N)_2$		
T/K	$10^6\chi'_M$/ c.g.s.u.	T/K	$10^6\chi'_M$/ c.g.s.u.	$\mu_{eff.}$/B.M.
309·2	730	309·2	312	0·88
294·7	837	294·8	343	0·90
266·8	846	263·9	386	0·91
229·8	996	227·4	480	0·94
200·6	1150	199·4	572	0·96
173·8	1319	171·4	686	0·97
144·3	1560	142·0	832	0·98
112·7	1911	114·0	1062	0·99
88·5	2362	88·0	1340	0·98

EXPERIMENTAL

Tetrachloro(2,2′-*bipyridyl*)*tungsten*(IV).—Freshly prepared WCl$_4$(CH$_3$CN)$_2$ (3 g) was dissolved in dry acetonitrile (50 ml) and added to 2,2′-bipyridyl (2 g) dissolved in acetonitrile (20 ml). The mixture was cooled and the resulting precipitate was filtered off and dried *in vacuo* (Found: C, 26·6; H, 2·6; Cl, 28·2; W, 37·5. $C_{10}H_8Cl_4N_2W$ requires C, 24·9; H, 1·7; Cl, 29·4; W, 38·1%). The compound is a non-electrolyte in pyridine.

Tetrachlorobis(*triphenylphosphine*)*tungsten*(IV).— Tetrachlorodi(n-propyl cyanide)tungsten(IV) (1·0 g) was completely dissolved in benzene (60 ml) and triphenylphosphine was added to the solution. The bright yellow precipitate which formed immediately was filtered off, washed with benzene, and dried *in vacuo* (Found: C, 50·2; H, 3·8; Cl, 16·6; P, 6·8; W, 22·4. $C_{36}H_{30}Cl_4P_2W$ requires C, 50·8; H, 3·5; Cl, 16·8; P, 7·1; W, 21·7%).

Tetrachloro(*n-propyl cyanide*)(*trimethylphosphine*)*tungsten*(IV).—Tetrachlorodi(n-propyl cyanide)tungsten(IV) (1·0 g) was dissolved in benzene (60 ml) and trimethylphosphine (15 ml) was added to the solution. The dark brown precipitate was washed with benzene and dried *in vacuo* (Found: C, 17·2; H, 4·3; Cl, 29·6; N, 3·1; P, 7·0; W, 39·0. $C_7H_{16}Cl_4NPW$ requires C, 17·8; H, 3·4; Cl, 30·1; N, 3·0; P, 6·6; W, 39·1%). The i.r. spectrum clearly shows the presence of co-ordinated n-propyl cyanide with strong absorptions at 2350 and 2275 cm^{-1}.

Tetrachlorotris(*trimethylamine*)*tungsten*(IV).— Tetrachlorodi(n-propyl cyanide)tungsten(IV) (1·0 g) was completely dissolved in benzene (60 ml), and trimethylamine (10 ml) was added to the solution. The green brown compound which precipitated immediately was filtered off, washed with benzene, and dried *in vacuo* (Found: C, 21·6; H, 4·4; Cl, 27·4; N, 7·6. $C_9H_{27}Cl_4N_3W$ requires C, 21·4; H, 4·9; Cl, 28·2; N, 8·3%). The magnetic susceptibility obeys the Curie–Weiss law over the range 88—311 K, with $\theta = 6°$. The electrical conductivity in dry nitromethane is dependent upon the concentration. At $2·8 \times 10^{-3}$, $0·40 \times 10^{-3}$, $0·36 \times 10^{-3}$, and $0·23 \times 10^{-3}$M, the conductivity was 26, 44, 47, and 57 cm^2 Ω^{-1} mol^{-1} respectively. The visible–u.v. spectrum shows bands at 23,500 and 14,000 cm^{-1} in the solid state, and at 22,000 and 13,500 cm^{-1} in nitromethane.

Trichloro(2,2′-*bipyridyl*)*tungsten*(III).—The procedure for the preparation of WCl$_4$(bipy) was repeated (see above), but in this case the mixture was refluxed for 3 days (Found: C, 26·9; H, 1·9; Cl, 23·5; W, 40·1. $C_{10}H_8Cl_3N_2W$ requires C, 26·9; H, 1·8; Cl, 23·8; W, 41·2%). The room-temperature effective magnetic moment is 1·48 B.M.

Trichlorobis(*trimethylamine*)*tungsten*(III).— Tetrachlorobis(n-propyl cyanide)tungsten(IV) (1·0 g) was dissolved in benzene (60 ml) and trimethylamine (10 ml) was added to the solution. The mixture was heated in a sealed tube at 120° for 36 h to precipitate the dark brown-green product; this was filtered off, washed with benzene, and dried *in vacuo* (Found: C, 18·2; H, 4·5; Cl, 26·7; W, 44·3. $C_6H_{18}Cl_3N_2W$ requires C, 17·7; H, 4·4; Cl, 26·0; W, 45·0%).

Trichlorodi(*acetonitrile*)(*trimethylamine*)*tungsten*(III).— Tetrachlorodi(acetonitrile)tungsten(IV) (1·0 g) and trimethylamine (30 ml) were placed in a sealed tube for 12 months at room temperature. The dark brown precipitate was washed with trimethylamine and dried *in vacuo* (Found: C, 18·5; H, 3·9; Cl, 23·9; N, 7·8; W, 42·0. $C_7H_{15}Cl_3N_3W$ requires C, 19·5; H, 3·5; Cl, 24·7; N, 9·7; W, 42·6%). The i.r. spectrum shows bands due to both co-ordinated trimethylamine and acetonitrile.

Pentachloro(o-*phenylenebisdimethylarsine*)*tungsten*(V).— Tungsten hexachloride (2·3 g) was dissolved in carbon tetrachloride (100 ml) and an excess of diarsine was added to the solution to precipitate the yellow complex; this was filtered off, washed with carbon tetrachloride, and pumped dry (Found: C, 18·3; H, 2·6; As, 21·2; Cl, 27·2; W, 27·9. $C_{10}H_{16}As_2Cl_5W$ requires C, 18·6; H, 2·5; As, 23·1; Cl, 27·4; W, 28·4%).

Oxotetrachloro(o-*phenylenebisdimethylarsine*)*tungsten*(VI). Diarsine (0·6 ml) in carbon tetrachloride (10 ml) was added to a hot solution of WOCl$_4$ (0·7 g) in carbon tetrachloride (100 ml). The red solution was immediately decolourised, and a pale green precipitate formed. This was filtered off, washed with carbon tetrachloride, and pumped dry (Found: C, 19·1; H, 3·0; As, 24·4; Cl, 22·2; W, 29·8. $C_{10}H_{16}As_2Cl_4OW$ requires: C, 19·1; H, 2·6; As, 23·9; Cl, 22·6; W, 29·3%).

Oxotrichloro(o-*phenylenebisdimethylarsine*)*molybdenum*(V). —*Method* 1. Molybdenum pentachloride (0·7 g) was dissolved in methanol under anhydrous oxygen-free conditions to give a bright green solution. Addition of diarsine (0·5 ml) to the solution produced a slow change to a yellow-brown colour, with eventual precipitation of a light brown solid. This was filtered off, washed with small amounts of methanol, and pumped dry (Found: C, 23·8; H, 3·5; As, 30·3; Cl, 21·9. $C_{10}H_{16}As_2Cl_3OMo$ requires C, 23·8; H, 3·7; As, 29·7; Cl, 21·1%). The magnetic moment at room temperature was 1·49 B.M. The conductivity of a 10^{-3}M-solution in acetonitrile was 17 cm^2 Ω^{-1} mol^{-1}. The solution spectrum in acetone shows bands at 15,600sh, 21,600, 30,000, and 34,400sh cm^{-1}.

Method 2. Molybdenum pentachloride (0·7 g) was dissolved in acetone (50 ml) under a nitrogen atmosphere. Diarsine (0·5 ml) was added to the solution which was pumped down until precipitation commenced. The light brown solid was filtered, washed with acetone, and pumped dry (Found: C, 24·0; H, 3·7; Cl, 23·6%).

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Method 3. Diarsine (0·5 ml) was added to a red solution of $MoOCl_3$ (1·0 g) in acetone (50 ml) under a nitrogen atmosphere. The yellow brown solution was evaporated to a small volume, and the brown precipitate was filtered off, washed with small amounts of acetone, and pumped dry (Found: C, 25·0; H, 3·1; Cl, 20·8%).

Method 4. Diarsine (0·5 ml) was added to a green solution of molybdenum pentachloride (1·0 g) in 10M-hydrochloric acid in the presence of air. The brown precipitate was filtered off, washed with ethanol and then a small amount of acetone, and then pumped dry (Found: C, 24·4; H, 3·8; Cl, 20·8%). The room-temperature magnetic moment was 1·40 B.M.

All these products have identical *X*-ray powder diffraction patterns and i.r. spectra.

Reaction of Molybdenum Pentachloride and o-*Phenylenebisdimethylarsine in Dioxan*.—An orange-red solid was precipitated immediately when dioxan solutions of molybdenum pentachloride and diarsine were mixed. The same compound was produced regardless of reactant stoicheiometry and reaction temperature. The same product was produced by $MoCl_4(MeCN)_2$ in dioxan [(Found: (average for six preparations) C, 25·1; H, 3·5; As, 26·0; Cl, 24·0; Mo, 16·2. $C_{24}H_{40}As_4Cl_8Mo_2O_3$ requires C, 25·0; H, 3·5; As, 26·0; Cl, 24·6; Mo, 16·7%]. The magnetic susceptibility of $10^6\chi_g = 1{\cdot}29$ c.g.s.u. corresponds to a magnetic moment of 1·54 B.M. based on a single molybdenum atom. The electrical conductivity of a 10^{-3}M-solution was 76 cm² Ω^{-1} mol^{-1} in acetonitrile and 30 cm² Ω^{-1} mol^{-1} in nitromethane, indicating a 1 : 1 electrolyte for a dimeric formula.

Tetrachloro(o-*phenylenebisdimethylarsine*)*tungsten*(IV).—The yellow WCl_5(diars) above was thoroughly washed with acetonitrile and the light brown product was dried *in vacuo* (Found: C, 19·4; H, 3·1; As, 24·1; Cl, 22·1; W, 29·8. $C_{10}H_{16}As_2Cl_4W$ requires C, 19·6; H, 2·6; As, 24·5; Cl, 23·3; W, 30·0%). The magnetic susceptibility of $10^6\chi_g = 2{\cdot}04$ c.g.s.u. corresponds to an effective magnetic moment of 1·88 B.M., which is normal for octahedral tungsten(IV).[1,2,8-11] The complex is a non-electrolyte in acetonitrile.

Tetrachloro(o-*phenylenebisdimethylarsine*)*molybdenum*(IV).—Diarsine (3·0 ml) in acetonitrile (20 ml) was added with stirring to a solution of molybdenum pentachloride (2·0 g) in acetonitrile (100 ml), which had been previously heated and pumped to remove chlorine. The orange-brown precipitate was filtered off, washed with acetonitrile, and pumped dry (Found: C, 23·1; H, 3·4; Cl, 27·1; Mo, 17·7; $C_{10}H_{16}As_2Cl_4Mo$ requires C, 22·9; H, 3·1; Cl, 27·1; Mo, 18·3%). The conductivity of a 10^{-3}M-solution in acetonitrile was 18 cm² Ω^{-1} mol^{-1}, indicating only slight dissociation in this solvent. The room-temperature effective magnetic moment was 1·88 B.M.

Bis(o-*dimethylarsinophenyl*)*methylarsine* (*or Triarsine*).—To (diarsine)(triarsine)nickel(II) perchlorate[28] (0·1 g) dissolved in water (20 ml) was added a solution of sodium cyanide (0·06 g) in water. The free ligands were extracted with diethyl ether (20 ml) and diarsine and triarsine were detected (v.p.c.) and isolated (distillation). The mass spectrum of triarsine showed the presence of all expected daughter ions.

Tetrachlorobis(o-*phenylenebisdimethylarsine*)*rhenium*(V) *Chloride*.—This preparation was similar to that used for the corresponding perchlorate[7] (Found: C, 24·6; H, 3·6; Cl, 19·2. $C_{20}H_{32}As_4Cl_5Re$ requires C, 25·3; H, 3·4; Cl, 19·0%).

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