Oxidation of Diamagnetic Octa-μ_3-chloro-*octahedro*-hexamolybdenum(II) and -tungsten(II) Clusters to Paramagnetic Dodeca-μ_2-chloro-*octahedro*-hexamolybdenum(3+) and -tungsten(III) Clusters

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Oxidation of tungsten dichloride, $[W_6Cl_8]Cl_4$, with octachlorocyclopentene at 270 °C yields tungsten trichloride, $[W_6Cl_{12}]Cl_6$. This complex is paramagnetic, containing two unpaired electrons. Similar oxidation of molybdenum dichloride, $[Mo_6Cl_8]Cl_4$, yields $[Mo_6Cl_{12}]Cl_3$ in which the average oxidation state of molybdenum is +2·5. The salt $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ is also readily obtained.

OCTAHEDRAL M_6 clusters of metal atoms occur in the halogeno-complexes $[M_6X_8]^{x+}$, in which one halogen atom X is situated above each of the eight octahedral faces, and in $[M_6X_{12}]^{x+}$, in which one halogen atom is situated above each of the twelve octahedral edges.[1] The $[M_6X_8]^{x+}$ clusters contain a relatively large number of electrons available for metal–metal bonding, and relatively short metal–metal bond lengths. For example metal–metal distances of 2·62 Å are found in $[Mo_6Cl_8]^{4+}$ clusters in which there are 24 electrons available for metal–metal bonding.[2] The strength of the metal–metal bonding in these clusters appears relatively insensitive to the metal atom (Mo or W), to the number of electrons available for metal–metal bonding, and to the nature of the ligand (L) in $[(M_6X_8)(L)_6]^{z\pm}$ complexes.[2] Known $[M_6X_{12}]^{x+}$ clusters contain fewer electrons available for metal–metal bonding, *e.g.* 14, 15, and 16 electrons in $[Nb_6Cl_{12}]^{4+}$, $[Nb_6Cl_{12}]^{3+}$, and $[Nb_6Cl_{12}]^{2+}$ respectively. These complexes have relatively long metal–metal distances which depend on both the metal atom and the number of electrons available for bonding (*e.g.* 2·91 Å in $[Nb_6Cl_{12}]^{2+}$, 3·02 Å in $[Nb_6Cl_{12}]^{4+}$, and 2·96 Å in $[Ta_6Cl_{12}]^{4+}$),[3] and moreover the metal–metal bonding is sensitive to the nature of the ligand in $[(M_6X_{12})(L)_6]^{z\pm}$ complexes.[4]

The nature of the metal–metal bonding in these clusters has been considered in some detail,[5] although the ordering of the molecular orbitals has not yet been unambiguously determined. An important prediction from these theories [5] is that the next most stable molecular orbital over the 16-electron configuration of the cluster $[Nb_6Cl_{12}]^{2+}$ is triply degenerate, suggesting that it may be possible to prepare paramagnetic

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[1] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London, 1972.

[2] P. C. Healy, D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, 1973, 646 and references therein.

[3] R. A. Field, D. L. Kepert, B. W. Robinson, and A. H. White, *J.C.S. Dalton*, 1973, 1858, and references therein.

[4] R. A. Field, D. L Kepert, and D. Taylor, *Inorg. Chim. Acta*, 1970, **4**, 113.

[5] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 10; D. J. Robbins and A. J. Thomson, *J.C.S. Dalton*, 1972, 2350.

clusters containing more than one unpaired electron. A preliminary note[6] has reported the preparation of the ion $[W_6Cl_{12}]^{6+}$ from $[W_6Cl_8]^{4+}$ and liquid chlorine at 100 °C.

RESULTS

A new synthesis of tungsten trichloride, $[W_6Cl_{12}]Cl_6$, from tungsten dichloride, $[W_6Cl_8]Cl_4$, has been devised using refluxing octachlorocyclopentene as an oxidising and chlorinating agent.[7] This technique avoids the necessity of heating liquid chlorine to 100 °C. Every line on a Guinier *X*-ray powder photograph was indexed on a rhombohedral hexagonal unit cell (Table 1) [$a = 14{\cdot}916(5)$, $c = 8{\cdot}454(2)$ Å], which is in excellent agreement with that obtained by Siepmann *et al.* ($a = 14{\cdot}91$, $c = 8{\cdot}45$ Å).[6] Similar reaction of molybdenum dichloride with octachlorocyclopentene yielded $[Mo_6Cl_{12}]Cl_3$, from which the salt $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ could readily be obtained. In these complexes the average oxidation state of molybdenum is +2·5. It is generally observed that oxidation of molybdenum compounds leads to lower oxidation states compared with the oxidation of analogous tungsten compounds.[1] This $[Mo_6Cl_{12}]^{3+}$ cluster is readily reduced to $[Mo_6Cl_8]^{4+}$.

TABLE 1

X-Ray powder data for tungsten trichloride

			$10^4 \sin^2 \theta$					$10^4 \sin^2 \theta$	
h	*k*	*l*	Obs.	Calc.	*h*	*k*	*l*	Obs.	Calc.
1	1	0	106·5	106·7	3	4	2	1 646·9	1 647·7
1	0	1	118·5	118·6	3	3	3	1 706·9	1 707·2
0	2	1	224·5	225·2	4	4	0		1 706·7
2	1	1	330·6	331·9	4	0	4	1 895·6	1 897·3
0	1	2	367·0	367·6	6	2	1	1 928·1	1 932·0
2	2	0	424·9	426·7	3	2	4	2 005·3	2 003·9
2	0	2	475·2	474·3	6	0	3	2 024·1	2 027·2
1	3	1	543·0	545·3	7	1	0		2 026·7
1	2	2	579·7	581·0	1	2	5	2 325·2	2 324·5
4	0	1	649·6	651·9	2	4	4		2 324·0
4	1	0	744·2	746·7	0	8	1	2 359·7	2 358·6
0	0	3		747·2	5	1	4	2 430·9	2 430·6
3	1	2	792·0	794·3	2	7	1	2 464·9	2 465·3
1	1	3	854·0	853·9	3	1	5	2 538·7	2 537·8
3	3	0	958·8	960·0	0	4	5	2 641·4	2 644·5
2	3	2	1 007·1	1 007·7	4	3	4		2 644·0
2	4	1	1 075·5	1 078·6	8	1	1	2 676·3	2 678·6
2	2	3	1 174·1	1 173·9	2	3	5	2 750·3	2 751·2
5	1	1	1 183·3	1 185·3	9	0	0	2 874·0	2 880·1
5	0	2	1 226·0	1 221·0	0	0	6	2 985·1	2 988·8
4	2	2	1 326·8	1 327·7	6	3	3		2 987·3
1	0	4	1 364·4	1 363·9	8	2	0		2 986·7
4	3	1	1 397·3	1 398·6	4	2	5	3 072·9	3 071·2
1	5	2	1 432·6	1 434·3	7	0	4		3 070·6
0	2	4	1 471·0	1 470·6	3	5	4		3 070·6
4	1	3	1 492·5	1 493·9					

DISCUSSION

Removal of electrons involved in metal–metal bonding on oxidation of the cluster $[M_6Cl_8]^{4+}$ (M = Mo or W; 24 electrons available for metal–metal bonding) leads to formation of $[M_6Cl_{12}]^{x+}$ (M = Mo, $x = 3$, 21 electrons available for metal–metal bonding; M = W, $x = 6$, 18 electrons available for metal–metal bonding). This change in structure is characteristic of weakening of the metal–metal bonding (see Introduction section).

Room-temperature effective magnetic moments of $[Mo_6Cl_{12}]Cl_3$ and $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ are 1·11 and 1·17 B.M. respectively. The latter is approximately independent of temperature (Table 2), and is consistent with the presence of one unpaired electron per cluster. These figures increase to 1·31 and 1·36 B.M. respectively if an arbitrary value of 200 c.g.s. units is added to $10^6\chi_M$ to correct for the diamagnetism of the Mo_6 core. Tungsten trichloride exhibits antiferromagnetic behaviour with a Néel temperature of *ca.* 218 K (Table 2). The effective magnetic moment per W_6Cl_{18} falls from 1·41 B.M. at 308 K to 0·65 B.M. at 84 K. These figures increase to 1·57 and 0·75 B.M. respectively if an arbitrary value of 200 c.g.s. units is added to $10^6\chi_M$ to correct for the diamagnetism of the W_6 core. This antiferromagnetic behaviour appears qualitatively consistent with an intramolecular spin–spin interaction between the expected[5] two unpaired electrons accommodated in either the $t_{2g}(d_{xy})$ or the $t_{2g}(d_{xz}, d_{yz})$ molecular orbitals, the latter being split by spin–orbit coupling.

TABLE 2

Magnetic data

$[W_6Cl_{12}]Cl_6$			$(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$		
$\frac{T}{K}$	$\frac{10^6\chi_M}{\text{c.g.s.u.}}$	$\frac{\mu_{eff}}{\text{B.M.}}$	$\frac{T}{K}$	$\frac{10^6\chi_M}{\text{c.g.s.u.}}$	$\frac{\mu_{eff}}{\text{B.M.}}$
308·4	387	1·41	300·0	−172	1·17
293·9	394	1·38	294·8	−137	1·20
265·8	407	1·32	269·7	−106	1·17
237·6	415	1·26	239·8	−34	1·17
225·3	416	1·22	219·8	34	1·17
220·7	418	1·21	199·6	131	1·18
217·6	418	1·20	179·4	206	1·17
214·4	416	1·19	162·8	275	1·15
201·7	414	1·16	139·3	461	1·16
186·2	409	1·11	119·6	599	1·13
165·3	392	1·03	100·0	756	1·10
142·4	358	0·94	83·5	1090	1·11
110·2	286	0·79			
3·9	222	0·65			

The metal–chlorine modes observed in the i.r. spectrum (>250 cm^{-1}) of the cluster $[Nb_6Cl_{12}]^{4+}$ (350 and 300 cm^{-1}) are shifted on reduction to $[Nb_6Cl_{12}]^{3+}$ (340 and 290 cm^{-1}) and $[Nb_6Cl_{12}]^{2+}$ (330 and 280 cm^{-1}),[8] which can be attributed to weaker metal–chlorine bonding resulting from stronger metal–metal bonding,[1,3] and/or to reduction of the positive charge on the cluster. These bands appear at 320 and 255 cm^{-1} in $[Mo_6Cl_{12}]^{3+}$, indicating that the increase in metal–metal bonding resulting from the extra electrons in the molybdenum complex compared with $[Nb_6Cl_{12}]^{3+}$ is greater than the decrease in metal–metal bonding for transition metals towards the right-hand side of the Periodic Table.[1,9] Tungsten–chlorine vibrations at 351 and 325 cm^{-1} in the cluster $[W_6Cl_{12}]^{6+}$ can be attributed to decreased metal–metal

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[6] R. Siepmann, H.-G. v. Schnering, and H. Schäfer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 637.

[7] A. F. Bardawil, F. N. Collier, and S. Y. Tyree, *J. Less-common Metals*, 1965, **9**, 20.

[8] P. B. Fleming, J. L. Meyer, W. K. Grindstaff, and R. E. McCarley, *Inorg. Chem.*, 1970, **9**, 1769.

[9] D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.*, 1968, **7**, 2091.

bonding compared with $[Mo_6Cl_{12}]^{3+}$ due to the loss of electrons, but more probably to the large increase in positive charge on the cluster.

The visible spectrum of the complex $[W_6Cl_{12}]Cl_6$ in dimethylformamide showed major absorbances at 27 500 and *ca.* 12 500 cm^{-1} with a long tail stretching to the i.r. region. In view of the difficulty of assigning bands in cluster complexes, the origin of these peaks remains unknown. The spectrum of the ion $[(Mo_6Cl_{12})Cl_6]^{3-}$ is featureless except for the edge of a c.t. band above 22 000 cm^{-1}.

EXPERIMENTAL

Tungsten Trichloride.—Tungsten dichloride (2·0 g) and octachlorocyclopentene (9·0 g, recrystallised from ethanol <35 °C) were heated at 270 °C for 6 h in an evacuated sealed tube. The organic material was distilled in the sealed tube at 270 °C for 3 h into a liquid-air trap, leaving the air-stable, black-brown product (Found: C, 35·0; W, 61·2; Cl/W = 2·97. Calc. for Cl_3W: Cl, 36·6; W, 63·4%). The far i.r. spectrum (500—250 cm^{-1}) showed strong absorption maxima at 351 and 325 cm^{-1}.

Pentadecachlorohexamolybdenum.—Molybdenum dichloride and octachlorocyclopentene were treated in the same manner as for the preparation of tungsten trichloride from tungsten dichloride (Found: Cl, 47·5; Mo, 52·0. Calc. for $Cl_{15}Mo_6$: Cl, 48·0; Mo, 52·0%). Satisfactory products (Cl/Mo = 2·45—2·50) were obtained if the heating was carried out within the range 230—270 °C. At higher temperatures, the product contained small amounts of carbon (Found: C, 1·5; H, 0·0; Cl, 47·2; Mo, 51·3%). The freshly prepared solid was amorphous to *X*-rays. The complex slowly decomposed in moist air to give a product identified by its *X*-ray powder pattern as $(H_3O)_2[(Mo_6Cl_8)Cl_6],6H_2O$. In contrast to Mo_6Cl_{12}, Mo_6Cl_{15} slowly liberates iodine from aqueous iodide solution. The far i.r. spectrum showed absorption maxima at 375, 340, 320, and 255 cm^{-1}.

Tris(*tetraethylammonium*) *Octadecachlorohexamolybdate*.—Mo_6Cl_{15} (0·3 g) was dissolved in dry, oxygen-free, ethanol (10 cm^3) saturated with chlorine. Tetraethylammonium chloride [0·3 g, in ethanol–light petroleum (1 : 3)] was added, and the immediate precipitate filtered off, pumped dry, and stored *in vacuo* (Found: C, 17·6; H, 3·5; Cl, 39·5; Mo, 36·8. Calc. for $C_{24}H_{60}Cl_{18}Mo_6N_3$: C, 18·0; H, 3·8; Cl, 39·8; Mo, 35·9%). The far i.r. spectrum (>255 cm^{-1}) showed a single strong band at 320 cm^{-1}, which is distinctly different to the 325 cm^{-1} absorption found in $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$. The *X*-ray powder pattern of the salt $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ showed no evidence for any $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ (Table 3), which is readily prepared from Et_4NCl and $[Mo_6Cl_8]Cl_4$ under the same conditions used to prepare $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$. The electrical conductivity of the salt $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ in dry acetonitrile at $1·56 \times 10^{-4}$M was 359 Ω^{-1} cm^2 mol^{-1}, compared with that of $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ at $1·11 \times 10^{-3}$M of 237 Ω^{-1} cm^2 mol^{-1}, confirming that these complexes are 3 : 1 and 2 : 1 electrolytes respectively.[10] The magnetic susceptibility of the salt $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ as a function of temperature is given in Table 2; corresponding values for $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ at 298 and 85 K were $10^6\chi_M = -370$ and -340 c.g.s. units respectively.

TABLE 3

X-Ray powder data ($10^4 \sin^2 \theta$) for the salts $(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$ and $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$

$(Et_4N)_2[(Mo_6Cl_8)Cl_6]$	$(Et_4N)_3[(Mo_6Cl_{12})Cl_6]$
	44·76
53·58	
56·25	
	77·44
	89·68
104·0	
120·3	
	122·5
138·1	
153·0	
	165·6
193·8	
	218·7
231·9	
	258·9
	307·6
	353·4
	396·0
	461·8
	522·4
560·7	
625·5	
	647·7
	703·3
742·0	
	753·0
	857·9
894·0	
	907·2
	1 040·7
1 076·4	
	1 145·1
1 169·6	
1 238·0	
	1 275·9
1 296·0	
	1 513·2
1 587·0	

A Phillips Debye–Scherrer camera, 114·8 mm in diameter, was used to obtain *X*-ray powder photographs, using nickel-filtered copper K_α radiation. The *X*-ray powder photograph of tungsten trichloride was obtained with a Hägg–Guiner camera with monochromatic copper radiation [$\lambda(K_{\alpha 1}) = 1·5406$ Å][11] and calibrated using thoria as internal standard.[12] Molybdenum, tungsten, and chlorine were determined by standard methods after decomposition of the given complex with concentrated sulphuric or nitric acid. Carbon, hydrogen, and nitrogen were determined by C.S.I.R.O. Microanalytical Services, Melbourne. Magnetic susceptibilities were measured by the Faraday method using a Teflon bucket calibrated with high-purity silver shot.[13] Standard diamagnetic corrections[14] were used, but no correction was applied for metal-core diamagnetism or temperature-independent paramagnetism unless otherwise stated. I.r. spectra were measured as Nujol mulls between

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[10] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

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[13] M. Garber, W. G. Henry, and H. G. Hoeve, *Canad. J. Phys.*, 1960, **38**, 1595.

[14] B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 400.

Polythene plates using a Perkin-Elmer 521 spectrophotometer which was flushed continuously with dry air. Water vapour was used to calibrate the instrument below 450 cm^{-1}.[15] Conductivities were measured in dry oxygen-free acetonitrile using bright platinum electrodes and a Phillips model GM 4246 resistance bridge.

We thank the Australian Research Grants Committee and Imperial Chemical Industries of Australia and New Zealand Ltd. for support.

[3/1800 *Received, 29th August,* 1973]

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