

## Oxidation and Reduction of Some Tungsten, Molybdenum, and Vanadium Chlorides by Chlorinated Alkyl Cyanides

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Tungsten(v) chloride is oxidised by trichloroacetonitrile to give a tungsten(vi) complex containing a tungsten-nitrogen triple bond,  $\text{CCl}_3\cdot\text{CCl}_2\text{NWCl}_4\cdot\text{CCl}_3\text{CN}$ ; tungsten(vi) chloride gives the same complex with trichloroacetonitrile and analogous complexes with monochloroacetonitrile and 1-cyano-1,1,2-trichloroethane. The i.r. spectra of molybdenum(v) complexes formed in the reactions of trichloroacetonitrile with molybdenum(v) chloride and molybdenum(iv) chloride are interpreted on the basis of a triple molybdenum-nitrogen bond being formed. Molybdenum(v) oxytrichloride forms simple adducts with trichloroacetonitrile, but no complex could be isolated from the reaction of this ligand or 1-cyano-1,1,2-trichloroethane with vanadium(iv) chloride; this halide was reduced with mono- or di-chloroacetonitrile to give vanadium(III) adducts  $\text{VCl}_3\cdot 3\text{L}$ .

We reported<sup>1</sup> the oxidation by trichloroacetonitrile of tungsten(vi) chloride to  $\text{WCl}_6\cdot 2\text{CCl}_3\text{CN}$ , molybdenum(iv) chloride to  $\text{MoCl}_5\cdot 2\text{CCl}_3\text{CN}$ , and titanium(III) chloride to  $\text{TiCl}_4\cdot\text{CCl}_3\text{CN}$ . A full study of the reactions of titanium(III) and (IV) chlorides has been reported<sup>2</sup> and single-crystal X-ray studies have confirmed<sup>3</sup> the presence of the trichloroacetonitrile group in the titanium complex, but have further shown<sup>4</sup> that in  $\text{WCl}_6\cdot\text{CCl}_3\text{CN}$  (derived from the species formulated as  $\text{WCl}_6\cdot 2\text{CCl}_3\text{CN}$ ) the CN group has been chlorinated and that the compound is best considered as  $(\text{C}_2\text{Cl}_5\text{NWCl}_4)_2$  with a multiple nitrogen-tungsten bond.

We present the results of detailed studies of the reactions of several chlorinated alkyl cyanides with tungsten(v), tungsten(vi), molybdenum(iv), molybdenum(v), and vanadium(IV) chlorides.

### EXPERIMENTAL

Reactions were normally carried out in evacuated sealed Pyrex ampoules with 4–5 g of halide and 40–50 cm<sup>3</sup> of ligand; any solid that formed was isolated by filtration on a vacuum line.

(i)  $\text{WCl}_6$  and  $\text{CCl}_3\text{CN}$ .—Reaction for 4 days at room temperature gave a crystalline yellow solid which became powdery when kept under vacuum; it was sealed in a tube and heated to 45 °C for 1 h to remove excess of free ligand (Found: Cl, 30.7; W, 27.0. Calc. for  $\text{C}_4\text{Cl}_{12}\text{N}_2\text{W}$ : Cl, 31.0; W, 26.8%). The complex lost  $\text{CCl}_3\text{CN}$  when heated *in vacuo* to 150 °C for 1 h and became orange (Found: Cl, 39.0; W, 34.3. Calc. for  $\text{C}_2\text{Cl}_5\text{NW}$ : Cl, 39.3; W, 34.0%). No further weight loss was observed when the orange solid was heated to 200 °C. When the yellow compound ( $\text{C}_4\text{Cl}_{12}\text{N}_2\text{W}$ ) was recrystallised slowly from  $\text{CH}_2\text{Cl}_2$  in an evacuated double ampoule, a mole of  $\text{CCl}_3\text{CN}$  was lost and orange crystals formed whose analysis corresponded to  $\text{C}_2\text{Cl}_5\text{NW}$ .

(ii)  $\text{WCl}_6$  and  $\text{CH}_2\text{Cl}\cdot\text{CCl}_2\text{CN}$ .—These reacted to give a canary-yellow complex; the same compound formed when the reaction was carried out by mixing isopentane solutions containing stoichiometric amounts of reactants (Found: Cl, 29.5; W, 25.9. Calc. for  $\text{C}_6\text{H}_4\text{Cl}_{12}\text{N}_2\text{W}$ : Cl, 28.9; W, 25.8%).

(iii)  $\text{WCl}_6$  and  $\text{CH}_2\text{ClCN}$ .—These gave a dark red solid which was recrystallised from n-pentane and dichloro-

methane (Found: C, 10.5; H, 1.4; Cl, 38.6; N, 5.1; W, 33.8. Calc. for  $\text{C}_4\text{H}_4\text{Cl}_8\text{N}_2\text{W}$ : C, 9.0; H, 0.8; Cl, 38.8; N, 5.1; W, 33.6%).

(iv)  $\text{WCl}_5$  and  $\text{CCl}_3\text{CN}$ .—These gave a green solution which on heating to 50 °C for 2 weeks deposited a yellow solid analysing as  $\text{C}_4\text{Cl}_{12}\text{N}_2\text{W}$  (Found: Cl, 31.0; W, 26.8%); oxidation state, 6.0. The i.r. spectrum of the product was identical with that of the yellow product isolated from reaction (i).

(v)  $\text{MoCl}_5$  and  $\text{CCl}_3\text{CN}$ .—These gave a dark brown solution which deposited a yellow powder after several hours (Found: Cl, 31.6; Mo, 17.1; N, 5.4;  $\mu$ , 1.80 B.M. Calc. for  $\text{C}_4\text{Cl}_{11}\text{MoN}_2$ : Cl, 31.5; Mo, 17.1; N, 5.0%).

(vi)  $\text{MoCl}_4$  and  $\text{CCl}_3\text{CN}$ .—When heated together under reflux at 50 °C for 2 days these gave a pale brown solid (Found: Cl, 34.2; Mo, 17.2; N, 4.7%;  $\mu$ , 1.82 B.M.) whose i.r. spectrum was identical with that obtained from reaction (v).

(vii)  $\text{MoCl}_5$  and  $\text{CH}_2\text{ClCN}$ .—These reacted in n-pentane to give a black tar which gradually disappeared during 9 days to give a brown powder (Found: Cl, 41.8; Mo, 22.2; N, 6.5;  $\mu$ , 1.82 B.M. Calc. for  $\text{C}_4\text{H}_4\text{Cl}_7\text{MoN}_2$ : Cl, 42.2; Mo, 22.1; N, 6.6%).

(viii)  $\text{MoOCl}_3$  and  $\text{CCl}_3\text{CN}$ .—These reacted to give a grass-green solid (Found: Cl, 29.2; Mo, 26.6. Calc. for  $\text{C}_2\text{Cl}_6\text{MoNO}$ : Cl, 29.3; Mo, 26.5%).

(ix)  $\text{VCl}_4$  and  $\text{CH}_2\text{ClCN}$  or  $\text{CHCl}_2\text{CN}$ .—These reacted to give green compounds of stoichiometry  $\text{VCl}_3\cdot 3\text{L}$  [Found (from  $\text{CH}_2\text{ClCN}$  reaction): Cl, 55.4; V, 13.1. Calc. for  $\text{C}_6\text{H}_6\text{Cl}_6\text{N}_3\text{V}$ : Cl, 55.4; V, 13.3%. Found (for the  $\text{CHCl}_2\text{CN}$  reaction): Cl, 21.7; V, 10.4. Calc. for  $\text{C}_6\text{H}_3\text{Cl}_9\text{N}_3\text{V}$ : Cl, 21.8; V, 10.5%]. Reaction of stoichiometric quantities of reactants in isopentane gave non-stoichiometric products, whose analysis indicated that reduction was only partial.

*Physical Measurements.*—Magnetic susceptibilities were measured by the Gouy method at room temperature only. Electronic and i.r. spectra were measured as described previously.<sup>2</sup>

*Analyses.*—Samples for chloride determination were decomposed by 0.25M-NaOH and the chloride determined by the Volhard method or gravimetrically as AgCl. Control experiments showed that the carbon-chloride bonds in the ligands remained intact, so that ligand chlorine was not estimated in our analysis. The Discussion section reports the chlorination of the CN group in some reactions; the

<sup>1</sup> G. W. A. Fowles, D. A. Rice, N. Rolfe, and R. A. Walton, *Chem. Comm.*, 1970, 459.

<sup>2</sup> G. W. A. Fowles, K. C. Moss, D. A. Rice, and N. Rolfe, *J.C.S. Dalton*, 1972, 915.

<sup>3</sup> N. Rolfe, Ph.D. Thesis, University of Reading, 1971.

<sup>4</sup> M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and N. Rolfe, *Chem. Comm.*, 1971, 231.

chlorine-carbon bonds so formed (*i.e.*,  $-\text{CCl}_2\text{N}=\text{C}$ ) are labile and the chlorine was estimated by our procedure. Tungsten and molybdenum were determined by precipitation with oxine at the appropriate pH, the complexes being hydrolysed initially with 0.25M-NaOH; solutions of molybdenum samples were oxidised to the +6 state with  $\text{H}_2\text{O}_2$  before precipitation of the oxinate. Titanium and vanadium complexes were decomposed by concentrated  $\text{HNO}_3$  and ignited to  $\text{TiO}_2$  or  $\text{V}_2\text{O}_5$ .

While chlorine and metal analyses were reproducible with duplicate samples, carbon and hydrogen determinations (either by H. Bieler or in the Department by means of an F. and M. 'Scientific 185' apparatus) were not reproducible; the compounds were either extremely sensitive to hydrolysis or decomposed in the heating block. The nitrogen analyses (F. and M.) were reasonably reliable.

#### DISCUSSION

Complexes of general formula  $\text{WCl}_6 \cdot 2\text{L}$  have been isolated from the reactions of  $\text{WCl}_6$  with the ligands (L) monochloroacetonitrile, trichloroacetonitrile, and 1-cyano-1,1,2-trichloroethane, and of  $\text{WCl}_5$  with trichloroacetonitrile. In each case the product is in oxidation state +6. The trichloroacetonitrile complex was found to be monomeric and non-conducting in nitromethane solution and hence considered<sup>1</sup> eight-co-ordinate, but X-ray studies<sup>5</sup> have shown that the complex must be considered as  $\text{C}_2\text{Cl}_5\text{NWCl}_4 \cdot \text{CCl}_3\text{CN}$ . Thus the tungsten atom is six-co-ordinate with an approximately planar  $\text{WCl}_4$  unit and two *trans*-nitrogen atoms; the CN group of one ligand molecule has been chlorinated in the reaction and a multiple tungsten-nitrogen bond formed. When heated, the complex loses the co-ordinated molecule of trichloroacetonitrile and forms a complex of stoichiometry  $\text{WCl}_6 \cdot \text{CCl}_3\text{CN}$ , but with the structure  $(\text{C}_2\text{Cl}_5\text{NWCl}_4)_2$  in which the chlorinated nitrile remains linked to tungsten through a multiple nitrogen-tungsten bond and the tungsten atom maintains six-co-ordination through chlorine bridging.<sup>4</sup> This structure explains the absence of a CN stretching band around  $2300\text{ cm}^{-1}$  from the i.r. spectrum of the complex.

It is noteworthy that each compound had an analysis corresponding to  $\text{W}:\text{Cl} = 1:6$ , showing that the two chlorine atoms attached to the carbon atom of the CN group are readily removed by hydrolysis.

By comparison of the i.r. and Raman spectra of  $\text{C}_2\text{Cl}_5\text{NWCl}_4 \cdot \text{CCl}_3\text{CN}$ ,  $(\text{C}_2\text{Cl}_5\text{NWCl}_4)_2$ , and  $\text{CCl}_3\text{CN}$  it is possible to distinguish between the bands characteristic of the co-ordinated nitrile and those arising from the pentachloroethylimido-group. The spectra\* of the first two compounds show strong bands at  $1285$  and  $1290\text{ cm}^{-1}$  respectively which cannot be associated with the nitrile or the  $\text{C}_2\text{Cl}_5$  group. We suggest that these bands

may be tungsten-nitrogen stretching frequencies. For  $\text{C}_2\text{Cl}_5\text{NPCI}_3$  a similar band at  $1375\text{ cm}^{-1}$  has been assigned to the PN stretching mode.<sup>6,7</sup>

We believe that the other complexes of stoichiometry  $\text{WCl}_6 \cdot 2\text{L}$ , where  $\text{L} = \text{CH}_2\text{ClCN}$  and  $\text{CH}_2\text{ClCCl}_2\text{CN}$ , also contain one molecule of chlorinated nitrile, multiply bonded to tungsten, and a co-ordinated molecule of ligand and can be best represented as  $\text{RCCl}_2\text{NWCl}_4 \cdot \text{RCN}$  (with  $\text{R} = \text{CH}_2\text{Cl}$  and  $\text{CH}_2\text{ClCCl}_2$ ); thus the i.r. spectra show bands at  $1293$  and  $1296\text{ cm}^{-1}$ , respectively, and further evidence for the suggested structures is provided by the low-frequency spectra\* which show the similarity of metal-chlorine stretching frequencies for all the complexes. Attempts to remove the co-ordinated ligand molecule by heat led to decomposition.

Molybdenum(IV) and molybdenum(V) chloride each reacted with trichloroacetonitrile to give a compound of stoichiometry  $\text{MoCl}_5 \cdot 2\text{CCl}_3\text{CN}$ . Oxidation-state titrations showed both compounds to contain quinquevalent molybdenum and both had appropriate magnetic moments of *ca.* 1.80 B.M. at room temperature. Neither compound dissolved in organic solvents suitable for measurements of molecular weight or conductance, but they had identical i.r. spectra with a strong Raman-active band at  $1233\text{ cm}^{-1}$ . A similar band at  $1265\text{ cm}^{-1}$  was observed in the spectrum of  $\text{MoCl}_5 \cdot 2\text{CH}_2\text{ClCN}$ , which was the product of the monochloroacetonitrile-molybdenum(V) chloride reaction, and it seems reasonable to suppose that this peak is associated with a multiple nitrogen-molybdenum bond. The complexity of the low-frequency spectrum rules out a detailed structural assignment, but the most likely structure for each compound seems to be a chlorine-bridged dimer with a multiple nitrogen-molybdenum bond, *i.e.*,  $(\text{RCCl}_2\text{-NMoCl}_3 \cdot \text{RCN})_2$  where  $\text{R} = \text{CCl}_3$  and  $\text{CH}_2\text{Cl}$ .

The stabilisation of tungsten(VI) and molybdenum(V) by chlorinated nitriles through the formation of multiple metal-nitrogen bonds is also shown by  $\text{WOCl}_4 \cdot \text{MeCN}$ <sup>8,9</sup> and  $\text{MoOCl}_3 \cdot 2\text{MeCN}$ <sup>10</sup> which contain multiple metal-oxygen bonds; in contrast to this stability of oxychloro-species, the simple chlorides [tungsten(VI) chloride and molybdenum(V) chloride] are reduced by acetonitrile to give complexes of the quadrivalent elements,  $\text{MCl}_4 \cdot 2\text{MeCN}$ .<sup>11</sup> Further, molybdenum(V) oxytrichloride reacts with trichloroacetonitrile to give  $\text{MoOCl}_3 \cdot \text{CCl}_3\text{CN}$  which is dimeric in dichloromethane solution. The spectrum of this compound shows a typical multiple molybdenum-oxygen stretching frequency at  $1003\text{ cm}^{-1}$  ( $1002\text{ cm}^{-1}$  for  $\text{MoOCl}_3$ ) but no band in the  $1230\text{--}1260\text{ cm}^{-1}$  region. The structure is hence believed to be a chlorine-bridged dimer with a terminal  $\text{Mo}=\text{O}$  and a co-ordinated  $\text{CCl}_3\text{CN}$  group. The multiple metal-nitrogen bonds may be formally written  $\text{N} \rightleftharpoons \text{W}$  in which the

\* Tables of i.r. ( $2350\text{--}200\text{ cm}^{-1}$ ) and Raman spectra for the complexes have been deposited in Supplementary Publication No. 20747 (5 pp.). For details of the Supplementary Publications scheme see *J.C.S. Dalton*, 1972, Index issue (Items less than 10 pp. are supplied as full-sized copies).

<sup>5</sup> M. G. B. Drew, K. C. Moss, and N. Rolfe, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1219.

<sup>6</sup> V. I. Shevchenko, N. D. Bodnarchuk, and A. V. Kinsanov, *Zhur. obshchei Khim.*, 1963, **33**, 1591.

<sup>7</sup> V. I. Shevchenko and N. D. Bodnarchuk, *Zhur. obshchei Khim.*, 1966, **36**, 1645.

<sup>8</sup> H. Funk and G. Mohaupt, *Z. anorg. Chem.*, 1962, **315**, 204.

<sup>9</sup> G. W. A. Fowles and J. Frost, *J. Chem. Soc. (A)*, 1967, 671.

<sup>10</sup> D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1965, **27**, 303.

<sup>11</sup> E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531.

double bond is reinforced by  $p_{\pi}-d_{\pi}$  bonding with the electron pair coming from the nitrogen  $p$ -orbital lone pair. This is supported by the  $X$ -ray study<sup>4</sup> of the tungsten complex which shows the W-N bond length to be 1.71 Å, considerably shorter than the 1.92–1.95 Å assigned to a tungsten–nitrogen double bond.<sup>12</sup>

Summary of metal chloride–nitrile reactions indicating the oxidation state of the metal in the final product

Halide	Nitrile				
	CCl <sub>3</sub> CN	CHCl <sub>2</sub> CN	CH <sub>2</sub> ClCN	CHCl <sub>2</sub> CCl <sub>2</sub> CN	CH <sub>3</sub> CN
WCl <sub>6</sub>	VI <sup>a</sup>		VI <sup>a</sup>	VI <sup>a</sup>	IV
WCl <sub>5</sub>	VI <sup>a</sup>				IV
MoCl <sub>5</sub>	V <sup>a</sup>		V <sup>a</sup>		IV
MoCl <sub>4</sub>	V <sup>a</sup>				IV
W <sub>2</sub> Cl <sub>4</sub>					VI
MoOCl <sub>3</sub>	V				V
VCl <sub>4</sub>	<i>b</i>	III	III	<i>b</i>	III
TiCl <sub>4</sub>	IV	IV	IV	IV	IV
TiCl <sub>3</sub>	IV	IV	IV <sup>c</sup> and III	IV	III
ZrCl <sub>4</sub>	IV		IV		IV

<sup>a</sup> Addition across CN bond. <sup>b</sup> No products isolated.  
<sup>c</sup> Depending on reaction conditions.

Stable complexes of quadrivalent vanadium could not be obtained from reactions of vanadium(IV) chloride with

<sup>12</sup> D. C. Bradley, H. M. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Comm.*, 1969, 1261.

any of the chlorinated nitriles, although with mono- and di-chloroacetonitrile there is reduction and the formation of tervalent complexes VCl<sub>3</sub>·3L. The i.r. spectra of these complexes confirms the presence of the co-ordinated ligands and there show the same pattern of vanadium–chlorine frequencies as for VCl<sub>3</sub>·3MeCN<sup>13,14</sup> which has been assigned a *cis* structure. The electronic spectra of both complexes show a band at 14,700 cm<sup>-1</sup> that can be assigned to the  ${}^3T_{2g} \leftarrow {}^3T_{1g}(F)$  transition, but the  ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}$  transition expected around 20,000 cm<sup>-1</sup> is hidden by strong charge-transfer bands.

The Table summarises the oxidation states present in the products of the various metal chloride–nitrile reactions, from which it can be seen that whereas all the chlorinated nitriles oxidise titanium(III) chloride to give adducts of titanium(IV) chloride, analogous reactions with chlorides of tungsten(VI) and tungsten(V) and molybdenum(V) and molybdenum(IV) form products [of tungsten(VI) and molybdenum(V)] in which the cyanide bond has been chlorinated and a multiple metal–nitrogen bond formed.

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<sup>13</sup> M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *J. Chem. Soc.*, 1963, 5665.

<sup>14</sup> R. J. H. Clark, *Spectrochim. Acta*, 1965, 21, 955.