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

By **Gerald W. A. Fowles,*** **Kenneth C. Moss,** **David A. Rice,** and **Nicholas Rolfe,** Chemistry Department, University of Reading, Whiteknights, Reading RG6 2AD

Tungsten(V) chloride is oxidised by trichloroacetonitrile to give a tungsten(VI) complex containing a tungsten–nitrogen triple bond, $CCl_3 \cdot CCl_2NWCl_4, CCl_3CN$; 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 $VCl_3, 3L$.

WE reported [1] the oxidation by trichloroacetonitrile of tungsten(VI) chloride to $WCl_6, 2CCl_3CN$, molybdenum(IV) chloride to $MoCl_5, 2CCl_3CN$, and titanium(III) chloride to $TiCl_4, CCl_3CN$. A full study of the reactions of titanium(III) and (IV) chlorides has been reported [2] and single-crystal X-ray studies have confirmed [3] the presence of the trichloroacetonitrile group in the titanium complex, but have further shown [4] that in WCl_6, CCl_3CN (derived from the species formulated as $WCl_6, 2CCl_3CN$) the CN grouping has been chlorinated and that the compound is best considered as $(C_2Cl_5NWCl_4)_2$ 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 cm³ of ligand; any solid that formed was isolated by filtration on a vacuum line.

(i) WCl_6 *and* CCl_3CN.—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 $C_4Cl_{12}N_2W$: Cl, 31·0; W, 26·8%). The complex lost CCl_3CN when heated *in vacuo* to 150 °C for 1 h and became orange (Found: Cl, 39·0; W, 34·3. Calc. for C_2Cl_9NW: 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 ($C_4Cl_{12}N_2W$) was recrystallised slowly from CH_2Cl_2 in an evacuated double ampoule, a mole of CCl_3CN was lost and orange crystals formed whose analysis corresponded to C_2Cl_9NW.

(ii) WCl_6 *and* $CH_2Cl \cdot CCl_2CN$.—These reacted to give a canary-yellow complex; the same compound formed when the reaction was carried out by mixing isopentane solutions containing stoicheiometric amounts of reactants (Found: Cl, 29·5; W, 25·9. Calc. for $C_6H_4Cl_{12}N_2W$: Cl, 28·9; W, 25·8%).

(iii) WCl_6 *and* CH_2ClCN.—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 $C_4H_4Cl_8N_2W$: C, 9·0; H, 0·8; Cl, 38·8; N, 5·1; W, 33·6%).

(iv) WCl_5 *and* CCl_3CN.—These gave a green solution which on heating to 50 °C for 2 weeks deposited a yellow solid analysing as $C_4Cl_{12}N_2W$ (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) $MoCl_5$ *and* CCl_3CN.—These gave a dark brown solution which deposited a yellow powder after several hours (Found: Cl, 31·6; Mo, 17·1; N, 5·4; μ, 1·80 B.M. Calc. for $C_4Cl_{11}MoN_2$: Cl, 31·5; Mo, 17·1; N, 5·0%).

(vi) $MoCl_4$ *and* CCl_3CN.—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%; μ, 1·82 B.M.) whose i.r. spectrum was identical with that obtained from reaction (v).

(vii) $MoCl_5$ *and* CH_2ClCN.—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; μ, 1·82 B.M. Calc. for $C_4H_4Cl_7MoN_2$: Cl, 42·2; Mo, 22·1; N, 6·6%).

(viii) $MoOCl_3$ *and* CCl_3CN.—These reacted to give a grass-green solid (Found: Cl, 29·2; Mo, 26·6. Calc. for C_2Cl_6-MoNO: Cl, 29·3; Mo, 26·5%).

(ix) VCl_4 *and* CH_2ClCN *or* $CHCl_2CN$.—These reacted to give green compounds of stoicheiometry $VCl_3, 3L$ [Found (from CH_2ClCN reaction): Cl, 55·4; V, 13·1. Calc. for $C_6H_6Cl_6$-N_3V: Cl, 55·4; V, 13·3%. Found (for the $CHCl_2CN$ reaction): Cl, 21·7; V, 10·4. Calc. for $C_6H_3Cl_9N_3V$: Cl, 21·8; V, 10·5%]. Reaction of stoicheiometric quantities of reactants in isopentane gave non-stoicheiometric 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.[2]

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–chlorine 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

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[2] G. W. A. Fowles, K. C. Moss, D. A. Rice, and N. Rolfe, *J.C.S. Dalton*, 1972, 915.
[3] N. Rolfe, Ph.D. Thesis, University of Reading, 1971.
[4] 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.*, $^-CCl_2N=$) 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 H_2O_2 before precipitation of the oxinate. Titanium and vanadium complexes were decomposed by concentrated HNO_3 and ignited to TiO_2 or V_2O_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 $WCl_6,2L$ have been isolated from the reactions of WCl_6 with the ligands (L) monochloroacetonitrile, trichloroacetonitrile, and 1-cyano-1,1,2-trichloroethane, and of 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 [1] eight-co-ordinate, but X-ray studies [5] have shown that the complex must be considered as $C_2Cl_5NWCl_4,CCl_3CN$. Thus the tungsten atom is six-co-ordinate with an approximately planar 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 stoicheiometry WCl_6,CCl_3CN, but with the structure $(C_2Cl_5NWCl_4)_2$ 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.[4] This structure explains the absence of a CN stretching band around 2300 cm^{-1} from the i.r. spectrum of the complex.

It is noteworthy that each compound had an analysis corresponding to W : 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 C_2Cl_5-$NWCl_4,CCl_3CN$, $(C_2Cl_5NWCl_4)_2$, and CCl_3CN 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 cm^{-1} respectively which cannot be associated with the nitrile or the C_2Cl_5 group. We suggest that these bands

may be tungsten–nitrogen stretching frequencies. For $C_2Cl_5NPCl_3$ a similar band at 1375 cm^{-1} has been assigned to the PN stretching mode.[6,7]

We believe that the other complexes of stoicheiometry $WCl_6,2L$, where L = CH_2ClCN and CH_2ClCCl_2CN, also contain one molecule of chlorinated nitrile, multiply bonded to tungsten, and a co-ordinated molecule of ligand and can be best represented as $RCCl_2NWCl_4,RCN$ (with R = CH_2Cl and $CH_2Cl\cdot CCl_2$); thus the i.r. spectra show bands at 1293 and 1296 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 stoicheiometry $MoCl_5,2CCl_3CN$. 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 cm^{-1}. A similar band at 1265 cm^{-1} was observed in the spectrum of $MoCl_5,2CH_2ClCN$, 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.*, $(RCCl_2$-$NMoCl_3,RCN)_2$ where R = CCl_3 and CH_2Cl.

The stabilisation of tungsten (VI) and molybdenum(V) by chlorinated nitriles through the formation of multiple metal–nitrogen bonds is also shown by $WOCl_4,MeCN$ [8,9] and $MoOCl_3,2MeCN$ [10] which contain multiple metal–oxygen bonds; in contrast to this stability of oxychlorospecies, the simple chlorides [tungsten(VI) chloride and molybdenum(V) chloride] are reduced by acetonitrile to give complexes of the quadrivalent elements, MCl_4,-$2MeCN$.[11] Further, molybdenum(V) oxytrichloride reacts with trichloroacetonitrile to give $MoOCl_3,CCl_3CN$ which is dimeric in dichloromethane solution. The spectrum of this compound shows a typical multiple molybdenum–oxygen stretching frequency at 1003 cm^{-1} (1002 cm^{-1} for $MoOCl_3$) but no band in the 1230—1260 cm^{-1} region. The structure is hence believed to be a chlorine-bridged dimer with a terminal Mo=O and a co-ordinated CCl_3CN group. The multiple metal–nitrogen bonds may be formally written N $\Longrightarrow$ W in which the

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* Tables of i.r. (2350—200 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).

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double bond is reinforced by p_π–d_π bonding with the electron pair coming from the nitrogen p-orbital lone pair. This is supported by the X-ray study [4] 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.[12]

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

Halide	Nitrile				
	CCl₃CN	CHCl₂CN	CH₂ClCN	CHCl₂CCl₂CN	CH₃CN
WCl₆	VI [a]		VI [a]	VI [a]	IV
WCl₅	VI [a]				IV
MoCl₅	V [a]		V [a]		IV
MoCl₄	V [a]				IV
WOCl₄					VI
MoOCl₃	V				V
VCl₄	b	III	III	b	III
TiCl₄	IV	IV	IV	IV	IV
TiCl₃	IV	IV	IV [c] and III	IV	III
ZrCl₄	IV		IV		IV

[a] Addition across CN bond. [b] No products isolated. [c] Depending on reaction conditions.

Stable complexes of quadrivalent vanadium could not be obtained from reactions of vanadium(IV) chloride with any of the chlorinated nitriles, although with mono- and di-chloroacetonitrile there is reduction and the formation of tervalent complexes VCl₃,3L. 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 VCl₃,3MeCN [13,14] which has been assigned a *cis* structure. The electronic spectra of both complexes show a band at 14,700 cm⁻¹ that can be assigned to the $^3T_{2g} \longleftarrow \,^3T_{1g}(F)$ transition, but the $^3T_{1g}(P) \longleftarrow \,^3T_{1g}$ transition expected around 20,000 cm⁻¹ 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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