

863. *Reaction of Molybdenum and Tungsten Halides with Alkyl Cyanides.*

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Alkyl cyanides (RCN, R = Me, Et, and n-Pr) react with molybdenum(v) chloride, tungsten(vi) and tungsten(v) chloride, and tungsten(v) bromide, with reduction of the metal to the quadrivalent state and the formation of complexes $\text{MX}_4\cdot 2\text{RCN}$. These complexes have been characterised as 6-coordinate complexes, and the results of spectroscopic and magnetic susceptibility studies are discussed on the basis of an octahedral model. The use of these complexes as starting materials for the preparation of a large number of other complexes of quadrivalent molybdenum and tungsten is discussed.

ALKYL cyanides are known^{1,2} to react with the chlorides and bromides of quadrivalent titanium and zirconium to give compounds of the general formula $\text{MX}_4\cdot 2\text{RCN}$. The analogous vanadium compounds $\text{VCl}_4\cdot 2\text{RCN}$ can be prepared if the reactants are well diluted with an inert solvent,^{3,4} but excess of alkyl cyanide brings about reduction of vanadium to the trivalent state with the formation of the compounds $\text{VCl}_3\cdot 3\text{RCN}$. These compounds, their bromo analogues, and the corresponding compounds of trivalent titanium, have been prepared directly by the reaction of the alkyl cyanides with the appropriate trihalide.⁴ The pentachloride and pentabromide of niobium and tantalum are not reduced by alkyl cyanides, however, even when the reactants are heated in a sealed tube to 150°, but simple 1 : 1 adducts $\text{MX}_5\cdot \text{RCN}$ have been isolated and characterised.⁵

In this Paper we report on the reactions of alkyl cyanides with molybdenum(v) chloride, tungsten(vi) and tungsten(v) chloride, and tungsten(v) bromide. These reactions were carried out with considerable excess of alkyl cyanide, and in every case a dark brown solid was obtained which analysed to $\text{MX}_4\cdot 2\text{RCN}$ (cf. Table 2). All the compounds showed some solubility in the parent alkyl cyanide, and measurement of the conductance of the solutions (cf. Table 3) indicated that the compounds behaved essentially as non-electrolytes, the measured values of the molar conductivity in every case being less than 10, as compared to values of around 150 for typical 1 : 1 electrolytes. Unfortunately, only the n-propyl cyanide compounds were sufficiently soluble in solvents such as benzene for molecular weight measurements to be made but, in these cases at least, the compounds were monomeric. We propose accordingly that the compounds be considered as simple 6-co-ordinate complexes. It is worth noting that, whereas the molybdenum and tungsten

¹ Emeléus and Rao, *J.*, 1958, 4245; Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

² Fowles and Walton, *J.*, 1964, 2840.

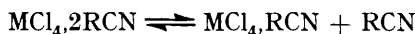
³ Funk, Mohaupt, and Paul, *Z. anorg. Chem.*, 1959, **302**, 199.

⁴ Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665; Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379; Scaife, 5th Internat. Conf. Co-ordination Chem., London, *Chem. Soc. Spec. Publ.*, 1959, **13**, 152; Nyholm, *Croat. Chem. Acta*, 1961, **33**, 157; Kern, *J. Inorg. Nuclear Chem.*, 1963, **25**, 5.

⁵ Feenan and Fowles, *J.*, 1964, 2842.

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compounds do not apparently dissociate, experiments with the alkyl cyanide adducts formed by titanium(IV) chloride,⁶ tin(IV) chloride,⁷ and vanadium(IV) chloride⁴ suggest that dissociation takes place in solution:



A consideration of the metal-chlorine stretching frequencies⁷ shows that the tin(IV) chloride complexes have a *cis* configuration and, while the evidence⁸ is not as unambiguous for the titanium(IV) and zirconium(IV) halide complexes, it again strongly suggests a *cis* configuration. A similar configuration is proposed for the molybdenum complex, $\text{MoCl}_4 \cdot 2\text{MeCN}$, which shows a strong band at 336 cm^{-1} with a shoulder at 311 cm^{-1} (compared with bands at 385s and 318w for $\text{TiCl}_4 \cdot 2\text{MeCN}$). The infrared spectra of the molybdenum and tungsten complexes show an increase in the $\nu_{\text{C}\equiv\text{N}}$ stretching frequency as is usual, the increase being in the range $20\text{--}30 \text{ cm}^{-1}$; this frequency increase is attributed to a kinematic effect. At high resolution, the $\nu_{\text{C}\equiv\text{N}}$ for $\text{MoCl}_4 \cdot 2\text{MeCN}$ can be resolved into two peaks.

The visible and ultraviolet spectra of these adducts, as measured in alkyl cyanide solution, are very complex (cf. Table 1), and it is not possible at this stage to make detailed assignments. The most noticeable point is the similarity in the spectra of all the compounds examined; thus six peaks were observed for all compounds except $\text{MoCl}_4 \cdot 2\text{EtCN}$, for which only five were found. The transition occurring around $20,000 \text{ cm}^{-1}$ for the molybdenum compounds has an extinction coefficient of 75 and corresponds to a *d-d* transition, but the remaining peaks have much higher intensities and must involve orbitals with appreciable ligand character (*i.e.*, be charge-transfer bands). Similarly, all the peaks observed for the tungsten bromide complexes have extinction coefficients greater than 2000 and must be charge-transfer in nature.

TABLE 1.

Visible and ultraviolet spectra of $\text{MX}_4 \cdot 2\text{RCN}$ complexes in RCN solution.

Compound	Peak positions (cm^{-1}) *
$\text{MoCl}_4 \cdot 2\text{MeCN}$...	20,200 (75); 25,000sh (~ 400); 27,800sh (~ 900); 31,800 (2900); 35,100 (2400); 41,700 (3000)
$\text{MoCl}_4 \cdot 2\text{EtCN}$...	19,800 (75); 25,300 (1800); 32,300 (5000); 34,500 (5000); 40,800 (4000)
$\text{MoCl}_4 \cdot 2n\text{-PrCN}$...	19,800; 25,000; 27,800; 31,800; 37,000; 40,800
$\text{WCl}_4 \cdot 2\text{EtCN}$	21,500 (400); 26,500 (400); 29,400sh (~ 4000); 31,000 (5500); 40,000 (13,400); 43,500 (9000)
$\text{WBr}_4 \cdot 2\text{MeCN}$...	22,100 (2600); 24,400 (3300); 29,800 (8100); 31,800 (7400); 34,500 (6000); 38,500 (17,000)
$\text{WBr}_4 \cdot 2\text{EtCN}$...	22,100 (2100); 24,400 (2300); 29,200 (7200); 31,550 (7100); 34,250 (6600); 39,500 (7200)
$\text{WBr}_4 \cdot 2n\text{-PrCN}$...	22,000 (3200); 24,400 (4200); 29,700 (12,000); 31,550 (11,000); 33,900 (9000); 39,700 (8700)

* Extinction coefficients given in parentheses.

The magnetic moments have been determined for all the compounds at room temperature (cf. Table 2). The molybdenum compounds have moments around 2.5 B.M., but the values found for the tungsten compounds are much lower, being in the range 1.78—2.07 B.M.; the tungsten bromide compounds have moments that are about 0.1—0.2 B.M. greater than those of the analogous chloride complexes. With all the compounds (but especially with the tungsten bromide compounds), there is a small increase in moment as the size of the alkyl group increases. With three compounds ($\text{MoCl}_4 \cdot 2\text{EtCN}$, $\text{WCl}_4 \cdot 2\text{EtCN}$, and $\text{WBr}_4 \cdot 2\text{MeCN}$) the variation of susceptibility has been studied over the temperature

⁶ Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, B, 17, 21.

⁷ Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.

⁸ Beattie, private communication.

TABLE 2.
Analytical data results.

Reaction		Found			Calculated for MX ₄ ·2RCN			Oxidation	μ
Halide	Alkyl cyanide	% M	% X	% N	% M	% X	% N	state	(B.M.)
MoCl ₅	MeCN	30.5	44.4	8.4	30.0	44.4	8.8	4.03	2.48
MoCl ₄	MeCN	30.0	43.2	8.9	30.0	44.4	8.8	—	—
MoCl ₅	EtCN	27.5	40.4	8.1	27.6	40.8	8.0	3.97	2.50
MoCl ₅	n-PrCN	24.8	37.6	7.4	25.5	37.8	7.4	4.13	2.52
WCl ₅	MeCN	45.6	34.7	—	45.1	34.8	6.9	4.15	—
WCl ₅	MeCN	45.3	34.2	6.8	45.1	34.8	6.9	4.07	1.78
WCl ₅	EtCN	41.5	32.2	6.5	42.2	32.6	6.4	—	1.84
WCl ₅	n-PrCN	40.1	30.5	6.0	39.7	30.6	6.0	—	1.85
WBr ₅	MeCN	31.7	54.7	4.9	31.4	54.6	4.8	—	1.89
WBr ₅	EtCN	29.7	52.1	4.5	30.0	52.1	4.6	—	1.97
WBr ₅	n-PrCN	28.3	50.2	4.4	28.6	50.0	4.4	3.82	2.07

range 90—295°K but only for a limited number (4) of temperatures. Plots of $1/\chi'_M$ with T give straight lines in every case, the θ values being 40° for the molybdenum compound and 250° for both tungsten complexes. Because the fields cannot be perfectly octahedral, accurate comparisons with the predictions for the behaviour of d^2 complexes by Kotani⁹ are not possible.

As the molybdenum and tungsten halides are reduced to the quadrivalent states upon reaction with alkyl cyanides, we attempted to ascertain the oxidation products of the latter, but without much success. Removal of all volatile material from the reaction mixture

TABLE 3.
Conductivity results.

Alkyl cyanide	Complex or salt	Molar conductivity (ohm ⁻¹ cm. ²)
MeCN	MoCl ₄ ·2MeCN	2.3
	WBr ₄ ·2MeCN	2.0
	Et ₄ NBr	159
EtCN	MoCl ₄ ·2EtCN	6.3
	WCl ₄ ·2EtCN	3.9
	Et ₄ NBr	156
n-PrCN	MoCl ₄ ·2n-PrCN	8.4
	Et ₄ NBr	157

gave the appropriate alkyl cyanide together with large amounts of the hydrogen halide. Examination of the infrared spectra of the volatile portion showed that it did not contain any halogenated species. Hydrogen chloride is known¹⁰ to form an unstable compound [MeCNH]⁺[HCl₂]⁻ with methyl cyanide, which readily loses hydrogen chloride *in vacuo*. The formation of hydrogen halide in the reaction of methyl cyanide with molybdenum or tungsten halides requires the extraction of a proton from the methyl group, leaving a ·CH₂·CN radical that could dimerise or initiate further polymerisation. It is worth noting that copper(II) bromide is reduced by methyl cyanide to the univalent state,¹¹ and here it is not hydrogen bromide but bromine that is formed.

The alkyl cyanide complexes, MX₄·2RCN, we report in this Paper, are the first authentic 6-co-ordinate complexes of the quadrivalent elements, apart from the hexahalogeno salts,^{12,13} [pyH]₂[Mo(NCS)₆],¹⁴ and MoBr₄·diars.¹⁵ and they form valuable starting materials for the preparation of other co-ordination compounds of molybdenum and tungsten in this

⁹ Kotani, *J. Phys. Soc., Japan*, 1949, **4**, 293.

¹⁰ Janz and Danyluk, *J. Amer. Chem. Soc.*, 1959, **81**, 3846.

¹¹ Schneider, 7th Internat. Conf. Co-ordination Chem., Stockholm, 1962, 27.

¹² Allen, Brisdon, Edwards, Fowles, and Williams, *J.*, 1963, 4649.

¹³ Edwards, Peacock, and Said, *J.*, 1962, 4643; Kennedy and Peacock, *J.*, 1963, 3392.

¹⁴ Mitchell and Williams, *J.*, 1962, 4570.

¹⁵ Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.

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oxidation state. Thus the n-propyl cyanide complexes, which are the most soluble in non-polar solvents, have been treated with a range of monodentate (L) and bidentate (B) ligands with the displacement of the n-propyl cyanide ligand from co-ordination. $\text{MoCl}_4 \cdot 2\text{L}$ have been prepared for L = tetrahydrofuran, pentamethyleneoxide, pyridine, pyrazine, 2,6-dimethylpyrazine, α -picoline, triphenylphosphine, triphenylarsine, and triphenylphosphine oxide.¹⁶ The tungsten compounds $\text{WCl}_4 \cdot 2\text{L}$ have been prepared¹⁷ in an analogous manner for L = triphenyl phosphine, triphenyl arsine, and triphenylphosphine oxide. The spectra and magnetic susceptibilities of these compounds have been measured and will be reported in full in a separate Paper.

EXPERIMENTAL

Materials.—Molybdenum(v) and tungsten(vi) chloride were prepared and purified as described previously.¹⁸ Tungsten(v) chloride was prepared by reduction of tungsten(vi) chloride with hydrogen at 380–400°, and purified by repeated sublimation in nitrogen. Found: W, 52.1; Cl, 49.1. Calculated for WCl_5 : W, 51.0; Cl, 49.0%. Tungsten(v) bromide was made by the action of bromine vapour (diluted with nitrogen) on tungsten metal powder at 1000°. Found: W, 31.5; Br, 68.8. Calculated for WBr_5 : W, 31.5; Br, 68.5%.

The alkyl cyanides (B.D.H. or Eastman Kodak) were fractionated and dried repeatedly with phosphoric oxide before use.

Analytical Methods.—Molybdenum, tungsten, halogen, and nitrogen were determined by the usual methods. Oxidation states were determined by treatment of the compounds with excess of standard cerium(iv) sulphate or potassium dichromate followed by back titration with iron(II) ammonium sulphate.

Magnetic Susceptibility.—Measurements were made on a Gouy balance at a field strength of 8000 gauss. Constant temperatures (90, 196, 251, and 295°K) were maintained by means of suitable slush baths.

Spectral Measurements.—Unicam S.P. 500 and S.P. 100 and Infracord (KBr) spectrophotometers were used. Special precautions were taken in view of the ease with which the compounds were hydrolysed.

Molecular Weight.—Determinations were made cryoscopically on benzene solutions with an apparatus (Beckmann) specially designed for incorporation in a vacuum line.

Reactions.—Reactions were carried out with excess of alkyl cyanide in an ampoule over a period of several days. The dark brown solid that separated from solution was filtered *in vacuo*, washed with benzene and then kept *in vacuo*. Table 2 summarises the analytical results. $\text{MoCl}_4 \cdot 2\text{MeCN}$ was also synthesised by the direct reaction of MeCN with molybdenum(iv) chloride. (Climax Molybdenum Co.)

Only the n-PrCN complexes were sufficiently soluble in benzene for molecular weight determinations to be made. Found: M, 370 (0.3% solution). $\text{MoCl}_4 \cdot 2\text{n-PrCN}$ requires: M, 376. Found: M, 433 (0.4% solution). $\text{WCl}_4 \cdot 2\text{n-PrCN}$ requires: M, 464. All the complexes were sufficiently soluble in the parent alkyl cyanide for conductivity measurements to be made. Table 3 lists values obtained at 25° for a selection of the compounds ($\sim 10^{-3}$ solutions), together with values measured for Et_4NBr , a typical 1 : 1 electrolyte.

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¹⁶ Allen, Feenan, and Fowles, unpublished observations.

¹⁷ Fowles and Kennedy, unpublished observations.

¹⁸ Fowles and Osborne, *J.*, 1959, 2275; Edwards and Fowles, *J.*, 1961, 24.