308. *Complex Compounds of Quadrivalent and Tervalent Molybdenum*

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A series of complex compounds of quadrivalent molybdenum of the types $MoCl_4,2L$ and $MoCl_4,B$ have been prepared, where L is one of a wide range of monodentate ligands and B is 2,2′-bipyridyl or 1,10-phenanthroline. Several complex compounds of tervalent molybdenum of the types $MoBr_3,3L$ and $MoBr_3,2L,RCN$ have also been prepared. The physical properties of these compounds, particularly spectra and magnetic susceptibilities, have been examined and the results interpreted.

The co-ordination chemistry of quadrivalent molybdenum has not been thoroughly investigated. Several 8-co-ordinate compounds have been prepared, of which the diamagnetic octacyanide complexes $M_4[Mo(CN)_8]$ have been particularly well characterised.[1] The oxalate [2] and triphenylarsine oxide [3] complexes $(NH_4)_4[Mo(C_2O_4)_4],8H_2O$, and $MoCl_4,4Ph_3AsO$, are well established, and there is some evidence [4] for the complex carbonate ion $[Mo(CO_3)_4]^{4-}$; all these compounds are diamagnetic.

6-Co-ordination has been established in the hexhalogeno-complex $[MoX_6]^{2-}$ ions (X = Br,[5] Cl,[5,6] and F [7]) and in the analogous thiocyanate species [8] $[Mo(NCS)_6]^{2-}$. The diarsine complex $MoBr_4$,diarsine had been reported,[9] and Muetterties has observed [10] the formation of complexes of molybdenum(IV) fluoride ($MoF_4,2L$, where L = Py, NMe_3,Me_2SO, and Me_2NCHO), where the molybdenum is formally 6-co-ordinate, although no structural information is available. Very recently,[11] molybdenum(IV) chloride has been prepared and shown to react with pyridine to give $MoCl_4,2Py$. A number of analogous alkyl cyanide complexes $MoCl_4,2RCN$ have recently been prepared [12] by the reaction of

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[1] I. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

[2] M. C. Steele, *Austr. J. Chem.*, 1957, **10**, 368.

[3] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1962, **1**, 947.

[4] M. C. Steele, *Austr. J. Chem.*, 1957, **10**, 367.

[5] A. J. Edwards, R. D. Peacock, and A. Said, *J.*, 1962, 4643.

[6] E. A. Allen, D. A. Edwards, and G. W. A. Fowles, *Chem. and Ind.*, 1962, 1026; E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J.*, 1963, 4649; S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1963, **2**, 568.

[7] A. J. Edwards and R. D. Peacock, *Chem. and Ind.*, 1960, 1441.

[8] G. A. Barbieri, *Atti Accad. naz. Lincei Rend. Classe Sci. fis. mat. nat.*, 1930, VI, **12**, 55; P. C. H. Mitchell and R. J. P. Williams, *J.*, 1962, 4570.

[9] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1960, 1806.

[10] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082, 6429.

[11] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1964, **3**, 285.

[12] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J.*, 1964, 4531.

molybdenum(V) chloride with excess of the alkyl cyanide, and molecular weight measurements have shown that these compounds are monomeric. We have found that the alkyl cyanide ligands are readily displaced by other ligands, and in this Paper we give an account of these new complex compounds of quadrivalent molybdenum. The compounds are mainly of the type $\mathrm{MoCl_4,2L}$, where L is one of the monodentate ligands: pyridine, α-picoline, tetrahydrofuran, pentamethylene oxide, triphenylphosphine oxide, triphenylphosphine, triphenylarsine, pyrazine, and 2,6-dimethylpyrazine, although two compounds $\mathrm{MoCl_4,B}$ have been made with B = 2,2′-bipyridyl and 1,10-phenanthroline.

We were unable to displace n-propyl cyanide by thioxan, but the required product $\mathrm{MoCl_4,2C_4H_8OS}$ was prepared by the direct reaction of molybdenum(IV) chloride with the ligand. Attempts to prepare the morpholine complex were unsuccessful because solvolysis took place.

Unfortunately, none of these compounds was sufficiently soluble in the usual non-co-ordinating organic solvents for molecular weights to be determined, so it is not possible to classify these compounds unambiguously as containing 6-co-ordinate molybdenum. Two compounds, $\mathrm{MoCl_4}$,2-tetrahydrofuran and $\mathrm{MoCl_4,2Ph_3As}$, were sufficiently soluble in methyl cyanide for conductivities to be measured, and Λ_M values of 7 and 33 were obtained respectively for ~10^{-3}M-solutions. Comparison of these values with that of 159 found for the 1 : 1 electrolyte $\mathrm{Et_4NBr}$ shows that the tetrahydrofuran compound does not give ions and that any dissociation of the triphenylarsine adduct is slight.

The infrared results, that have been obtained for all these compounds down to 400 cm.$^{-1}$ show peaks typical of the co-ordinated ligands, and provide no evidence for structures other than those in which the ligands are co-ordinated to molybdenum(IV) chloride; thus the spectra of the pyridine and α-picoline compounds completely eliminate the possibility of pyridinium and α-picolinium cations being present. The asymmetric C–O–C bands found at 1100 and 1075 cm.$^{-1}$, respectively, in pentamethylene oxide and tetrahydrofuran, shift to 1075 and 1000 cm.$^{-1}$ in the complex. Similarly, the P=O stretching frequency found at 1190 cm.$^{-1}$ in triphenylphosphine oxide shifts to 1125 cm.$^{-1}$ in the complex.

On the basis of the limited conductivity and spectra results, we suggest that in these compounds the molybdenum atoms are 6-co-ordinate. Additional co-ordination through chlorine–chlorine bridging is unlikely in the presence of strong electron donors such as pyridine, especially since the starting material ($\mathrm{MoCl_4,2Pr^nCN}$) is monomeric in solution.[12] The pyrazine and 2,6-dimethylpyrazine complexes could contain molybdenum with a higher co-ordination number, since both ligands are potentially bidentate and could link adjacent molybdenum atoms. Recent work [13] on compounds of these ligands with other transition metal halides, suggests that if pyrazine and 2,6-dimethylpyrazine bond through only one nitrogen atom, then bands should be observed at 980 and 1160 cm.$^{-1}$, respectively. The latter band is present in the $\mathrm{MoCl_4}$,2(2,6-dimethylpyrazine) complex, indicating that the ligand is monodentate, but in the analogous pyrazine complex the band at 980 cm.$^{-1}$ is quite weak and some ligand bridging may be present. As evidence against strong co-ordination, however, it may be noted that the reflectance spectrum of the adduct (cf. Table 1) is very similar indeed to that of $\mathrm{MoCl_4,2Py}$, which would suggest a similar arrangement of ligands around the molybdenum atom.

TABLE 1

Reflectance spectra of $\mathrm{MoCl_4,2L}$ complexes

Compound	Peak positions (cm.$^{-1}$)	Compound	Peak positions (cm.$^{-1}$)
$\mathrm{MoCl_4,2PPh_3}$	15,600; 20,000; 25,000; 27,800	$\mathrm{MoCl_4}$,2pyz	20,000; 23,500
$\mathrm{MoCl_4,2AsPh_3}$	15,600; 20,000; 24,400; 27,000	$\mathrm{MoCl_4}$,2dmp	20,000br.; 24,000br.
$\mathrm{MoCl_4}$,bipy	19,600sh; 25,000; 27,000	$\mathrm{MoCl_4,2OPPh_3}$	20,800sh; 27,000
$\mathrm{MoCl_4}$,2py	21,200sh; 24,700	$\mathrm{MoCl_4}$,2THF	20,800sh; 26,000—29,000br.
$\mathrm{MoCl_4}$,2(α-pic)	19,000; 25,000v.br.	$\mathrm{MoCl_4}$,2PMO	18,900; 23,200; 27,400

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[13] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J.*, 1962, 1235; 1963, 3156, 5042.

The thioxan adduct shows an unchanged C–O–C stretch at 1105 cm.$^{-1}$ indicating that co-ordination is through the sulphur atom. Unfortunately, C–S–C vibrations give bands of very low intensity,[14] and positive infrared evidence for co-ordination through sulphur could not be obtained. In the analogous adducts of the titanium(IV) halides,[15] the absence of unpaired electrons made nuclear magnetic resonance studies possible, and these showed fairly conclusively that bonding in those compounds was through the sulphur.

The far infrared spectrum (400—200 cm.$^{-1}$) of $MoCl_4$,bipy shows two strong bands (at 345 and 311 cm.$^{-1}$), and a similar spectrum was observed for $MoCl_4$,2MeCN [12] (peaks at 334 and 311 cm.$^{-1}$). $MoCl_4,2PPh_3$, on the other hand, shows two strong sharp peaks quite close together (342 and 334 cm.$^{-1}$), and we suggest that whereas the first compound has C_{2v} symmetry (and so therefore does $MoCl_4$,2MeCN), the triphenylphosphine compound may be D_{4h} (*i.e.*, *trans*). The bulky phosphine groups could lead to the *trans*-configuration, and it is perhaps significant that the triphenylphosphine and triphenylarsine adducts have different spectra from those of the remainder of the complexes.

All the compounds mentioned unquestionably contain quadrivalent molybdenum, as shown by the determination of their oxidation states, although prolonged reaction of $MoCl_4,2Pr^nCN$ with excess of α-picoline resulted in further reduction. We have been unable to isolate any pure compound of tervalent molybdenum from this reaction; the analogous reaction of $WCl_4,2Pr^nCN$ with excess of pyridine yields the tervalent tungsten adduct, WCl_3,3Py.[16]

The magnetic moments of the complexes (cf. Table 2) range from 2·71 B.M. for the pyridine adduct (Larson and Moore [11] found 2·52 B.M.) to 2·19 B.M. for the triphenylphosphine oxide complex, the majority being between 2·3 and 2·5 B.M. Spin-orbit coupling is no doubt responsible for these values being appreciably below the spin-only value,[17] but they are still higher than the values obtained for the salts of the hexachloromolybdates,[5,6] presumably because the $MoCl_4$,2L adducts are less symmetrical. The magnetic susceptibilities of three compounds have been measured over a temperature range, and the values obtained are given in Table 2. Plots of the reciprocal of the molar susceptibility with the absolute temperature show linear relationships, and the Curie–Weiss constant is small in each instance.

TABLE 2

Magnetic susceptibility of quadrivalent molybdenum compounds

	$10^6\chi_M$		
Temp. (°K)	$MoCl_4,2PPh_3$	$MoCl_4,2C_4H_8O$	$MoCl_4$,bipy
90	8414	7438	6334
195	3789	4087	3422
273	2705	2866	—
293	2504	2712	2354

All the complexes show two main peaks in their visible spectra (cf. Table 1 and Figures 1 and 2) around 20,000 and 25,000 cm.$^{-1}$; the first of these peaks sometimes appears only as a shoulder, and the second is generally broad and occasionally resolved into two. If we assume that the structures of the complexes are not too distorted from octahedral, then we may assign these two main peaks to the $3T_{2g} \longleftarrow 3T_{1g}$ and $3T_{1g}(P) \longleftarrow 3T_{1g}$ transitions, by analogy with recent assignments made for the hexachloromolybdate anion (which shows peaks at 21,510 and 25,640 cm.$^{-1}$). The triphenylphosphine and triphenylarsine complexes also show a very much weaker peak at 15,600 cm.$^{-1}$ (cf. Figure 2) which may be a spin-forbidden transition. It is noteworthy that this peak is found for a complex whose i.r. spectrum suggests that the local symmetry may be D_{4h} rather than C_{2v}.

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[14] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 353.

[15] G. W. A. Fowles and R. A. Walton, *J.*, 1964, 4330.

[16] G. W. A. Fowles and C. D. Kennedy, unpublished observations.

[17] B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," Interscience Publishers, New York, 1960, p. 427.

Several types of 6-co-ordinate complexes of tervalent molybdenum have been characterised. Thus, both cations $[MoB_3]^{3+}$ (with B = 2,2'-bipyridyl,[18] 1,10-phenanthroline,[18] and 2-aminomethylpyridine[19]) and anions $[MoX_6]^{3-}$ (with X = Br,[20] Cl,[21] and SCN[9,22]) are known, as well as the un-ionised complexes MoX_3,3L (with X = Cl, and Br, and L = pyridine[23,24] and urea[25]). Simple ammines have not been prepared, however, since ammonia, methylamine, and dimethylamine solvolyse molybdenum(III) bromide.[24] The acetylacetonate, $Mo(acac)_3$,[26] and related complexes formed from the substituted ketone[27] have also been prepared recently.

In this Paper we report the preparation of a series of complexes of the $MoBr_3$,3L type. The alkyl cyanide (R = Me, Et, and Pr^n) complexes have been prepared in good yield by the reaction of the tribromide with excess of alkyl cyanide in a sealed tube at 150°. These compounds appear to be simple adducts containing 6-co-ordinate molybdenum, since the n-propyl cyanide adduct is monomeric in benzene and the methyl cyanide compound gives a non-conducting solution in excess of the ligand. The analogous γ-picoline complex $MoBr_3$,3 γ-pic, which was readily prepared by the direct reaction of the bromide with excess of γ-picoline under reflux, was found to be monomeric in chloroform. Pyrazine and tetrahydrofuran complexes were prepared by displacing from co-ordination the alkyl cyanide in the $MoBr_3$,3RCN complexes. Triphenylphosphine and triphenylarsine did not, however, completely displace the alkyl cyanide ligands, but complexes of the type $MoBr_3$,2L,RCN were obtained; the presence of the remaining alkyl cyanide ligand was confirmed by the i.r. spectra of the complexes, which showed strong C≡N stretching frequencies. Similar experiments with bipyridyl yielded $MoBr_3$,bipy,MeCN, which is

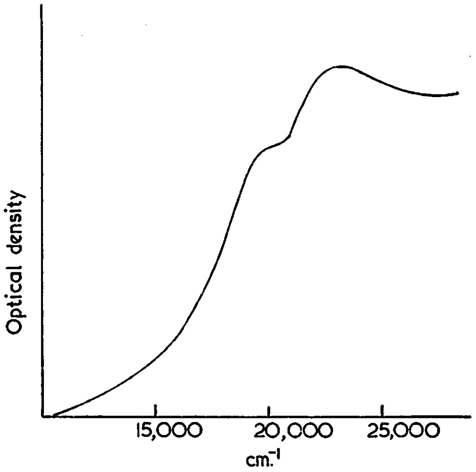

FIGURE 1. Diffuse reflectance spectrum of $MoCl_4$,2pyrazine

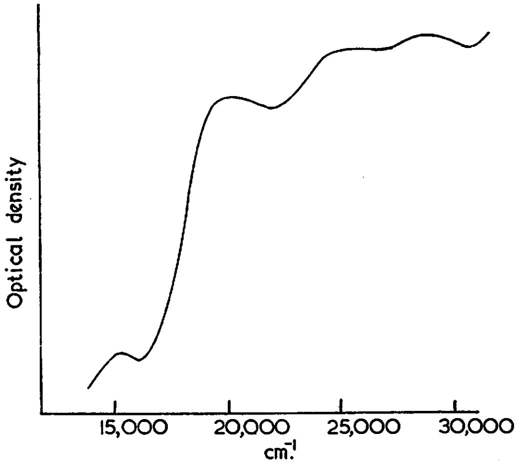

FIGURE 2. Diffuse reflectance spectrum of $MoCl_4$,2PPh_3

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[18] M. C. Steele, *Austr. J. Chem.*, 1957, **10**, 489.

[19] G. J. Sutton, *Austr. J. Chem.*, 1962, **15**, 232.

[20] W. Wardlaw and A. J. I. Harding, *J.*, 1926, 1592.

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[23] A. Rosenheim, G. Abel, and R. Lewy, *Z. anorg. Chem.*, 1931, **197**, 189; P. C. H. Mitchell, *J. Inorg. Nuclear Chem.*, 1961, **21**, 382.

[24] D. A. Edwards and G. W. A. Fowles, *J. Less-Common Metals*, 1962, **4**, 512.

[25] V. B. Evdokimov, V. V. Zelentsov, I. D. Kolli, W.-H. T'ang, and V. I. Spitsyn, *Doklady Akad. Nauk S.S.S.R.*, 1962, **145**, 1282.

[26] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1962, **1**, 856; J. H. Balthis, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1016.

[27] K. Christ and H. L. Schläfer, *Angew. Chemie* (*Int. Edn.*), 1963, **2**, 97.

analogous to the compounds $TiCl_3$,bipy,RCN obtained by the reaction of titanium(III) chloride with bipyridyl in alkyl cyanide solution.[28]

TABLE 3

Spectra of tervalent molybdenum complexes

Compound	Peak positions (cm.$^{-1}$) *
$MoBr_3$,3MeCN [a]	14,700sh; 21,000; 24,000; 25,200; 33,000sh; 34,200; 41,300
$MoBr_3$,3EtCN [b]	14,900; 21,000; 24,000; 26,400; 32,400; 33,800; 41,200
$MoBr_3$,2PPh_3,MeCN [c]	13,400; 14,900; 19,200sh; 23,200; 25,300
$MoBr_3$,2PPh_3,MeCN [a]	13,400(4); 15,100(4); —; 23,200(600); 26,000(1100)
$MoBr_3$,2$AsPh_3$,Pr^{n}CN [c]	13,300; 15,300; 20,000; 25,000
$MoBr_3$,2$AsPh_3$,Pr^{n}CN [d]	13,000(8); 15,000(5); 21,200(75)sh

* Extinction coefficients given in parentheses.

[a] MeCN soln. [b] EtCN soln. [c] Diffuse reflectance. [d] Pr^{n}CN soln.

The magnetic moments of all these tervalent molybdenum complexes are just below the spin-only value, in agreement with the predictions of Figgis and his co-workers.[29] The i.r. spectra of the complexes show the peaks to be expected for the ligands, modified slightly as would be expected.

The absorption spectra of several of the complexes have been measured (cf. Table 3 and Figure 3). A number of the peaks can be accounted for on the basis of an octahedral model, and by analogy with $[MoCl_6]^{3-}$. The spectrum of the latter complex shows three peaks at 15,000, 19,000, and 24,000 cm.$^{-1}$, which have been assigned[30] to the transitions $^2E_g \longleftarrow {}^4A_{2g}$, $^4T_{2g} \longleftarrow {}^4A_{2g}$, and $^4T_{1g} \longleftarrow {}^4A_{2g}$, the first being spin-forbidden. As the ligand-field order is RCN > Cl > Br,[31] so $MoBr_3$,3RCN might be expected to show peaks in approximately the same positions, and both the complexes show peaks at 15,000 and 21,000 cm.$^{-1}$ (the first being much the weaker in intensity). Both complexes also show a doublet of somewhat higher intensity around 25,000 cm.$^{-1}$. The other peaks observed, a doublet around 33,000 cm.$^{-1}$ and a peak close to 41,000 cm.$^{-1}$, are very much more intense and are evidently charge-transfer in origin. The spectra of the triphenylphosphine and

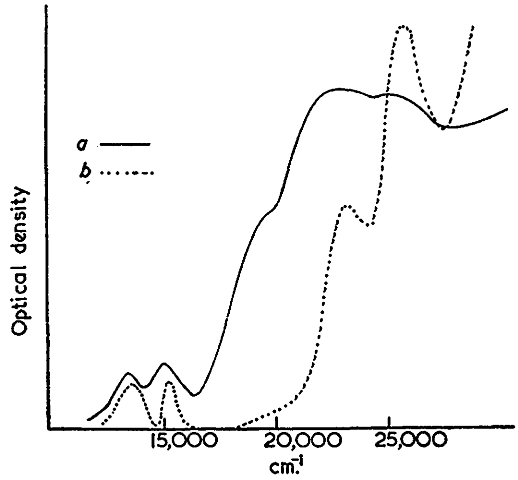

FIGURE 3. Spectra of $MoBr_3$,2PPh_3,MeCN (*a*) Diffuse reflectance. (*b*) In MeCN

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[28] G. W. A. Fowles, R. A. Hodless, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 391.

[29] B. N. Figgis, J. Lewis, and F. E. Mabbs, *J.*, 1961, 3138.

[30] H. Hartmann and H. J. Schmidt, *Z. phys. Chem. (Frankfurt)*, 1957, **11**, 234; H. Hartmann and H. L. Schläfer, *Angew. Chem.*, 1954, **66**, 768.

[31] G. W. A. Fowles and R. A. Walton, *J.*, 1964, 4953.

triphenylarsine complexes (studies up to 30,000 cm.$^{-1}$) are similar to those of the alkylcyanide complexes, except that the peak at 15,000 cm.$^{-1}$ now consists of two peaks of very low intensity; this splitting is not surprising in view of the low symmetry of the complexes.

EXPERIMENTAL

Materials.—Bis-(n-propyl cyanide)molybdenum(IV) chloride was prepared by treating molybdenum(V) chloride with excess of n-propyl cyanide for several days in a sealed ampoule, removing the excess *in vacuo*, and extracting the residue with chloroform.[12] The various solvents were purified by distillation and dried by repeated distillation from calcium hydride and phosphoric oxide.

Physical Measurements.—Because of possible hydrolysis or oxidation, all compounds were handled by techniques that have been developed to handle such sensitive materials. Infrared spectra were measured on Nujol mulls of the compounds by means of Unicam S.P. 100 and S.P. 200 and Perkin-Elmer (KBr) spectrophotometers. Visible spectra were measured on powdered specimens by means of a Unicam S.P. 500 spectrophotometer equipped with a diffuse reflectance attachment. Measurements of magnetic susceptibility were made by the Gouy procedure, constant temperatures being maintained with suitable slush baths; values were reproducible to 0·05 B.M.

Reactions.—*Preparation of complexes of quadrivalent molybdenum.* Chloroform solutions of the n-propyl cyanide adduct and the appropriate ligand were mixed in an ampoule and sealed under vacuum. The complexes that were precipitated (the time for precipitation varied from complex to complex), were filtered from the solution and kept *in vacuo* for at least 12 hr. before analysis. The results of the physical and chemical measurements on these compounds are given in Table 4.

TABLE 4

Properties of $MoCl_4,2L$ complexes

	Found (%)					Calc. (%)					Oxidation		μ
Ligand L	C	H	Cl	Mo	N	C	H	Cl	Mo	N	state	Colour	(B.M.)
C_5H_5N	—	—	35·8	24·3	7·2	—	—	35·9	24·2	7·1	—	Orange-brown	2·71
C_6H_7N	34·0	3·6	33·2	22·2	6·5	34·0	3·3	33·45	22·6	6·6	3·93	Yellow-orange	2·63
C_4H_8O	25·3	4·7	36·9	25·1	—	25·1	4·2	37·2	25·1	—	3·90	Pink	2·52
$C_5H_{10}O$	29·1	5·3	34·4	22·9	—	29·3	4·9	34·6	23·4	—	4·04	Yellow	2·45
$C_{18}H_{15}OP$	52·3	3·7	17·9	11·9	—	54·4	3·8	17·9	12·1	—	—	Yellow	2·19
$C_{18}H_{15}P$	56·3	4·2	19·3	12·7	—	56·7	4·0	18·6	12·6	—	—	Orange-brown	2·43
$C_{18}H_{15}As$	50·9	3·7	17·0	11·5	—	51·0	3·6	16·6	11·2	—	—	Brick-red	2·36
$C_4H_4N_2$	24·1	2·1	34·8	24·1	14·0	24·1	2·0	35·6	24·1	14·1	3·94	Red-brown	2·55
$C_6H_8N_2$	31·9	3·7	31·0	21·3	12·3	31·7	3·55	31·2	21·1	12·3	4·02	Orange-red	2·38
$1/2(C_{10}H_8N_2)$	—	—	36·9	24·0	7·3	—	—	36·0	24·4	7·1	4·05	Dark brown	2·36
$1/2(C_{12}H_8N_2)$	—	—	34·3	22·6	7·0	—	—	34·0	23·0	6·7	—	Dark brown	2·28

Preparation of complexes of tervalent molybdenum. (*i*) *Alkyl cyanide complexes.* Molybdenum(III) bromide did not react with any alkyl cyanide (RCN; R = Me, Et, and Pr^n) at room temperature even during several weeks, and reaction (in a Carius tube) was very slow at 100°. 150° proved to be the optimum temperature for maximum reaction and minimum breakdown of the ligands, and dark brown solutions were formed. Any unchanged bromide was filtered off and excess of alkyl cyanide was removed from the filtrate to leave a yellow-brown solid $MoBr_3,3RCN$ in each case [Found (for R = Me): Br, 51·5; Mo, 21·5; N, 9·0%; μ 3·76 B.M.; Λ_M, 19 ohm^{-1} cm.^{2} for $\sim10^{-3}$M-MeCN solution. $MoBr_3,3MeCN$ requires: Br, 52·3; Mo, 20·9; N, 9·1%. Found (for R = Et): Br, 47·5; Mo, 19·0; N, 8·2%; μ, 3·51 B.M. $MoBr_3,3EtCN$ requires: Br, 47·8; Mo, 19·2; N, 8·4%. Found (for R = Pr^n): Br, 43·9; Mo, 17·8; N, 7·7%; μ, 3·61 B.M. *M*, 496 (5% solution in benzene). $MoBr_3,3Pr^nCN$ requires: Br, 44·2; Mo, 17·7; N, 7·7%; *M*, 543].

(*ii*) *γ-Picoline complex.* Molybdenum(III) bromide and γ-picoline were heated under reflux for 1 week and yielded a greenish-yellow solution and a yellow-green solid. The product obtained by evaporation of the solution was extracted with chloroform and yielded a yellow-green solid [Found: Br, 37·2; Mo, 15·5; N, 7·0%; μ, 3·86 B.M.; *M*, 654 (5% solution in $CHCl_3$). $MoBr_3,3\gamma\text{-}C_6H_7N$ requires: Br, 39·0; Mo, 15·6; N, 6·8%; *M*, 615].

(*iii*) *Pyrazine complex.* The reaction of $MoBr_3,3Pr^nCN$ and pyrazine in benzene gave a dark yellow solid (Found: C, 25·0; H, 2·2; Br, 41·8; Mo, 16·4; N, 14·3%; μ, 3·67 B.M. $MoBr_3,3C_4H_4N_2$ requires: C, 25·0; H, 2·1; Br, 41·6; Mo, 16·7; N, 14·6%).

(*iv*) *Triphenylphosphine complexes.* Reaction of triphenylphosphine with the alkyl cyanide complex $MoBr_3,3RCN$ (for R = Me and Pr^n), in methyl cyanide and benzene solutions, respectively, yielded the yellow adducts $MoBr_3,2PPh_3,RCN$ (Found: C, 50·9; H, 3·5; Br, 26·6; Mo, 10·5; N, 1·4; P, 6·8%; μ, 3·89 B.M. $MoBr_3,2PPh_3,MeCN$ requires: C, 50·6; H, 3·7; Br, 26·6; Mo, 10·6; N, 1·5; P, 6·9%. Found: C, 54·3; H, 4·5; Br, 25·3; Mo, 9·4; N, 1·9; P, 7·9. $MoBr_3,2PPh_3,Pr^nCN$ requires: C, 51·7; H, 4·0; Br, 25·8; Mo, 10·3; N, 1·5; P, 6·7%). (The analysis indicates a little contamination of the product with triphenylphosphine.)

(*v*) *Triphenylarsine complex.* Reaction of triphenylarsine with $MoBr_3,3Pr^nCN$ in benzene gave an orange-yellow solid (Found: C, 47·9; H, 3·8; Br, 23·8; Mo, 9·1; N, 1·2%; μ, 3·83 B. M. $MoBr_3,2AsPh_3,Pr^nCN$ requires: C, 47·2; H, 3·7; Br, 23·6; Mo, 9·4; N, 1·4%).

(*vi*) *Tetrahydrofuran complex.* Reaction of tetrahydrofuran with $MoBr_3,3MeCN$ in benzene gave a small yield of a salmon-pink solid (Found: C, 26·2; H, 4·4; Br, 42·8; Mo, 17·2; N, 0·9. $MoBr_3,3C_4H_8O$ requires: C, 26·1; H, 4·4; Br, 43·4; Mo, 17·4%).

(*vii*) 2,2′-*Bipyridyl complex.* Reaction of bipyridyl and $MoBr_3,3MeCN$ in methyl cyanide solution gave a cherry-red solution which deposited a reddish-brown precipitate after several days. Excess of ligand was removed from the solid by extraction with benzene (Found: Br, 44·1; Mo, 17·6; N, 8·0%; μ, 3·82 B.M. $MoBr_3$,bipy,MeCN requires: Br, 45·0; Mo, 18·0; N, 7·9%).

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