Molybdenum-95 Nuclear Magnetic Resonance and Vibrational Spectroscopic Studies of Molybdenum(VI) Species in Aqueous Solutions and Solvent Extracts from Hydrochloric and Hydrobromic Acid: Evidence for the Complexes $[Mo_2O_5(H_2O)_6]^{2+}$, $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br), and $[MoO_2Cl_4]^{2-}$

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Aqueous molybdate solutions which contain a series of polymeric oxomolybdenum(VI) complex ions have been investigated conjointly by ^{95}Mo and ^{17}O n.m.r. and Raman spectroscopy. The spectra provide evidence of the species $[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$, $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ believed to be formed successively prior to the point at which hydrous MoO_3 ('molybdic acid') precipitates from the acidified solution. This solid will redissolve and a further complex, probably $[Mo_2O_5(H_2O)_6]^{2+}$, is the predominant form of Mo^{VI} in 2—6 mol dm^{-3} nitric or perchloric acid solutions. This species has characteristic vibrational frequencies ν_{sym}(Mo–O) 952, ν_{asym} (Mo–O) 925, and ν(Mo–O–Mo) 830 cm^{-1}, and gives a ^{95}Mo n.m.r. signal at δ −63 p.p.m. In halogen acid solutions additional complexes exist and spectroscopic evidence shows these to be polymeric oxohalogenomolybdenum(VI) species and the discrete complexes $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br). Oxygenated organic solvents efficiently extract Mo^{VI} from halogen acid solutions in this form and the vibrational spectra of ether or ketone phases show the $[MoO_2X_2(H_2O)_2]$ complexes to have *cis-trans-cis* disposition of ligands. Characteristic ^{95}Mo chemical shifts of the halogeno-complexes $[MoO_2X_2(H_2O)_2]$ occur at δ 157 (X = Cl), 217 (X = Br), and 187 p.p.m. for the mixed halide $[MoO_2ClBr(H_2O)_2]$. I.r. and Raman spectra of the *cis*-$[MoO_2Cl_4]^{2-}$ anion have been observed and assigned by studying the crystalline Cs^+ salt, but this complex is not present in significant amounts in molybdenum(VI) solutions in concentrated hydrochloric acid.

Aqueous solutions of molybdenum(VI), which are an important starting point for the preparation of molybdenum catalysts, involve a series of equilibria between isomolybdate polymers, and despite many investigations knowledge of the structures concerned is incomplete.[1,2] Recent studies by ^{95}Mo n.m.r.[3,4] and Raman[5,6] spectroscopy show that $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ anions coexist in the range of pH 4.5—6.5. Acidification produces higher polymers, probably $[Mo_8O_{26}]^{4-}$ and $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ or protonated forms of these ions.[1] Beyond the isoelectric point, at which molybdic acid tends to precipitate, the species in solution become cationic and are expected to contain the molybdenyl ion, $[MoO_2]^{2+}$. Various techniques indicate the predominance of dimeric species in nitric or perchloric acid solutions.[7–9] Solutions of molybdenum(VI) in hydrochloric acid have been examined by u.v.–visible absorption[10,11] and Raman spectroscopy,[9,12–14] revealing the presence of chloro complexes. A study of Mo^{VI} in hydrobromic acid was chiefly concerned with the facile reduction to Mo^V which occurs in this solution.[15]

We have extended the earlier Raman analysis of molybdenum(VI) solutions alongside a study of their ^{95}Mo n.m.r. spectra which provides the first n.m.r. data for the polymerised molybdenum(VI) species in strongly acid systems. Because the time-scales of vibrational and n.m.r. spectra differ, the latter may record average signals for the mixtures of species in equilibrium while the characteristic Raman bands of the different structures continue to be observed and, subject to the problem of overlapping of bands, can be used to identify the species. Molybdenum in the +6 state is efficiently extracted from aqueous HCl or HBr into an ether or ketone phase and this procedure provides a useful method of separation, the basis of which is not fully understood.[16,17] As part of the present study, we have investigated the solvent extraction of molybdenum and found that the extracted complex is of the type *cis*-$[MoO_2X_2(H_2O)_2]$ (X = Cl or Br). The molybdenum(VI) nuclear shielding of these complexes and the mixed halide $[MoO_2BrCl(H_2O)_2]$ displays an inverse halogen dependence,[18,19] and these are the simplest molybdenum structures in which this effect has been observed.

Results and Discussion

Molybdenum-95 and ^{17}O N.M.R. Spectra of Molybdenum(VI) Species in Aqueous Solutions.—Figure 1 depicts the ^{95}Mo n.m.r. spectra of solutions of Na_2MoO_4 containing HCl or HBr, ranging from a composition where simple molybdate and heptamolybdate are present to solutions in the concentrated acids. At least seven species appear to be involved. The $[MoO_4]^{2-}$ ion and the species (**G**), (**G′**), and (**G″**), which we show to be halogeno-complexes, exhibit discrete resonances, but species (**A**), which is the heptamolybdate ion $[Mo_7O_{24}]^{6-}$,[3,4] and the other species (**B**)—(**F**) give signals which merge with one another successively as the composition of the solution is changed. Some broadening of the signals will be the consequence of loss of symmetry due to protonation, as is well documented for molybdate and heptamolybdate ions,[3,4] but the major factor, which results in very broad resonances, is the existence of equilibria between the various polymeric isomolybdate and molybdenyl ions. In HCl solution, species (**G**) with δ 152 p.p.m. is a mononuclear complex $[Mo_2O_2Cl_2(H_2O)_2]$, its identity being firmly established by the solvent extraction experiments described later.

The n.m.r. spectra of hydrobromic acid solutions (dotted traces in Figure 1) show that a similar series of species is involved. The solution in concentrated hydrobromic acid reveals the signal (**G′**) at 218 p.p.m. attributable to

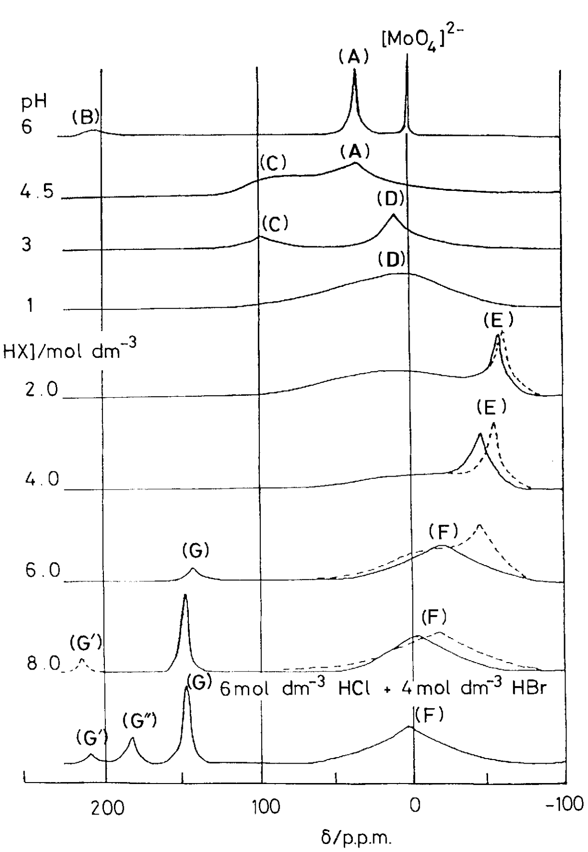

Figure 1. Molybdenum-95 n.m.r. spectra of molybdenum(VI) species in aqueous HCl (——) or HBr (– – –) solutions of $Na_2[MoO_4]$ (0.5 mol dm^{-3}). Species (**A**)—(**G**) are identified in the text

$[MoO_2Br_2(H_2O)_2]$. Mixing of this solution with that of molybdenum(VI) in concentrated HCl leads to the appearance of $[MoO_2BrCl(H_2O)_2]$ (**G″**) at 186 p.p.m. alongside the dichloro- and dibromo-complexes. Solutions of Mo^{VI} (0.5 mol dm^{-3}) in nitric acid, or perchloric acid, differ from the halogen acid systems in that excess of HNO_3 or $HClO_4$ produces little change to the n.m.r. spectrum. A strong signal at δ −60 p.p.m. is present when $[HNO_3] = 2.0$ mol dm^{-3}. This peak, attributed to species (E), becomes sharper on dilution of the solution, and moves slightly to δ −63 p.p.m. in the presence of 6.0 mol dm^{-3} HNO_3. Attempts to raise the nitric acid concentration any higher cause the precipitation of a white solid. A similar peak at −63 p.p.m. constitutes the ^{95}Mo n.m.r. spectrum of molybdenum(VI) solutions in 3.0 or 4.5 mol dm^{-3} $HClO_4$ and again a solid is formed if more acid is added. Raman evidence suggests that this signal arises from molybdenyl ions, probably in the form of a solvated $[Mo_2O_5]^{2+}$ complex.

The ^{17}O n.m.r. spectra of the molybdenum(VI) species were also sought. At 20 °C in an aqueous solution of pH 5.5 where the heptamolybdate ion is predominant we recorded sharp ^{17}O peaks at 122, 339, 397, 758, and 823 p.p.m., in agreement with prior work.[20,21] On adding small amounts of nitric acid to the solution several of these peaks altered significantly to give 122, 325, 391, 765, 819, and 826 p.p.m. at pH 4.5, and 121, 313, 387, 771, 822, and 827 p.p.m. at pH 4, an effect which has been noted before (although without the chemical shift data being cited) and attributed to protonation of the $[Mo_7O_{24}]^{6-}$ anion.[21] At pH 3, which is in the region where heptamolybdate undergoes a transition to octamolybdate,[4,21] only the ^{17}O n.m.r. signals of the solvent water at 0 p.p.m. and the nitrate ion at 416 p.p.m. were detected. We also attempted to obtain the ^{17}O n.m.r. spectrum of the solution of Mo^{VI} in concentrated HCl believed to contain $[MoO_2Cl_2(H_2O)_2]$, and of the solution in nitric acid whose ^{95}Mo signal at −63 p.p.m. we attribute to a molybdenyl cation. However, in neither case were there ^{17}O peaks other than those of solvent or NO_3^-. The failure to detect resonances of oxygen as part of a molybdenum complex under these conditions can be ascribed to low symmetry and/or fast exchange of ligand atoms between the complex and the solvent.[20]

Raman Spectra and Structures of the Molybdenum(VI) *Species in Acidic Aqueous Solutions.*—Sodium molybdate dissolves in water to give an alkaline solution with the Raman spectrum of the tetrahedral $[MoO_4]^{2-}$ ion.[5] When acid is added to this solution, new frequencies due to $[Mo_7O_{24}]^{6-}$, notably that of symmetric Mo–O stretching at 939 cm^{-1},[5,22] are detected at pH 6.5 and then increase at the expense of the molybdate spectrum [ν_{sym}(Mo–O) at 896 cm^{-1}] until at pH 5 only the heptamolybdate remains. Proton acceptance by the molybdate ion takes place in this range, leading to condensation (1).

$$7[MoO_4]^{2-} + 8H^+ \longrightarrow [Mo_7O_{24}]^{6-} + 4H_2O \quad (1)$$

As already noted, the ^{95}Mo n.m.r. spectra of molybdate–heptamolybdate mixtures display two separate resonances at 20 °C. Published results[23] show that these coalesce as the temperature is increased progressively to 50 °C, proving that the Mo_1 and Mo_7 species are then exchanging rapidly on the n.m.r. time-scale. Closer examination of the spectrum of the mixture of $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ (**A**) at pH 6 reveals an additional weak signal (**B**) at 220 p.p.m. (see Figure 1). A recent study of molybdenum(VI) solutions also recorded this peak and attributed it to heptamolybdate along with the major peak at 35 p.p.m.[4] However, we find that the signal at 220 p.p.m. is present over a narrower range of pH than the strong $[Mo_7O_{24}]^{6-}$ peak, implying that it is due to a separate species, and we think that this signal may show the presence in small amounts of a protonated entity $[HMoO_4]^-$ as an intermediate in the aggregation of $[MoO_4]^{2-}$ to form $[Mo_7O_{24}]^{6-}$. Prior evidence indicates an expansion of co-ordination number and according to Pope[1] the actual formula of $[HMoO_4]^-$ may be $[MoO_2(OH)_3(H_2O)]^-$. Unfortunately the amount of species (**B**) is insufficient for its Raman spectrum to be identified.

The Raman data for solutions of sodium molybdate with added hydrochloric or hydrobromic acid are given in Table 1. They are substantially in agreement with earlier work.[5,9,12–14] By correlating these spectra with the n.m.r. findings there is now a firmer basis for the structural conclusions. Except for the molybdate ion, which is present only in the least acidic solution of the series, all the molybdenum(VI) species involve octahedral co-ordination and the ν_{sym}(Mo–O) frequencies by which they are detected occur in the restricted range 939—982 cm^{-1}. In 0.8 mol dm^{-3} HCl solution, with $[Mo^{VI}] = 0.5$ mol dm^{-3}, corresponding to a degree of acidification[2] of 1.6 protons per molybdate ion, the intense ν_{sym} molybdenum–oxygen stretching band at 950 cm^{-1} has a shoulder at 970 cm^{-1}. This is in agreement with previous Raman spectra of molybdate solutions where the octamolybdate anion $[Mo_8O_{26}]^{4-}$ is expected to be present.[4,5,22] The n.m.r. spectrum shows that heptamolybdate (**A**) (δ 35 p.p.m.) is replaced by peaks at 10 and 100 p.p.m. The $[Mo_8O_{26}]^{4-}$ ion as the α form in acetonitrile solution gives ^{95}Mo n.m.r. signals at 24.2 and −4.2 p.p.m.[24] Failure to detect these particular signals does not exclude this species in the presence of water, since it is likely to be involved in exchange processes as previously demonstrated.[20,25] Increase in the degree of acidification to 1.8 (pH 0.95) has a pronounced effect on the Raman spectrum which now has bands at 954 and 982 cm^{-1}. These bands and others at lower frequency, attributable to ν_{asym}(Mo–O) stretching and bending vibrations, are part of a complicated spectrum given in the present work by molybdate

Table 1. Raman spectra (cm^{-1}) of molybdenum(VI) species in aqueous acidic solutions[a]

Acid	$\frac{[HX]}{\text{mol dm}^{-3}}$	ν_{sym}(Mo–O)	ν_{asym}(Mo–O)	ν(Mo–O–Mo)	δ_{sym}(Mo–O)	ν_{sym}(Mo–X)	Other bands	Major species[b]
HCl	0.5	939s, 896s	(895),[c] 845m	760w	360m	—	455w, 318m, 220m	$[MoO_4]^{2-}$ and **(A)**
HCl	0.8	970w, 950vs	920w, 900s	760w		—		**(A)** and **(C)**
HCl or HBr	1.0	982m, 954vs	920w, 900s	850w, 800w	370m	—	230m	**(D)**
HCl or HBr	2.0	953vs	920w	820w	370m	—	230m	**(E)**
HCl	4.0	955vs	920m	820w	370m	297m	430w, 250w, 220w	**(E)** and **(F)**
HBr	4.0	953vs	925m	830w	375m	190m	220m	**(E)** and **(F)**
HCl	6.0	955vs	920m	820w	372m	295m	430w, 220m	**(F)**
HBr	6.0	955vs	920m	830w	380m	190m	440w, 220m	**(F)**
HCl	8.0	960vs	922s	—	395m	310s	252m, 225m	**(G)**
HBr	8.0	955vs	918s	—	385m	198s	250m, 225m	**(G′)**
HNO_3	2.0—6.0	952vs	925m	830w	370m	—	450vw, 250vw, 220m	**(E)**

[a] $Na_2[MoO_4]$ = 0.5 mol dm^{-3}. [b] See text. [c] Masked by $[MoO_4]^{2-}$ peak.

solutions in 0.9—1.5 mol dm^{-3} HCl, and previously ascribed to $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$.[26] A molecular mass of 5 620 and spectroscopic and *X*-ray evidence of the sodium salt which crystallises from these solutions provide the previous support for this polymer.[26] We attribute the ^{95}Mo n.m.r. spectrum, centred at 10 p.p.m., to this complex [species **(D)**], while recognising that the broad signal indicates that a range of molybdenum environments are involved. A recent study assigned both the peak at 10 and the less intense peak at 100 p.p.m. to the $[Mo_8O_{26}]^{4-}$ ion.[4] However, assignment of a major peak to octamolybdate contradicts the molecular weight evidence[5,26] which indicates the presence of species with an average mass of *ca.* 5 000 whereas that of $[Mo_8O_{26}]^{4-}$ is 1 184. The nature of the molybdenum isopolyanions in aqueous solution has been a controversial subject.[1,2] Our results are consistent with the conversion of heptamolybdate into octamolybdate and the further reaction to yield a higher polymer.

Acidification to the equivalence point of the reaction (2)

$$[MoO_4]^{2-} + 2H^+ \longrightarrow H_2MoO_4 \qquad (2)$$

produces a white precipitate of hydrous MoO_3 ('molybdic acid') which redissolves when mixing is complete. Further changes to the spectra occur in the region where acid is in excess. For 0.5 mol dm^{-3} Mo^{VI} in 2.0 mol dm^{-3} HCl or HBr the ^{95}Mo n.m.r. spectrum reveals a new signal *ca.* δ −60 p.p.m. as well as an underlying very broad resonance. In the Raman spectrum we observe ν_{sym}(Mo–O) 953 cm^{-1}, ν_{asym}(Mo–O) 920 cm^{-1}, and several other bands (Table 1). These characteristics are similar to those of the complex which is present in nitric or perchloric acid solutions and we return to the question of the identity of this complex [species **(E)**] later. In 4.0—6.0 mol dm^{-3} halogen acid solutions the n.m.r. peak moves to lower field and tends to merge with the underlying resonance. A significant change in the Raman spectrum is the appearance in the low-frequency range of a band at 297 (HCl solution) or 190 cm^{-1} (HBr solution) of medium intensity and polarised, which clearly suggests that halogenomolybdenum complexes are being encountered. The spectra do not provide enough information to determine the structure of species **(F)**, although the ν(Mo–O) values indicate octahedral co-ordination and the presence of a band at 820 cm^{-1} in the ν(Mo–O–Mo) stretching region shows that the species probably has a bridged or polymeric structure. Support for this interpretation is provided by Raman studies of molybdenum(V) in HCl solutions for which frequencies ν(Mo–O) 982—997, ν(Mo–O–Mo) 742—870, and ν(Mo–Cl) 323—334 cm^{-1} were observed.[27] Himeno and Hasegawa[27] concluded that dimeric complexes with the Mo_2O_3 and Mo_2O_4 cores were present in 1—5 mol dm^{-3} HCl solutions and were replaced by monomeric molybdenum(V) chloro-complexes above 8 mol dm^{-3}.

On increasing the halogen acid concentration of the present molybdenum(VI) solutions to 8.0 mol dm^{-3} the ν_{sym}(Mo–O) and ν_{sym}(Mo–X) frequencies occur at 960 and 310 cm^{-1} in HCl, or 955 and 198 cm^{-1} in HBr, respectively. The ν(Mo–O–Mo) band is no longer observed. We are now dealing with the spectra of species **(G)** for which practically the same vibrational frequencies and ^{95}Mo chemical shifts are encountered when we examine either the halogen acid solutions or solvent extracts of these solutions. Investigations of the spectra of the solvent extracts, described below, identify the species as *cis*-dioxomolybdenum complexes, $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br).

The species **(E)** present in HCl or HBr solutions at low halide concentration appears to be identical with that found in nitric or perchloric acid solutions where the anion does not take part in complexing, and our Raman spectra agree with earlier findings.[9] The n.m.r. and Raman spectra in Figure 2 are those of a molybdenum(VI) solution in 6.0 mol dm^{-3} HNO_3 and show the species clearly. The Mo–O Raman bands, 952vs, polarised, and 925m, depolarised, establish octahedral co-ordination of the molybdenum atoms, and the band at 830 cm^{-1} suggests an oxo-bridged structure. This eliminates the ion $[MoO_2]^{2+}$ {or $[MoO_2(H_2O)_4]^{2+}$} and we favour the dinuclear structure $[(H_2O)_3O_2MoOMoO_2(H_2O)_3]^{2+}$. It is consistent with the Raman spectrum which includes bands at 370m (MoO_2 in-plane bending) and 220m cm^{-1} (out-of-plane bending), as well as a weak band at 450 cm^{-1} which is reasonably assigned to Mo–OH_2 stretching. The proposed structure has a Mo_2O_5 core and a number of complexes of this type are known,[13,28,29] *e.g.* $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$. *X*-Ray studies show the molybdenum–oxygen bond lengths vary considerably; Mo–O (terminal) 169, Mo–O(bridge) 190, and Mo–OH_2 233 pm, and the widely differing Mo–O frequencies are consistent with these distances. The average molecular weights of the molybdenum(VI) species as a function of the pH of the solution[5] are in line with the deductions from the spectroscopic data. For molybdate solutions acidified with HCl, the apparent molecular weight increases to a maximum of 5 200 at a pH of 1.1 then decreases to a local minimum of 800 around the isoelectric point (pH 0.9), followed by a sharp increase to 2 500 at pH 0.8.[5] The complex $[Mo_2O_5(H_2O)_6]^{2+}$ has a formula weight of 380; hence if this species is present in the HCl solutions of low pH, as the Raman spectra suggest, it must be accompanied by high-molecular-weight material. Our ^{95}Mo n.m.r. spectrum shows

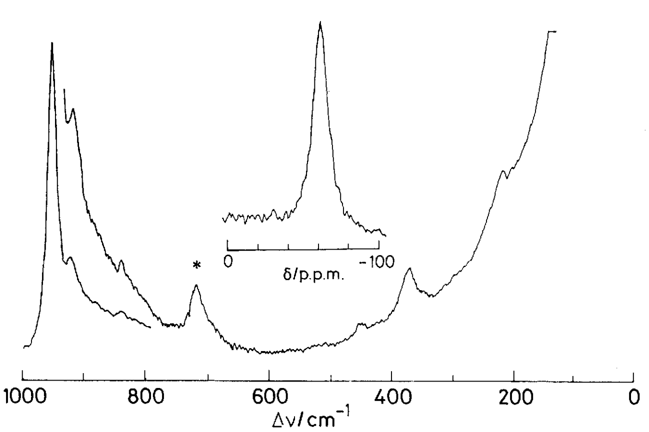

Figure 2. Raman and (inset) ^{95}Mo n.m.r. spectra of $[Mo_2O_5(H_2O)_6]^{2+}$ in 6 mol dm^{-3} HNO_3 solution. Slit width: 6 (150—930), 2 cm^{-1} (800—1 000 cm^{-1}). * Indicates peak due to ν_4 mode of NO_3^- ion

this to be the case by revealing an underlying broad resonance which can be attributed to polymeric species.

In summary, the following species appear to be present in acidified aqueous molybdate solutions ($[Mo^{VI}] = 0.5$ mol dm^{-3}) whose spectra are given in Table 1 and Figures 1 and 2.

The molybdate anion $[MoO_4]^{2-}$ is present above pH 4.5. It is characterised by vibrational frequencies ν_{sym}(Mo–O) 896, ν_{asym}(Mo–O) 845 cm^{-1}, and ^{95}Mo n.m.r. resonance $\delta = 0$ (linewidth < 10 Hz at pH 9). At pH 5 the linewidth increases to *ca.* 80 Hz without altering the chemical shift or appreciably changing the Raman frequencies.

Species (**A**) is the heptamolybdate ion, $[Mo_7O_{24}]^{6-}$,[30] which is present between pH 3 and 6.5. Vibrational frequencies are ν_{sym}(Mo–O) 939, ν_{asym}(Mo–O) 894, and $\delta(MoO_2)$ 360 cm^{-1}; the ^{95}Mo n.m.r. resonance occurs at δ 35 (linewidth 200—500 Hz, increasing as protonation occurs at lower pH). A series of ^{17}O n.m.r. resonances are found for this species.

Species (**B**) is revealed by a weak ^{95}Mo n.m.r. peak at 220 p.p.m. A tentative suggestion is that it may be an octahedral molybdenum(VI) monomer, such as $[MoO_2(OH)_3(H_2O)_2]^-$. Alternatively this signal could be associated with a subsidiary molybdenum environment in the heptamolybdate ion.

Species (**C**) is believed to be the octamolybdate ion, $[Mo_8O_{26}]^{4-}$.[31] It is detected by ν_{sym}(Mo–O) 970 cm^{-1} as a shoulder on the main Raman band at 950 cm^{-1} to which species (**A**) also contributes. A ^{95}Mo n.m.r. signal at +100 p.p.m. is assigned to this species in equilibrium with heptamolybdate and species (**D**).

Species (**D**) appears to be the polymolybdate ion, $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$.[32] Characteristics are ν_{sym}(Mo–O) 982 and 954, ν_{asym}(Mo–O) 900 cm^{-1}, and other Raman bands of lower frequency. A broad ^{95}Mo n.m.r. resonance centred at 10 p.p.m. and extending from +80 to −60 p.p.m. in solutions near the molybdic acid composition is attributed to this polymer and its protonated forms.

Species (**E**), the first beyond the isoelectric point, is believed to be a dimeric molybdenum(VI) cation, probably $[Mo_2O_5(H_2O)_6]^{2+}$. It is the predominant molybdenum(VI) species in nitric or perchloric acid solutions. Characteristics are ν_{sym}(Mo–O) 952, ν_{asym}(Mo–O) 925, ν(Mo–O–Mo) 830, $\delta(MoO_2)$ 370 and 220 cm^{-1}; ^{95}Mo n.m.r. δ −63 (linewidth 300 Hz). In HCl or HBr solutions this species is converted into the polymeric species (**F**).

Species (**F**) are cationic *cis*-dioxomolybdenum(VI) polymers involving octahedrally co-ordinated molybdenum. The ^{95}Mo n.m.r. resonance extends from +100 to −100 p.p.m. The frequencies ν_{sym}(Mo–O) 955, ν_{asym}(Mo–O) 920, and ν(Mo–O–Mo) 820 cm^{-1} are similar to those of species (**E**), with the addition of a molybdenum–halogen stretching band at 297 (HCl solutions) or 190 cm^{-1} (HBr solutions) showing the replacement of water molecules as ligands by halide ions.

Species (**G**) is $[MoO_2Cl_2(H_2O)_2]$. It is detected in aqueous solution above 6 mol dm^{-3} HCl and is the species which is extracted into an ether or ketone phase: ν_{sym}(Mo–O) 960, ν_{asym}(Mo–O) 922, and ν_{sym}(Mo–Cl) 310 cm^{-1}; ^{95}Mo n.m.r. δ 152 (linewidth 225 Hz).

Species (**G′**) is $[MoO_2Br_2(H_2O)_2]$: ν_{sym}(Mo–O) 955, ν_{asym}(Mo–O) 918, and ν_{sym}(Mo–Br) 198 cm^{-1}; ^{95}Mo n.m.r. δ 218 (linewidth 400 Hz).

Species (**G″**) is $[MoO_2BrCl(H_2O)_2]$: ν_{sym}(Mo–O) 958, ν_{asym}(Mo–O) 920, ν(Mo–Cl) 320, and ν(Mo–Br) 216 cm^{-1}; ^{95}Mo n.m.r. δ 186 (linewidth 540 Hz).

Solvent Extraction of Mo^{VI} *in the Form of Halide Complexes.*—Molybdenum(VI) is extracted from hydrochloric or hydrobromic acid solutions by ether or ketone solvents.[16] Typical values of the distribution ratio into diethyl ether are 2.1:1 from 7 mol dm^{-3} HCl solution and 1.4:1 from 5 mol dm^{-3} HBr solution. Isobutyl methyl ketone is a particularly efficient extractant and provides a distribution ratio of 29:1 from 7 mol dm^{-3} HCl.[17] Diamond[33] studied the extraction of molybdenum(VI) from solutions comprising LiCl + HCl at a total concentration of 6 mol dm^{-3}, and also measured the conductances of ether extracts, showing that the extracting species is not a strong acid, in contrast to other systems such as iron(III) which is extracted as $[H_3O]^+[FeCl_4]^-$.[34] The constancy of the distribution ratio while the molybdenum concentration was varied from 10^{-9} to 10^{-2} mol dm^{-3} implies that the extracting complex is monomeric. Analysis of ether extracts yielded the Mo:halide ratio of 1:2.0 leading to the conclusion that the extracting species was a chloro (or bromo) compound MoO_2X_2 with an undetermined amount of water and solvent also involved.[17] Other workers have proposed the formula $MoO_2Cl_2L_2$ in which the extra ligands L are molecules of the extracting solvent.[35]

Our n.m.r. spectra of molybdenum(VI) solutions demonstrate the presence of halide complexes [species (**G**)] with δ 152 p.p.m. in concentrated HCl or δ 218 p.p.m. in concentrated HBr solutions. Diethyl ether or isobutyl methyl ketone extracts from these solutions display strong, sharp resonances in almost the same place; δ 157 p.p.m. for the chloride and δ 216 p.p.m. for the bromide system. When samples of the chloride and bromide extracts are mixed an additional band appears at δ 187 p.p.m. as shown in Figure 3. This new signal is also observed along with the two original resonances, in the spectrum of extracts from a molybdate solution in a mixture of concentrated HCl and HBr. The formation of only one mixed halide species is confirmation that we are dealing with a dihalide complex. If the species being combined were of MoX_3 and MoY_3 types, *e.g.* $[MoO_2X_3(H_2O)]^-$, then a pair of mixed halides of the type MoX_2Y and $MoXY_2$ would be produced and two new resonances should be seen, not just one. Tin(II) complexes $[SnX_3]^-$ (X = Cl or Br) are a case in point.[36]

Following extraction of the molybdenum complex from the aqueous phase, it becomes possible to measure the i.r. as well as the Raman spectrum, and the spectral data obtained in ether and ketone extracts are in Table 2. The spectra are attributed to $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br) and can be assigned by comparison with that of $[MoO_2Cl_2(dmf)_2]$ (dmf = dimethylformamide), which is supported by *X*-ray structure determination and normal co-ordinate calculations.[37] This compound contains the *cis*-MoO_2 unit of widespread occurrence,[38] with the Cl ligands *trans* to one another, and the solvent extractable complex appears to have a similar structure. For $[MoO_2Cl_2(H_2O)_2]$, the Raman frequency at 310 cm^{-1} (polarised) and the i.r. frequency at 346 cm^{-1} agree with those of $[MoO_2Cl_2(dmf)_2]$ and are due to the modes ν_{sym}(Mo-Cl) and ν_{asym}(Mo–Cl),

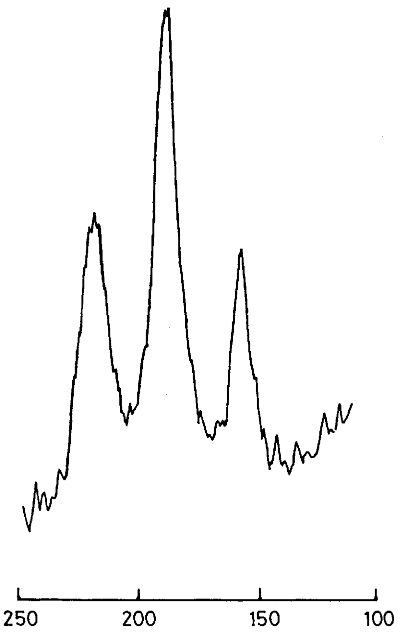

Figure 3. Molybdenum-95 n.m.r. spectrum of an isobutyl methyl ketone extract from a molybdenum(VI) solution in HCl (6 mol dm^{-3}) + HBr (4 mol dm^{-3}) showing the presence of three species, $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br)

respectively. For $[MoO_2Br_2(H_2O)_2]$ the corresponding bands occur at 192 and 255 cm^{-1}. Samples which are shown by their n.m.r. spectra to contain the mixed halide complex exhibit extra bands at 216 cm^{-1}, ν(Mo–Br), and 320 cm^{-1}, ν(Mo–Cl), in the Raman and i.r. spectra.

Strong bands at 960 and 922 cm^{-1} which alter very slightly with change of halide are due to the Mo–O stretches of the *cis*-MoO_2 group of $[MoO_2X_2(H_2O)_2]$. The corresponding frequencies of $[MoO_2Cl_2(dmf)_2]$ are at 940 and 905 cm^{-1}. Previous workers have studied a series of complexes $[MoO_2X_2L_2]$ (X = Cl or Br).[37] For L = MeCN, EtCN, PrCN, tetrahydrofuran (thf), dmf, or dimethyl sulphoxide (dmso), they observed a dependence of ν(Mo–O) on ligand donicity, and it is interesting to find that the frequencies of the present species with L = H_2O, which has a donicity of 18.0, fall into this sequence between PrCN (962 and 922 cm^{-1}; donicity = 16.6) and thf (958 and 920 cm^{-1}; donicity = 20.1). We find precisely the same ν(Mo–O) frequencies for the extracted species from HCl solutions into isobutyl methyl ketone, diethyl ether, or tributyl phosphate, the donicities of which range from 17.0 to 23.7, and this is part of our argument for excluding the extracting solvent from a role of inner-sphere co-ordination in the present complexes. Other points are that we observe absorptions due to the H_2O ligand at 1 635, 3 200, and 3 380 cm^{-1} in the spectra of solvent extracts, and that bands at low frequency, additional to the Mo–X stretches and Mo–O bands, can be reasonably assigned to modes involving the pair of co-ordinated water molecules. At least 12 modes of the *cis-trans-cis*-$[MoO_2X_2(OH_2)_2]$ complex can be assigned in the spectra of the extracted species (Table 2); C_{2v} symmetry requires 15 vibrations, however the missing modes are likely to give weak bands by analogy with the spectrum of $[MoO_2Cl_2(dmf)_2]$.[37]

The identification of the extracted species as $[MoO_2X_2(H_2O)_2]$ assists in understanding the composition of the molybdenum(VI) halogen acid solutions. The ^{95}Mo n.m.r. resonances differ slightly from the values measured in the solvent extracts, but no more than can be expected through a change in the dielectric constant of the medium. Several investigators have suggested that anionic halide complexes might be present in these aqueous solutions, *e.g.* $[MoO_2Cl_3(H_2O)]^-$ and $[MoO_2Cl_4]^{2-}$.[13,39,40] The present results show that in the highest attainable HCl (or HBr) concentrations only the $[MoO_2X_2(H_2O)_2]$ complex is produced in appreciable quantities, and is the form in which molybdenum(VI) is extracted by oxygenated organic solvents.

The ^{95}Mo chemical shift, δ 157 p.p.m. in $[MoO_2Cl_2(H_2O)_2]$, moves by 60 p.p.m. to δ 217 in $[MoO_2Br_2(H_2O)_2]$. This is in the direction of *decreased* shielding of the molybdenum nucleus. It provides an example of *inverse halogen dependence* in the chemical shift which is associated with compounds of transition metals in which the valence shell is either half-filled or complete.[18] For molybdenum(VI) the effect has been reported once before in the compounds MoO_2XL, where L = tris(3,5-dimethylpyrazol-1-yl)borate and X = Cl or Br, for which the chemical shift increases by 44 p.p.m. when Cl^- is replaced by Br^-.[19]

Vibrational Spectra and Assignment of the $[MoO_2Cl_4]^{2-}$ *Anion.*—The compound $Cs_2[MoO_2Cl_4]$ is obtained as a pale yellow crystalline solid by adding caesium chloride to a solution of sodium molybdate in concentrated hydrochloric acid.[40] This has led to the spectrum of this solution being attributed to the $[MoO_2Cl_4]^{2-}$ complex anion,[38,40] but this is incorrect because the Raman spectrum is that of $[MoO_2Cl_2(H_2O)_2]$. We have repeated the preparation of the solid $Cs_2[MoO_2Cl_4]$ and our product is similar in its i.r. and Raman spectra to that described by Griffith.[40] The spectra, including low-frequency data not reported before, are in Table 2. The presence of the *cis*-MoO_2 group is established by the pair of Mo–O bands which appear strongly in both i.r. and Raman spectra. The frequencies, 919 (symmetric stretching) and 883 cm^{-1} (antisymmetric stretching), are 40 cm^{-1} less than those of $[MoO_2Cl_2(H_2O)_2]$, which is consistent with the structure concerned being anionic. The expected MoO_2 bending frequency occurs at 382 cm^{-1} as a medium-intensity band in the i.r. and Raman spectra. Assuming C_{2v} symmetry for the complex anion $[MoO_2Cl_4]^{2-}$, the 15 vibrational modes consist of $6A_1 + 2A_2 + 4B_1 + 3B_2$ (the A_2 modes are i.r. inactive). A reasonable assignment of the observed frequencies can be made as shown in Table 2. Only solid state data are available; $Cs_2[MoO_2Cl_4]$ is insoluble in solvents of low polarity and is decomposed by donor solvents such as dmf or MeCN yielding a solution of the co-ordination complex $[MoO_2Cl_2L_2]$ (L = dmf or MeCN) and leaving a residue of CsCl.

Butcher *et al.*[37] performed a normal-co-ordinate analysis of $[MoO_2Cl_2(dmf)_2]$, and calculated the force constant f(Mo–O) 682 N m^{-1} for the molybdenum–oxygen bond. Assuming this force constant to be mainly determined by the Mo–O stretching frequencies, since these are well removed from the rest of the spectrum, we estimate f(Mo–O) values of 650 N m^{-1} for $[MoO_2Cl_4]^{2-}$ and 710 N m^{-1} for $[MoO_2Cl_2(H_2O)_2]$ or $[MoO_2Br_2(H_2O)_2]$. Because the separation of the ν_{sym} and ν_{asym} frequencies, 35—40 cm^{-1}, hardly changes, the same value of the interaction constant, f(Mo–O, Mo–O) = 47 N m^{-1}, can be assumed for all four complexes. The MoO_2 bending frequency at *ca.* 380 cm^{-1} is another useful characteristic by which to recognise the *cis*-MoO_2 group, and like the set of Mo–O stretching frequencies near 900 cm^{-1}, is a feature of all the octahedral molybdenum(VI) species identified in the present work.

Experimental

The commercial materials $Na_2[MoO_4]\cdot 2H_2O$ and $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ were used to prepare molybdenum(VI)

Table 2. Vibrational spectra and assignments for $[MoO_2Cl_4]^{2-}$ and $[MoO_2X_2(H_2O)_2]$ (X = Cl or Br)

Mode and symmetry[a]	$[MoO_2Cl_2(dmf)_2]$[b]	$[MoO_2Cl_4]^{2-}$		$[MoO_2Cl_2(H_2O)_2]$[c]		$[MoO_2Br_2(H_2O)_2]$[c]		$[MoO_2BrCl(H_2O)_2]$[c]		Description of vibration[d]
	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	
$\nu_1\ A_1$	940s	919vs	919s	960vs, p	960s	958vs, p	958s	960vs	960s	$\nu_{sym}(Mo–O_t)$
$\nu_9\ B_1$	905s	886m	883vs	923s, dp	922vs	918s, dp	918vs	920s	920vs	$\nu_{asym}(Mo–O_t)$
$\nu_2\ A_1$	416s			415w		410w		410w		$\nu_{sym}(Mo–O_l)$
$\nu_{10}\ B_1$	390m				390w		390w		390w	$\nu_{asym}(Mo–O_l)$
$\nu_3\ A_1$	378m	381m	382m	390m, p		385m, p		385m		$\delta_{sym}(Mo–O_t)$
$\nu_{13}\ B_2$	340s	325w	325s	348w	346s	—	—	—	—	$\nu_{asym}(Mo–Cl)$
$\nu_4\ A_1$	310w	308m	310(sh)	310s, p	305w	—	—	320w	320m	$\nu_{sym}(Mo–Cl)$
$\nu_7\ A_2$	278w	—	—	280w		280w				$\rho_t(Mo–O_t)$
$\nu_{11}\ B_1$	265w									$\delta(O_t–Mo–O_l)$
$\nu_{14}\ B_2$	252s	239m	239s	255s, dp?	255m	(252)[e]	(255)[e]	255m	255m	$\rho_r(Mo–O_t)$
$\nu_5\ A_1$	213m	214s	214w	224m, p?	225w	220w		224w		$\delta_{sym}(Mo–O_l)$
$\nu_{13}\ B_2$	—	—	—	—	—	252w, dp	255s	—	—	$\nu_{asym}(Mo–Br)$
$\nu_4\ A_1$	—	—	—	—	—	192s, p	190w	216s	215w	$\nu_{sym}(Mo–Br)$
$\nu_{15}\ B_2$	197m	180m	178s	185w						$\rho_r(Mo–O_t)$
$\nu_8\ A_2$	166m	172w		165w		160w		160w		$\rho_t(Mo–O_t)$
$\nu_{12}\ B_1$	145w	143w	146w	147w		—	—	—		$\delta_{asym}(Mo–Cl)$
$\nu_6\ A_1$	133w		130vw	136m		—	—	132w		$\delta_{sym}(Mo–Cl)$
$\nu_{12}\ B_1$	—	—	—	—	—	—	100w	—		$\delta_{asym}(Mo–Br)$
$\nu_6\ A_1$	—	—	—	—	—	90m		97w		$\delta_{sym}(Mo–Br)$

[a] Numbered according to C_{2v} symmetry. [b] Ref. 37. [c] Absorptions due to the H_2O ligand occur at 1 635, 3 200, and 3 380 cm^{-1}. [d] O_l refers to donor ligand, O_t to *cis*-MoO_2 group. [e] Coincides with $\nu_{asym}(Mo–Br)$ band.

solutions; 0.5 mol dm^{-3} solutions of $Na_2[MoO_4]$ in water or 2, 4, or 8 mol dm^{-3} HX (X = Cl, Br, NO_3, or ClO_4) were prepared, and these were mixed to furnish intermediate acid concentrations. Equilibration of polymeric molybdate species is complete within a matter of minutes. Consequently no changes in the spectra with time were observed. Molydenum(VI) solutions (*ca.* 1 mol dm^{-3}) in concentrated HCl or HBr were prepared using $Na_2[MoO_4]{\cdot}2H_2O$; some NaCl (or NaBr) crystals separated and the resulting solutions were pale yellow and yellow, respectively. The salt $Cs_2[MoO_2Cl_4]$ was prepared by adding CsCl to a hydrochloric acid solution of $Na_2[MoO_4]$.[40] The resulting precipitate dissolved on heating and recrystallised as a yellow solid. Attempts to prepare a corresponding bromide, $M_2[MoO_2Br_4]$ (M = Cs or NMe_4), were unsuccessful. Some attempts to introduce iodide into molydenum(VI) solutions led to dark blue or black mixtures due to a spontaneous redox reaction which yields molybdenum(V) or mixed-valence products. Diethyl ether, isobutyl methyl ketone, and tributyl phosphate were laboratory reagents, used without purification. Organic extracts were prepared by shaking equal volumes of the solvent and the particular aqueous phase.

N.m.r. spectra were obtained using a 10-mm broad-band probe in a Bruker AM400 spectrometer operating at 295 K. Molybdenum-95 n.m.r. spectra at 26.08 MHz were collected with 8K data points over 20 000 Hz using a 50° pulse (25 μs). Typically, the pulse repetition rate was 0.5 s and the data were processed using a line broadening of 30 Hz. Oxygen-17 n.m.r. spectra at 54.24 MHz were collected with 4K data points over 84 000 Hz using a 50° pulse (7 μs). The pulse repetition rate was 0.11 s. The typical line-broadening factor used was 50 Hz. Deuterium oxide was added to aqueous solutions to provide a locking signal. For ether extracts, $CDCl_3$ was added as an internal lock, and for isobutyl methyl ketone extracts, $CDCl_3$ in a concentric 5-mm tube provided the lock. Spectra were referenced to external 2 mol dm^{-3} $Na_2[MoO_4]$ in D_2O at pH 11 for ^{95}Mo or to water at 295 K for ^{17}O. Raman spectra of samples in glass capillary tubes were recorded using a Jasco R300 or modified Cary 81 spectrometer with Coherent Radiation argon (488 or 514 nm) or krypton (647 nm) laser excitation (50—200 mW of power at the sample). Molybdenum(VI) bromide solutions, and solid $Cs_2[MoO_2Cl_4]$, were subject to photochemical reduction becoming blue under argon laser irradiation, or on prolonged standing. Infrared spectra were recorded with Nicolet 5DX and Digilab FTS-60 Fourier-transform i.r. systems for the ranges 4 000—400 and 400—50 cm^{-1}, respectively. Solvent extract samples were sealed within cells fabricated from thin Polythene sheet for the i.r. spectroscopic measurements.

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