Lindqvist-Type (Aryldiazenido)polyoxomolybdates − Synthesis, and Structural and Spectroscopic Characterization of Compounds of the Type $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ar})]$

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Keywords: Molybdenum / NMR spectroscopy / Polyoxometalates / N ligands

A series of aryldiazenido compounds of the type $(n\mathrm{Bu}_4\mathrm{N})_3$-$[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ar})]$ have been prepared by treatment of $(n\mathrm{Bu}_4\mathrm{N})_4$-$[\mathrm{Mo}_8\mathrm{O}_{26}]$ with the appropriate arylhydrazines in acetonitrile or in methanol. All these compounds are isostructural. Two members of the series, the *o*-nitro and the *p*-carboxy derivatives, have been characterized by single-crystal X-ray diffraction. The aryl ring in the first anion lies in a mirror plane of the polyoxometalate, while in the second one it is tilted, allowing hydrogen bonding between the carboxylic acid function and a neighbouring anion. The aryldiazenido ligands exhibit the characteristic features of the singly bent coordination mode with short Mo–N and N–N bond lengths indicative of multiple bond character. The compounds have been characterized by ^{95}Mo and ^{17}O NMR spectroscopy in acetonitrile. Their spectra indicate C_{4v} symmetry, and hence stereochemical nonrigidity in solution. The ^{95}Mo chemical shifts are mainly determined by variation in the paramagnetic shielding term, σ_{para}. The strongly deshielded resonance of the $\mathrm{Mo}^{\mathrm{II}}$ centre spans a large range (600–1100 ppm).

Introduction

The functionalization of polyoxometalates (i.e., the replacement of one or several oxo ligands by other ligands) allows their properties to be tuned and provides a route to their application in supramolecular chemistry through the introduction of suitable pendent functions.[1,2] As part of a broad program centred on the functionalization of polyoxometalates, we have for some time been interested in the replacement of terminal oxo ligands by other multiply bonded ligands such as nitrosyl,[3−7] imido[8,9] and nitrido[10] ligands. From electronic considerations, these ligands fall into two categories, the first being the π-donor imido and nitrido ligands, RN^{2-} and N^{3-}, respectively, which can substitute for oxo ligands without a change in the oxidation state of the metal atom − although reduction of $\mathrm{Mo}^{\mathrm{VI}}$ to Mo^{V} is sometimes observed in the course of the reactions of polyoxomolybdates with precursors of imido and nitrido ligands − and the second being the π-acceptor nitrosyl ligand, which cannot bind to a d^0 metal centre. Consequently, (nitrosyl)polyoxometalates always contain reduced centres, for example, d^4 (M^{II}) and d^6 (M^0) in $\{\mathrm{M(NO)}\}^{3+}$ [3−7] and $\{\mathrm{M(NO)}_2\}^{2+}$ [11] units (M = Mo, W), respectively. Because of the analogy between nitrosyl and diazenido ligands,[12] there should be structurally related pairs of nitrosyl and diazenido derivatives of polyoxometalates, which might be obtained − at least in principle − through analogous reactions between hydroxylamine or monosubstituted hydrazines and polyoxomolybdates. However, the reactivity of hydrazines towards polyoxomolybdates contrasts with that of hydroxylamine. Nitrosyl derivatives containing $\{\mathrm{M(NO)}\}^{3+}$ units are quite easily obtained by treatment of polyoxomolybdates with hydroxylamine in nonaqueous solvents,[3,4,6] while the incorporation of $\{\mathrm{Mo(NO)}_2\}^{2+}$ units in polyoxomolybdates requires the use of additional ligands, such as amidoximes.[11] In contrast, the products of the reactions between hydrazines and polyoxomolybdates most often contain $\{\mathrm{Mo(N_2Ar)_2}\}^{2+}$ units,[13] while derivatives containing $\{\mathrm{Mo(N_2Ar)}\}^{3+}$ units are not easily obtained. The phenyldiazenido Lindqvist-type molybdate $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ph})]$ was described as early as 1986,[14] but in our hands the reported procedure failed to give the expected compound. The perfluoro derivative, $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{F}_5)]$, was reported soon after, but without full details about its preparation.[15] This latter paper also included a preliminary study of these compounds by ^{95}Mo NMR spectroscopy. In our experience, the synthesis of $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ar})]$ is quite sensitive to the boundary conditions. We report here the synthesis and characterization of an extended series of these compounds (Scheme 1).

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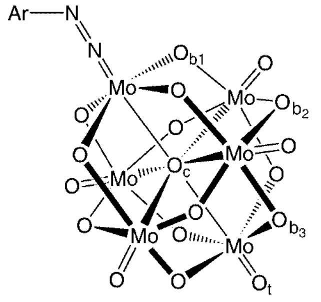
DOI: 10.1002/ejic.200300112



Ar	Compound	Ar	Compound
C_6H_5	**1**	C_6H_4-*m*-NO_2	**8**
C_6H_4-*p*-CH_3	**2**	C_6F_5	**9**
C_6H_4-*p*-F	**3**	C_6H_4-*o*-NO_2	**10**
C_6H_4-*p*-CN	**4**	C_6H_4-*p*-NO_2	**11**
C_6H_4-*p*-CF_3	**5**	C_6H_3-*o*,*p*-$(NO_2)_2$	**12**
C_6H_4-*p*-OCH_3	**6**	C_6H_4-*p*-CO_2H	**13**
C_6H_4-*o*-Cl	**7**		

Scheme 1

Results and Discussion

Synthesis

Arylhydrazines, $ArNHNH_2$, react with dioxomolybdenum(VI) complexes, $[MoO_2L_x]$, to give bis(aryldiazenido)molybdenum complexes of the type $[Mo(N_2Ar)_2L_x]$. While sulfur- and/or nitrogen-ligated ancillary ligands[16,17] are usually not displaced in the course of the reaction, oxygen-ligated ligands such as acetylacetone[18] and 2,3-butanediol[19] may be displaced. When the reaction is carried out in methanol this eventually produces tetranuclear complexes of the type $[Mo_4O_8(OMe)_2(N_2Ar)_4]^{2-}$.[19,20] These complexes are also easily obtained by treatment of $(nBu_4N)_4[Mo_8O_{26}]$ with arylhydrazines in refluxing MeOH,[13] and this approach can be generalized, compounds of the type $(nBu_4N)_2[Mo_4O_8(OR)_2(N_2Ar)_4]$ being obtainable from the reaction between an arylhydrazine and an isopolyoxomolybdate such as $(nBu_4N)_2[Mo_6O_{19}]$ or $(nBu_4N)_4[Mo_8O_{26}]$ in an alcohol (ROH). It was originally thought that the formation of Lindqvist-type derivatives, $(nBu_4N)_3[Mo_6O_{18}(N_2Ar)]$, would be favoured in acetonitrile, but complexes containing $\{Mo(N_2Ar)_2\}^{2+}$ moieties, such as $[Mo_8O_{20}(N_2Ar)_6]^{4-}$,[21] are again the major compounds formed. We have now found that the solvent is not critical. Indeed, $[Mo_6O_{18}(N_2C_6H_4\text{-}p\text{-}NO_2)]^{3-}$ can be obtained in acetonitrile as well as in MeOH or EtOH. In fact, the formation of the $\{Mo(N_2Ar)\}^{3+}$ unit, and hence the $[Mo_6O_{18}(N_2Ar)]^{3-}$ complexes **1**−**13**, depends critically upon the temperature and the composition of the reactant mixture. In a typical preparation, the arylhydrazine was added to a solution of $(nBu_4N)_4[Mo_8O_{26}]$ in degassed acetonitrile and the mixture was stirred at ca. 50 °C for a short period of time. Heating must not be prolonged after the colour of the mixture has changed to red-brown. Addition of triethylamine, even if the arylhydrazine was not introduced in the form of its hydrochloride, is beneficial to the reaction. It has also been found that the yield of $(nBu_4N)_3[Mo_6O_{18}(N_2Ar)]$ can be significantly increased by addition of $(nBu_4N)Br$, which is likely to help precipitation of the target compounds.

The $[Mo_6O_{18}(N_2Ar)]^{3-}$ derivatives **1**−**13** are only moderately stable in solution. In most cases, the progressive increase of the ^{95}Mo NMR signals of $[Mo_6O_{19}]^{2-}$ and α-$[Mo_8O_{26}]^{4-}$ indicates decomposition. For example, at 50 °C the parent complex $[Mo_6O_{18}(N_2Ph)]^{3-}$ was found to transform mainly into $[Mo_6O_{19}]^{2-}$ in DMF while α-$[Mo_8O_{26}]^{4-}$ was the major decomposition product in acetonitrile.

X-ray Diffraction Analysis

The *o*-nitro (**10**), *p*-nitro (**11**) and *p*-carboxy (**13**) derivatives have been characterized by single-crystal X-ray diffraction. Soon after the study of **11** had been completed, we became aware of the report by Li et al.[22] on the same compound. As there are no significant differences between the two sets of data, we will not enlarge on the crystal structure of **11**. Three other compounds of the type $(nBu_4N)_3[Mo_6O_{18}(N_2Ar)]$, namely **1**,[14] **9**[15] and **12**,[23] had been characterized previously. With the exception of **13**, all the compounds of the type $(nBu_4N)_3[Mo_6O_{18}(N_2Ar)]$ characterized to date are isomorphous (space group *Pmcn*) and the anion displays C_s symmetry with the aryl group lying in the plane of symmetry passing through the two apical Mo centres and two bridging oxygen atoms of the equatorial belt (Mo1, O33, Mo6 and O44 in Figure 1). Compound **13** crystallizes in the $P2_1cn$ space group, the noncentrosymmetric counterpart of the *Pmcn* space group. In this structure, the aromatic ring does not lie in the plane defined above. Instead, it lies almost in the plane of an $\{Mo_4O_4\}$ ring comprising Mo1, Mo2, Mo4 and Mo6 (Figure 2), the deviation being fairly small (13.5°) and the arrangement perhaps being the result of intermolecular interactions in the solid. The anions are linked into chains through O−H···O bonds involving the carboxylic acid function of one anion and a terminal oxygen atom of another anion [O···O 2.796(16) and 2.788(16) Å]. The aryldiazenido ligands in $[Mo_6O_{18}(N_2Ar)]^{3-}$ exhibit the characteristic features of the singly bent coordination mode with a linear Mo−N−N arrangement and short Mo−N and N−N bond lengths indicative of multiple-bond character (Table 1).[13−17] The bond angle at the β-nitrogen atom is around 120° as expected for an sp^2-hybridized atom. The Mo−O distance between the functionalized Mo centre and the central oxygen atom (O_c, see Scheme 1) is significantly shorter than other Mo−O_c distances. Analogous contractions have been observed in other monofunctionalized Lindqvist-type hexamolybdates such as $[Mo_6O_{18}(NNMePh)]^{2-}$,[24] $[Mo_6O_{18}(NC_6H_4\text{-}p\text{-}CH_3)]^{2-}$ [25] and $[Mo_6O_{18}(\eta^5\text{-}C_5Me_5)]^{-}$,[26] reflecting the weaker *trans* influence of diazenido, hydrazido, imido and cyclopentadienyl ligands relative to the oxo ligand. Inspection of bond lengths in the Mo_4O_4 rings going through Mo(1) (Figures 1 and 2) reveals the same pattern of bond length alternation as observed in other monosubstituted hexamolybdates.[24−27] Because of the disorder in the solid-state structure of $(n\mathrm{Bu_4N})_3[\mathrm{Mo_6O_{18}(NO)}]$,[5] no accurate comparison can be made between the structural parameters of $[\mathrm{Mo_6O_{18}(N_2Ar)}]^{3-}$ and those of $[\mathrm{Mo_6O_{18}(NO)}]^{3-}$. However, there is no doubt that the bonding features within the $\{\mathrm{Mo(N_2Ar)}\}^{3+}$ unit are quite similar to those of the $\{\mathrm{Mo(NO)}\}^{3+}$ unit. In such coordination modes, diazenido and nitrosyl ligands are commonly regarded as $\mathrm{RN_2}^+$ and NO^+ species, respectively. According to this formalism, $\{\mathrm{Mo(N_2Ar)}\}^{3+}$ and $\{\mathrm{Mo(NO)}\}^{3+}$ units contain $\mathrm{Mo^{II}}$ centres.

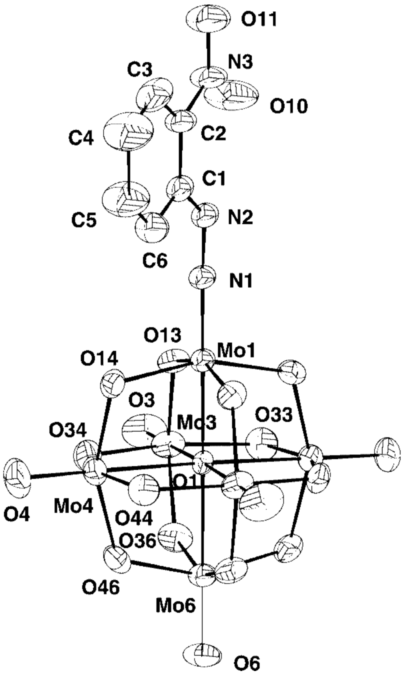


Figure 1. Molecular structure of $[\mathrm{Mo_6O_{18}(N_2C_6H_4\text{-}\mathit{o}\text{-}NO_2)}]^{3-}$; thermal ellipsoids are drawn at the 30% probability level

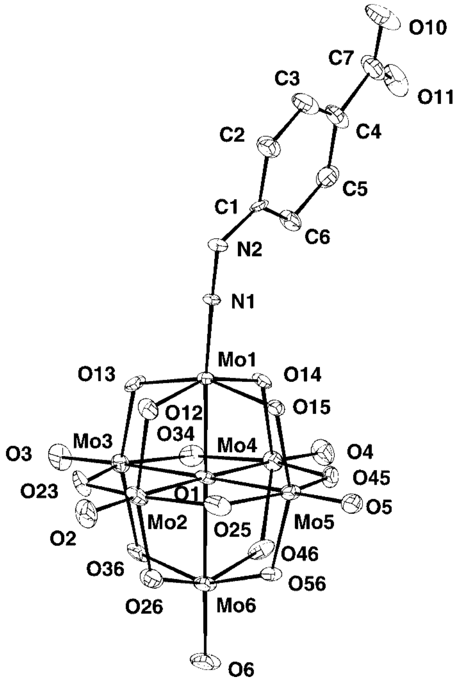


Figure 2. Molecular structure of $[\mathrm{Mo_6O_{18}(N_2C_6H\text{-}\mathit{p}\text{-}CO_2H)}]^{3-}$; thermal ellipsoids are drawn at the 30% probability level

Table 1. Geometric features of the $\mathrm{MoN_2Ar}$ groups in $(n\mathrm{Bu_4N})_3[\mathrm{Mo_6O_{18}(N_2Ar)}]$

Compound	Mo−N [Å]	N−N [Å]	Mo−N−N [°]	Ref.
1	1.76(2)	1.31(3)	178.7(19)	[14]
9	1.75(2)	1.30(3)	170.6(21)	[15]
10	1.75(1)	1.285(14)	173.9(10)	this work
11	1.74(2)	1.29(2)	178(2)	[22]
12	1.762	1.292	176.03	[23]
13	1.76(1)	1.246(13)	174.7(10)	this work

IR Spectroscopy

In the low-wavenumber region of the IR spectra ($\tilde{\nu} < 1000\ \mathrm{cm^{-1}}$), all the $(n\mathrm{Bu_4N})_3[\mathrm{Mo_6O_{18}(N_2Ar)}]$ compounds **1**−**13** display similar patterns characteristic of the Lindqvist structure. Actually, the IR bands of the aryldiazenido ligand in this region (mostly C−C and C−H deformations) are of low intensity with respect to those of the polyoxometalate framework. $(n\mathrm{Bu_4N})_3[\mathrm{Mo_6O_{18}(N_2Ar)}]$ presents more complex features than $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{19}}]$, especially in the 1000−700 $\mathrm{cm^{-1}}$ range characteristic of Mo−O stretchings. In particular, the strong $\nu_{as}(\mathrm{Mo{-}O_t})$ band observed at 958 $\mathrm{cm^{-1}}$ in $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{19}}]$[28] splits into two more or less resolved bands ($\Delta\tilde{\nu} \approx 20\ \mathrm{cm^{-1}}$) in the aryldiazenido derivatives. Similarly, the broad band observed at 796 $\mathrm{cm^{-1}}$ in the parent hexamolybdate and assigned to a $\mathrm{Mo{-}O_b}$ stretching mode, also splits into two components ($\Delta\tilde{\nu} \approx 25\ \mathrm{cm^{-1}}$) in $(n\mathrm{Bu_4N})_3[\mathrm{Mo_6O_{18}(N_2Ar)}]$ (Figure 3). Such splittings are commonly observed in monofunctionalized hexamolybdates, such as imido,[8,9] nitrosyl,[4,5] and cyclopentadienyl[26] derivatives, and they have been ascribed to the reduction in symmetry of the oxometalate framework from O_h to C_{4v} upon the substitution of MoX for MoO. According to group theory, this should result in the splitting of all IR-active triply degenerated F_2 modes into A_1 and E modes. A detailed analysis, using Mo−N and $\mathrm{Mo{-}O_t}$ internal coordinates, allows four IR-active modes to be predicted: one Mo−N and three $\mathrm{Mo{-}O_t}$, according to the following representation:[8]

$$\Gamma(\mathrm{Mo{-}O_t}) = 2\mathrm{A_1(IR, R)} + \mathrm{B_1(R)} + \mathrm{E(IR, R)}$$

$$\Gamma(\mathrm{Mo{-}N}) = \mathrm{A_1(IR, R)}$$

In the approximation of separate $\mathrm{Mo{-}O_t}$ and Mo−N vibrators, the stronger band, at low energy ($\tilde{\nu} \approx 940\ \mathrm{cm^{-1}}$), should be assigned to the E-type $\nu_{as}(\mathrm{Mo{-}O_t})$ mode, whereas the less intense band ($\tilde{\nu} \approx 965\ \mathrm{cm^{-1}}$) might correspond to an $\mathrm{A_1}$-type mode, associated principally with the Mo−N vibrator. Mechanical coupling between the $\mathrm{Mo{-}O_t}$ and Mo−N vibrators are not excluded, however. Isotopic

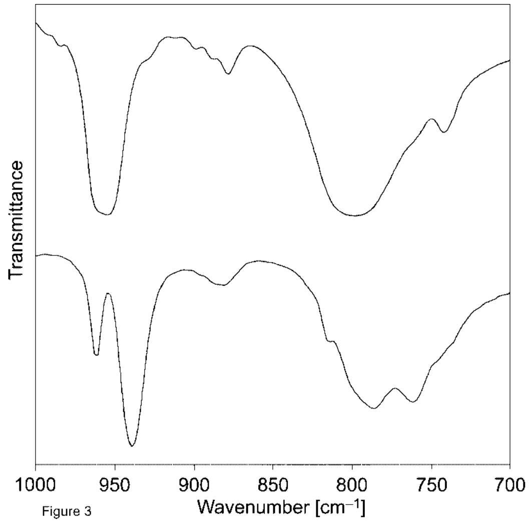


Figure 3. Part of the IR spectra of $[Mo_6O_{19}]^{2-}$ (top) and $[Mo_6O_{18}(N_2C_6H$-*p*-$CH_3)]^{3-}$ (bottom); note the splitting of the Mo=O (left) and Mo−O−Mo (right) bands in the diazenido complex

^{15}N and/or ^{18}O labelling is needed to reach a definite conclusion.

In all compounds **1**−**13**, the aromatic ν(C−H) bands ($\tilde{\nu} > 3000$ cm^{-1}) are hardly visible, due to their low intensity, and the complex pattern around 2900 cm^{-1} contains aliphatic ν(C−H) bands both of the tetrabutylammonium cation and of the substituent on the aromatic ring. The IR spectra of compounds **1**−**13** differ markedly in their band positions but also in their intensities in the medium-frequency region (1650−1300 cm^{-1}) where ν(N=N) and various bands from the arene occur.[29] It should be noted that this part of the IR absorption spectrum is more complex and more intense for a given (aryldiazenido)hexamolybdate than for the (arylimido)hexamolybdate $[Mo_6O_{18}(NAr)]^{2-}$ with the same Ar group.[8,30] By use of extensive isotopic labelling on mononuclear (aryldiazenido)metal complexes, Ibers and co-workers have shown that the intensity of the intrinsically weak ν(N=N) band may be considerably enhanced by resonance interaction with phenyl modes. This also results in differences between the experimentally observed band position and the real ν(N=N) frequency.[29] Apparently, resonance interactions also occur in the aryldiazenido hexamolybdates, because of the intense features observed between 1650 and 1300 cm^{-1}. Without isotopic labelling it is then impossible to determine the exact frequency of the N=N stretching mode, and thus the strength of the N=N bond.

UV/Vis Spectroscopy

The UV/Vis electronic spectra were recorded in acetonitrile solutions at room temperature. Slow changes were observed on standing, in line with the ^{95}Mo NMR study, indicating progressive transformation mainly into α-$[Mo_8O_{26}]^{4-}$. The electronic spectrum of the phenyldiazenido derivative **1** was recorded in different solvents, and almost identical spectra were obtained except in methanol, in which a fast transformation occurs. The electronic spectra of compounds **1**−**13** split into two groups. Those of compounds **1**−**3** and **5**−**9** exhibit two bands at ca. 390 and 290 nm, the second being more intense than the first. In addition, there are two shoulders on the lower energy side of each main band. The second group of compounds comprises the nitro derivatives **10**−**12**, for which the more intense band lies in the visible region. Compounds **4** and **13** are somewhat intermediate. The lower energy absorptions are clearly associated with the $\{Mo(N_2Ar)\}$ chromophore and their high molar absorptivity is indicative of charge-transfer character. This contrasts with $[Mo_6O_{18}(NO)]^{3-}$ and other polyoxomolybdates containing $\{Mo(NO)\}^{3+}$ units, which display a band most probably associated with a $d_{xz},d_{yz} \rightarrow d_{xy}$ transition.[3−6] Although we prefer not to speculate extensively on the origin of the absorption bands until a theoretical study has been performed, the difference between nitrosyl and diazenido derivatives might be related to the change from C_{4v} to C_s symmetry on going from $[Mo_6O_{18}(NO)]^{3-}$ to $[Mo_6O_{18}(N_2Ar)]^{3-}$. Indeed in six-coordinate complexes, bending of the diazenido ligand has a stabilizing effect on the π* N_2Ar orbital in the plane of bending.[31,32]

NMR Spectroscopy

The characterization of compounds **1**−**13**, $(n\text{Bu}_4N)_3$-$[Mo_6O_{18}(N_2Ar)]$, by multinuclear NMR (^{17}O and ^{95}Mo) spectroscopy was carried out in the same way as used for the nitrosyl derivatives $(n\text{Bu}_4N)_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W)[6] and the imido derivatives $(n\text{Bu}_4N)_2[Mo_6O_{19-x}(NR)_x]$ (x = 1−6):[8,9] in acetonitrile and at elevated temperatures (usually 50 °C). This allows the relaxation rate of the quadrupolar nuclei (^{17}O and ^{95}Mo) to be decreased and the linewidths of the resonance signals to be reduced. Even under these conditions, some of the expected ^{95}Mo resonances were not observed, probably because of extreme broadening. In some cases, such as **8**, **9** and **11**, however, full ^{95}Mo spectra could be obtained at room temperature, although the signals were significantly broadened with respect to the high-temperature spectra. Unlike the nitrosyl and imido derivatives, the diazenido compounds proved to be only fairly stable at 50 °C, even in dried acetonitrile. Decomposition was evident from the progressive growth of the ^{95}Mo NMR signals characteristic of $[Mo_6O_{19}]^{2-}$ (δ = 125 ppm) and of α-$[Mo_8O_{26}]^{4-}$ (δ = 21 and −11 ppm). In particular, decomposition could not be avoided for compounds with a donor substituent on the aryl group, and in some cases it was nearly complete during the time required for the acquisition of the ^{95}Mo spectrum, so measurement of a full set of NMR spectroscopic data was not possible for each member of the series $(n\text{Bu}_4N)_3$-$[Mo_6O_{18}(N_2Ar)]$. Results are listed in Tables 2 and 3. No significant data could be collected for **3** and **6**, and nearly complete sets of ^{17}O and ^{95}Mo data were obtained only for

7, **8**, **9** and **12**. Nevertheless, this allows a comparison with $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{NO})]$ and reveals some trends within the series of diazenido compounds.

Table 2. ^{95}Mo NMR spectroscopic data for (aryldiazenido)hexamolybdates $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ar})]^{3-}$[a][b]

Compound	δ(Mo^{II})	δ(Mo^{VI}) eq.	 ax.	$\Delta\delta_{\mathrm{eq.-ax.}}$
1	[c]	214	155	59
2	[c]	214	156	58
4	998	202	153	49
5	1100	206	153	53
7	[c]	208	155	53
8	1092	206	151	55
9	961	202	154	48
10	940	201	154	47
11	845	197	150	47
12	600	185	149	36

[a] Spectra recorded at 50 °C in acetonitrile solutions. [b] Chemical shifts in ppm with respect to external aqueous alkaline solution of 2 M $\mathrm{Na}_2\mathrm{MoO}_4$. [c] Not observed.

Table 3. ^{17}O NMR spectroscopic data for (aryldiazenido)hexamolybdates $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{Ar})]^{3-}$[a][b]

Compound	T [°C]	δ(O$_t$) eq.	 ax.	δ(O$_b$)			δ(O$_c$)
7	25	892.5	877.7	603.3	564.5	530.6	[c]
8	25	891.3	876.8	599.1	562.0	528.9	−37.1
9	50	892.6	878.7	603.3	563.0	531.8	ca. −30
12	50	902.6	888.8	593.1	566.6	538.6	−26

[a] Spectra recorded in acetonitrile solutions. [b] Chemical shifts in ppm with respect to neat $\mathrm{H_2O}$. [c] Not observed.

Before discussing the NMR spectroscopic data in detail, let us remember briefly the two terms determining the shielding (σ) and the chemical shift ($\delta = -\sigma$) of a given nucleus.[33] Shielding is usually expressed as the sum of two opposite terms: the diamagnetic term σ_{dia} (positive) and the paramagnetic term σ_{para} (negative).

$$-\delta = \sigma = \sigma_{\mathrm{dia}} + \sigma_{\mathrm{para}}$$

An increase in the electron density at the nucleus results in an increase in the diamagnetic contribution and hence shifts the resonance to lower chemical shifts. In contrast, an enhanced paramagnetic contribution results in reduced shielding and shifts the NMR line to higher δ values. Furthermore, σ_{para} depends on all electronic excitation energies; in favourable cases it is inversely proportional to the HOMO−LUMO gap. Then, within a congruent set of complexes, the net deshielding of the NMR signal may reflect the decrease in the HOMO−LUMO gap through the increase of the paramagnetic contribution.

^{95}Mo NMR Spectroscopy

The ^{95}Mo NMR spectrum of $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)]$ (**11**) in acetonitrile displays three signals in an approximate ratio of 1:4:1 in order of increasing shielding (Figure 4). This spectrum is quite similar to that of $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{NO})]$, so the two more-shielded signals at δ = 197 ppm (4 Mo, $\Delta\nu_{1/2} \approx 200$ Hz) and at δ = 150 ppm (1 Mo, $\Delta\nu_{1/2} \approx 350$ Hz) may be assigned to the equatorial and axial Mo^{VI} centres, respectively, while the strongly deshielded and broad signal ($\Delta\nu_{1/2} \approx 600$ Hz) at δ = 845 ppm may be assigned to the Mo^{II} centre. According to these data, the apparent symmetry of $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)]^{3-}$ in solution is C_{4v}, while its actual symmetry is at most C_s, as observed in the solid state.[22] Because other members of the series behave similarly, and because analysis of the ^{17}O NMR spectra suggests the same conclusion (see below), accidental degeneracy of signals can be ruled out. The NMR spectroscopic data in solution thus indicate fast rotation of the aryldiazenido ligand on NMR timescales. There is precedent for such a rotation.[34]

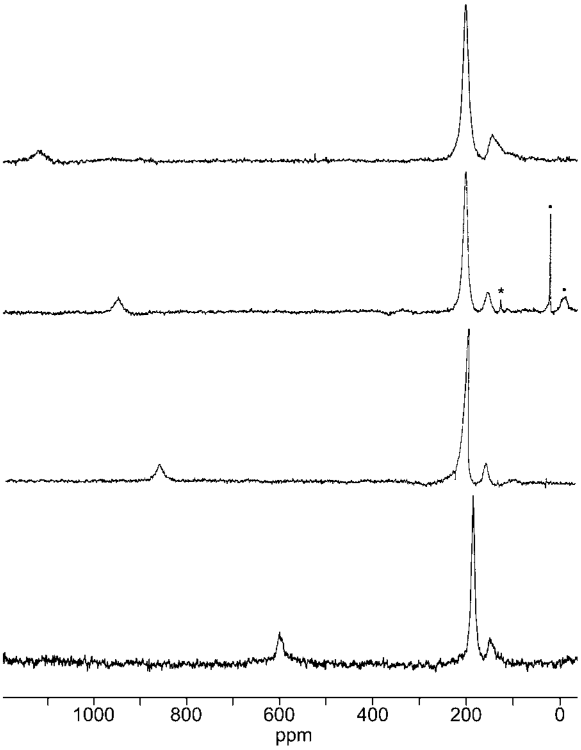


Figure 4. 32.6 MHz ^{95}Mo NMR spectra of all NO$_2$-substituted diazenido hexamolybdates; from top to bottom: $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}m\text{-}\mathrm{NO}_2)]^{3-}$ (**8**), 25 °C, 20 mM, 288·10^3 transients; $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}o\text{-}\mathrm{NO}_2)]^{3-}$ (**10**), 50 °C, 50 mM, 77·10^3 transients; $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)]^{3-}$ (**11**), 50 °C, 28 mM, 120·10^3 transients; $[\mathrm{Mo}_6\mathrm{O}_{18}\{\mathrm{N}_2\mathrm{C}_6\mathrm{H}_3\text{-}o,p\text{-}(\mathrm{NO}_2)_2\}]^{3-}$ (**12**), 50 °C, 20 mM, 54·10^3 transients; note the relative broadness of the room-temperature spectrum of **8** and the spurious signals from $[\mathrm{Mo}_6\mathrm{O}_{19}]^{2-}$ (*) and of α-$[\mathrm{Mo}_8\mathrm{O}_{26}]^{4-}$(·) in the spectrum of **10**; general conditions for all spectra: spectral width 45 kHz (ca. 1400 ppm); pulse width 10 µs (ca. 30° flip angle); acquisition time 45 ms; no relaxation delay; the time domain data (4 K points) were multiplied by an exponential window (LB, 20 Hz) prior to Fourier transformation without zero-filling; baseline distortions were corrected by use of the Bruker software

The deshielding of the functionalized Mo can be attributed to the dominant role of the paramagnetic contribution. In addition, the similarity between the chemical shifts supports similar electronic structures (i.e., d^4 Mo^{II} centres) both in $[Mo_6O_{18}(N_2C_6H_4\text{-}p\text{-}NO_2)]^{3-}$ and in $[Mo_6O_{18}(NO)]^{3-}$ compounds. Any compound of the type $(n\mathrm{Bu}_4N)_3[Mo_6O_{18}(N_2Ar)]$ should display the same type of ^{95}Mo spectrum, with a strongly deshielded signal and two resonances at $\delta \approx 200$ and 150 ppm. The deshielded resonance is always quite broad and could not be observed for compounds **1**, **2** and **7**. Otherwise, all data agree with the typical spectra of Figure 4. Let us note that Zubieta and Ellis have already reported ^{95}Mo NMR spectroscopic data on compound **1**.[15] Like us, they only observed two signals, lying in a range typical of Mo^{VI} centres, though their reported chemical shifts are not in agreement with our observations. In our hands, $[Mo_6O_{18}(N_2Ph)]^{3-}$ proved to be amongst the less stable diazenido complexes, and the data reported by Zubieta and Ellis might correspond to decomposition products.

The chemical shifts for both equatorial and axial $\{^{95}MoO\}$ sites in the diazenido derivatives are uniformly deshielded with respect to those of $[Mo_6O_{19}]^{2-}$. In contrast to the wide variance of the $\{^{95}MoN_2Ar\}$ resonances, the $\{^{95}MoO\}$ resonances fall within a narrow range: δ = 185−214 ppm for the equatorial sites, and δ = 149−156 ppm for the axial site. A trend can be established for those compounds in which the three signals are observed: deshielding of the $\{^{95}MoN_2Ar\}$ resonance is accompanied by definite, albeit smaller, deshielding of the $\{^{95}MoO\}$ resonances (Figure 5). By extrapolation of this trend to all the members of the series, the $\{^{95}MoN_2Ph\}$ resonance for **1** would be expected at $\delta \approx 1300$ ppm.

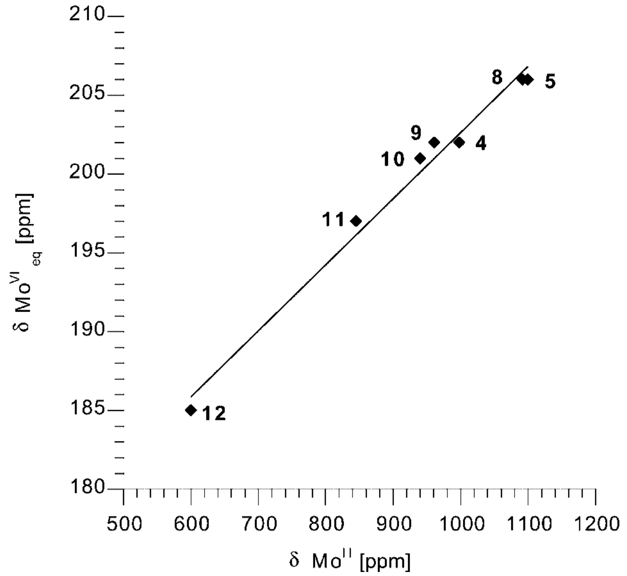


Figure 5. Plotting of the ^{95}Mo chemical shifts of the equatorial Mo^{VI} centres as a function of those of the Mo^{II} centre in the (diazenido)hexamolybdates; the heavy line represents the best fit from a linear regression $\delta(Mo^{VI}) = 4.19\cdot10^{-2}\ \delta(Mo^{II}) + 160.7$ ppm ($R = 0.993$)

It may be inferred from these observations, and from comparison with the nitrosyl complexes $[M_5O_{18}\{M'(NO)\}]^{3-}$ (M, M′ = Mo, W)[6] and the imido complexes $[Mo_6O_{18}(NR)]^{2-}$,[8,9] that all the ^{95}Mo chemical shifts for $[Mo_6O_{18}(N_2Ar)]^{3-}$ are mainly determined by variation in the paramagnetic shielding term, σ_{para}. While imido ligands are superior to oxo ligands as electron donors, nitrosyl and diazenido ligands − to be regarded as NO^+ and RN^{2+}, respectively − are strong Lewis acids and their complexes have low-lying excited states. Accordingly, there is a bathochromic shift of the lower energy absorptions of $[M_5O_{18}\{M'(NO)\}]^{3-}$ and $[Mo_6O_{18}(N_2Ar)]^{3-}$ in relation to $[Mo_6O_{18}(NR)]^{2-}$. While the $\{^{95}MoN\}$ chemical shifts correlate with λ_{max} for the arylimido complexes $[Mo_6O_{18}(NAr)]^{2-}$,[9,30] no such correlation could be found for the aryldiazenido complexes $[Mo_6O_{18}(N_2Ar)]^{3-}$, whether the lowest energy transition (which most often appears as a shoulder) or the next one is considered. Attempts were also made to correlate the ^{95}Mo chemical shifts of the *p*-substituted compounds with either Hammett function σ_p or σ_p^+: although there is no evident correlation, it is clear that both $\{^{95}MoN\}$ and $\{^{95}Mo_{eq}O\}$ resonances move to lower frequency on going from electron-donating (Me) to electron-withdrawing substituents (CN, CF_3, NO_2). For the (dinitrophenyl)diazenido species **12**, the cumulative effect of the two strongly electron-withdrawing substituents produces the most shielded spectrum of the series. A similar trend has been observed for $\delta\{^{95}MoN\}$ in the (arylimido)hexamolybdates $(n\mathrm{Bu}_4N)_2[Mo_6O_{18}(NC_6H_4\text{-}p\text{-}X)]$,[8,9,30] as well as for $\delta(^{51}V)$ in the (arylimido)vanadium(v) complexes $[VCl_3(NC_6H_4N\text{-}p\text{-}X]$,[35] and was explained by variations in the paramagnetic shielding term. We therefore suggest that the same effect is likely to apply to the aryldiazenido series. Nevertheless, further studies, in particular theoretical calculations, are needed to provide a full account of the variation of the ^{95}Mo chemical shifts in this series.

^{17}O NMR Spectroscopy

As noted above, the low solubilities and the long-term instabilities of the diazenido complexes hampered the acquisition of natural-abundance ^{17}O spectra. Moreover the sensitivity of most of these compounds to hydrolysis did not allow ^{17}O-enriched samples to be obtained. ^{17}O NMR spectra were therefore obtained only for **7**, **8**, **9** and **12** (Table 3). As a typical example, the room-temperature spectrum of $[Mo_6O_{18}(N_2C_6H_4\text{-}m\text{-}NO_2)]^{3-}$ (**8**) is displayed in Figure 6. This spectrum is very similar to that of $[Mo_6O_{18}(NO)]^{3-}$ [5] and is consistent with the C_{4v} symmetry of the species. The ^{17}O spectra of **8**, **9** and **12** all display six signals in an approximate intensity ratio of 4:1:4:4:4:1, which may be assigned to the terminal (O_t) resonances at $\delta \approx 880-900$ ppm, to the bridging (O_b) resonances between δ = 530 and 600 ppm and to the central (O_c) resonance at $\delta \approx -30$ ppm (Table 3). The signal of O_c in **7**, and also those of the nitro groups in **7** and **12**, were not detected. The four diazenido compounds measured here and the

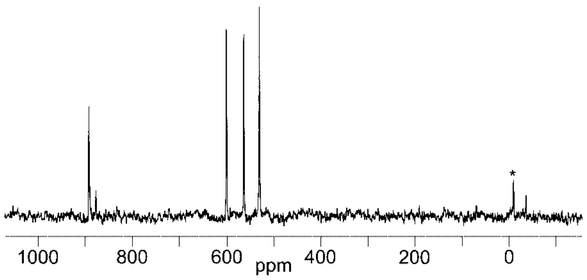


Figure 6. 67.8 MHz natural-abundance ^{17}O NMR spectrum of a 20 mM solution of $[Mo_6O_{18}(N_2C_6H_4\text{-}m\text{-}NO_2)]^{3-}$ (**8**) in CH_3CN; experimental conditions: spectral width 83 kHz (> 1200 ppm); pulse width 20 µs (ca. 45° flip angle); acquisition time 25 ms; no relaxation delay; $1.8 \cdot 10^6$ transients were acquired for a total spectrometer time of 12.5 h; the time domain data (4 K points) were multiplied by an exponential window (LB, 40 Hz) prior to Fourier transformation without zero-filling; baseline distortions were corrected by use of the Bruker software; the signal marked with an asterisk corresponds to H_2O

nitrosyl derivative provide a homogeneous set of ^{17}O data, again not in agreement with those reported by Zubieta and Ellis for $[Mo_6O_{18}(N_2C_6F_5)]^{3-}$.[15]

According to Klemperer,[36,37] the general pattern of the ^{17}O NMR spectra of polyoxometalates is determined by the paramagnetic shielding term, which accounts for the sequence $\delta(O_t) > \delta(O_b) > \delta(O_c)$, following decreasing π-bond order. However, variations in the diamagnetic term must be considered in order to explain the relatively subtle chemical shift modulations within each group. As with the nitrosyl derivatives, the signals of the terminal oxygen atoms in the diazenido derivatives are shielded with respect to that of $[Mo_6O_{19}]^{2-}$, in keeping with the net increase in negative charge over the polyoxometalate framework when $[Mo^{II}NO]^{3+}$ or $[Mo^{II}NNAr]^{3+}$ is substituted for $[Mo^{VI}O]^{4+}$. In contrast to the ^{95}Mo chemical shifts, the most deshielded O_t resonances in the series are shown by the dinitro derivative (**12**). This is in accordance with IR data, which indicate the highest $Mo-O_t$ stretching energy, and thus the strongest $Mo-O_t$ bond, for this compound.

With regard to the O_b signals, one appears at higher frequency than the unique O_b resonance of $[Mo_6O_{19}]^{2-}$; it had already been assigned to the oxygen atoms (O_{b1}) bridging Mo^{II} and the four equatorial Mo^{VI}.[5] The central O_b resonance does not move significantly throughout the series: it lies approximately at the same position, within ± 3 ppm, as the hexamolybate signal, a situation already encountered in the monoimido series.[8,9] Finally, the most shielded O_b signal, at −25 to −30 ppm from the previous one, seems to be the only one reflecting the overall negative charge increase.

Conclusion

A series of aryldiazenido compounds of the type $(nBu_4N)_3$-$[Mo_6O_{18}(N_2Ar)]$ has been prepared by treatment of $(nBu_4N)_4[Mo_8O_{26}]$ with the appropriate arylhydrazines in acetonitrile or in methanol. All these compounds are isostructural and belong to the family of Lindqvist-type polyoxometalates. Two members of the series, the *o*-nitro and *p*-carboxy derivatives, have been characterized by single-crystal X-ray diffraction. The first anion displays C_s symmetry, in the second one the aromatic ring is tilted and thus allows hydrogen bonding of the carboxylic acid to a neighbouring anion. The aryldiazenido ligands exhibit features characteristic of the singly bent coordination mode with short Mo−N and N−N bonds indicative of multiple-bond character. The compounds have been characterized by ^{95}Mo NMR spectroscopy in acetonitrile. Their spectra are normally composed of three signals in an intensity ratio of 1:4:1, although the strongly deshielded resonance ($\delta \approx 1100-600$ ppm) is quite broad and was not always observed. The large deshielding of the Mo^{II} centre arises from paramagnetic contributions.

We have shown here the possibility of obtaining a family of functionalized polyoxometalates differing in the substituents on the aromatic rings. These substituents influence the physical and chemical properties of the hexamolybdate, as can be seen by the spectroscopic characterization of the compounds and their different stabilities in solution. The presence of reactive groups on the aromatic ring allows further derivatization, and we are now investigating the possibilities of carbon−carbon coupling and elaboration on the carboxylic acid.

Experimental Section

General Procedures and Materials: All reactions were performed under dry nitrogen. Reagents and chemicals were purchased from commercial sources and were used as received. Solvents were purified and dried by standard procedures. $(nBu_4N)_4[Mo_8O_{26}]$ was prepared as reported in the literature.[38] IR spectra were recorded in KBr pellets with a BioRad FTS 165 FT-IR spectrophotometer. UV/Vis spectra were recorded in acetonitrile solutions (concentration ca. $2.5 \cdot 10^{-4}$ M) with a Shimadzu UV-2101 spectrophotometer. Natural-abundance ^{17}O and ^{95}Mo NMR spectra were recorded at 67.8 and 32.6 MHz, respectively, by use either of a Bruker AM 500 or of a Bruker DRX 500 spectrometer. All spectra were obtained without lock from nearly saturated acetonitrile solutions in 10-mm o.d. tubes. Sample concentrations ranged from 40 to 200 mg in 2.5 mL of CH_3CN (from 0.01 to 0.05 M). Chemical shifts δ are reported in ppm with respect to external H_2O (^{17}O) and external aqueous alkaline solution of 2 M Na_2MoO_4 (^{95}Mo) according to the IUPAC recommendation. Positive δ corresponds to high frequency shift (deshielding) with respect to the reference. Elemental analyses were performed by the "Service de microanalyse", Université Pierre et Marie Curie, Paris, France and by the "Service central d'analyse", CNRS, Vernaison, France.

Syntheses: The preparations of the compounds $(nBu_4N)_3$-$[Mo_6O_{18}(N_2Ar)]$ divide into two groups, differing mainly in the solvent used, and in the presence of base.

Compounds 1−8: $(nBu_4N)_4[Mo_8O_{26}]$ (2.15 g, 1.00 mmol), twice the molar amount of the appropriate arylhydrazine ($C_6H_5NHNH_3Cl$, 0.289 g; *p*-Me-$C_6H_4NHNH_3Cl$, 0.317 g; *p*-F-$C_6H_4NHNH_3Cl$, 0.325 g; *p*-NC-$C_6H_4NHNH_3Cl$, 0.339 g; *p*-F_3C-$C_6H_4NHNH_2$, 0.352 g; *p*-MeO-$C_6H_4NHNH_3Cl$, 0.349 g; *o*-Cl-$C_6H_4NHNH_3Cl$, 0.358 g; *m*-O_2N-$C_6H_4NHNH_3Cl$, 0.379 g), $(nBu_4N)Br$ (0.50 g, 1.55 mmol) and NEt_3 (2.8 mL, 20 mmol) were added to MeCN

(15 mL). The mixture was vigorously stirred and heated at ca. 50 °C until its colour had turned dark brown (20 min at most). The product sometimes started to precipitate at this stage. Filtration was carried out after the solution had been concentrated to ca. 10 mL and cooled to room temperature. The collected solid was washed with a 1:1 mixture of MeCN and Et_2O, then with pure Et_2O, and dried under vacuo. In some cases (**1**, **3**, **5**, **6**), the solid had to be washed with cold MeCN to remove traces of $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Mo}_8\mathrm{O}_{26}]$. Each compound was recrystallized from MeCN by slow diffusion of Et_2O.

Compounds 9−13: $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Mo}_8\mathrm{O}_{26}]$ (2.15 g, 1.00 mmol) and twice the molar amount of the appropriate arylhydrazine [$\mathrm{C_6F_5NHNH_3Cl}$, 0.408 g; o-$\mathrm{O_2N}$-$\mathrm{C_6H_4NHNH_2}$, 0.306 g; p-$\mathrm{O_2N}$-$\mathrm{C_6H_4NHNH_2}$, 0.306 g; o,p-$(\mathrm{O_2N})_2$-$\mathrm{C_6H_3NHNH_2}$, 0.396 g] were added to MeOH (30 mL). The mixture was vigorously stirred and heated at reflux for 30 min at the most. The solution was concentrated to about 15 mL, and the precipitate was then collected by filtration, washed with MeOH and Et_2O, and dried in vacuo. The products were recrystallized by diffusion of Et_2O into MeCN solutions. The preparation of **13** required some modifications in the above procedure. A mixture of $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Mo}_8\mathrm{O}_{26}]$ (2.15 g, 1.00 mmol) and p-$\mathrm{HO_2C}$-$\mathrm{C_6H_4NHNH_2}$ (0.152 g, 1.00 mmol) was heated at ca. 50 °C for ca. 20 min, during which time its colour had changed to dark brown. The methanol was removed in vacuo and the residue was extracted with several portions (20 mL) of acetone. The extracts were combined and concentrated to ca. 10 mL. The insoluble material was removed by filtration and the filtrate was exposed to vapours of Et_2O. The complex may be recrystallized by diffusion of Et_2O in MeCN or Me_2CO solutions.

Only IR bands that could be unambiguously assigned are listed below. All spectra display the bands characteristic of the tetrabutylammonium cations.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_5)]$ (1): Yield: 1.49 g (66% based on Mo). $\mathrm{C_{54}H_{113}Mo_6N_5O_{18}}$ (1696.17): calcd. C 38.24, H 6.72, Mo 33.94, N 4.13; found C 37.99, H 6.68, Mo 33.78, N 4.14. UV/Vis (MeCN): λ_{max} (log ε) = 486 (sh, 3.49), 383 (4.26), 331 (sh, 4.32), 286 nm (4.62). IR (KBr): $\tilde{\nu}_{max}$ = 962 (m), 939 (s) [ν(Mo=O,Mo=N)], 786 (s), 762 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}$-$p$-$\mathrm{Me})]$ (2): Yield: 1.28 g (56% based on Mo). $\mathrm{C_{55}H_{115}Mo_6N_5O_{18}}$ (1710.19): calcd. C 38.63, H 6.78, Mo 33.66; N 4.10; found C 38.70, H 6.79, Mo 33.30, N 4.04. UV/Vis (MeCN): λ_{max} (log ε) = 498 (sh, 3.41), 385 (4.19), 331(4.26), 284 nm (4.55). IR (KBr): $\tilde{\nu}_{max}$ = 962 (m), 939 (s) [ν(Mo=O,Mo=N)], 786 (s), 762 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}$-$p$-$\mathrm{F})]$ (3): Yield: 1.33 g (58% based on Mo). $\mathrm{C_{54}H_{112}FMo_6N_5O_{18}}$ (1714.15): calcd. C 37.84, H 6.59, F 1.17, Mo 33.58, N 4.08; found C 37.97, H 6.60, F 1.21, Mo 33.49, N 4.03. UV/Vis (MeCN): λ_{max} (log ε) = 483 (sh, 3.42), 378 (sh, 4.15), 325 (sh, 4.25), 283 nm (4.55). IR (KBr): $\tilde{\nu}_{max}$ = 963 (m), 940 (s) [ν(Mo=O,Mo=N)], 788 (s), 763 (s) cm^{-1} [ν(MoOMo)].

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$p$-$\mathrm{CN})]$ (4): Yield: 1.35 g (59% based on Mo). $\mathrm{C_{55}H_{112}Mo_6N_6O_{18}}$ (1721.18): calcd. C 38.38, H 6.56, Mo 33.44, N 4.88; found C 38.31, H 6.49, Mo 33.52, N 4.93. UV/Vis (MeCN): λ_{max} (log ε) = 421 (4.48), 308 nm (4.30). IR (KBr): $\tilde{\nu}_{max}$ = 2207 (m) [ν(C≡N)], 965 (m), 941 (s) [ν(Mo=O,Mo=N)], 788 (s), 762 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$p$-$\mathrm{CF}_3)]$ (5): Yield: 1.22 g (52% based on Mo). $\mathrm{C_{55}H_{112}F_3Mo_6N_5O_{18}}$ (1764.16): calcd. C 37.45, H 6.40, F 3.23, Mo 32.63, N 3.97; found C 37.27, H 6.62, F 3.34, Mo 32.44, N 3.92. UV/Vis (MeCN): λ_{max} (log ε) = 481 (sh, 3.69), 400 (4.37), 330 (sh, 4.27), 296 nm (4.46). IR (KBr): $\tilde{\nu}_{max}$ = 965 (s), 942 (s) [ν(Mo=O,Mo=N)], 788 (s), 764 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$p$-$\mathrm{OMe})$ (6): Yield: 0.86 g (38% based on Mo). $\mathrm{C_{55}H_{115}Mo_6N_5O_{19}}$ (1726.19): calcd. C 38.27, H 6.72, Mo 33.35, N 4.05; found C 38.22, H 6.71, Mo 33.27, N 4.09. UV/Vis (MeCN): λ_{max} (log ε) = 509 (sh, 3.37), 388 (sh, 4.30), 327 (sh, 4.26), 284 nm (4.58). IR (KBr): $\tilde{\nu}_{max}$ = 961 (m), 939 (s) [ν(Mo=O,Mo=N)], 787 (s), 762 (s) cm^{-1} [ν(MoOMo)].

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$o$-$\mathrm{Cl})$ (7): Yield: 1.22 g (53% based on Mo). $\mathrm{C_{54}H_{112}ClMo_6N_5O_{18}}$ (1730.61): calcd. C 37.48, H 6.52, Cl 2.28, Mo 33.26, N 4.05; found C 37.40, H 6.50, Cl 2.07, Mo 33.16, N 4.07. UV/Vis (MeCN): λ_{max} (log ε) = 491 (sh, 3.61); 390 (4.36), 334 (sh, 4.36), 288 nm (4.68). IR (KBr): $\tilde{\nu}_{max}$ = 963 (m), 941 (s) [ν(Mo=O,Mo=N)], 788 (s), 761 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2. ^{17}O NMR: see Table 3.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$m$-$\mathrm{NO}_2)]$ (8): Yield: 1.74 g (75% based on Mo). $\mathrm{C_{54}H_{112}Mo_6N_6O_{20}}$ (1741.16): calcd. C 37.25, H 6.48, Mo 33.06, N 4.83; found C 37.31, H 6.52, Mo 33.12, N 4.52. UV/Vis (MeCN): λ_{max} (log ε) = 487 (sh, 3.67), 383 (4.38), 281 nm (4.71). IR (KBr): $\tilde{\nu}_{max}$ = 965 (s), 940 (s) [ν(Mo=O,Mo=N)], 788 (s), 763 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2. ^{17}O NMR: see Table 3.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{F}_5]$ (9): Yield 1.60 g (67% based on Mo). $\mathrm{C_{54}H_{108}F_5Mo_6N_5O_{18}}$ (1786.12): calcd. C 36.31, H 6.09, F 5.32, Mo 32.23, N 3.92; found, C 36.21, H 5.95, F, 5.12, Mo 31.90, N 3.94. UV/Vis (MeCN): λ_{max} (log ε) = 467 (sh, 3.48), 379 (4.19), 279 nm (4.50). IR (KBr): $\tilde{\nu}_{max}$ = 964 (m), 942 (s) [ν(Mo=O,Mo=N)], 792 (s), 768 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2. ^{17}O MNR: see Table 3.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$o$-$\mathrm{NO}_2)]$ (10): Yield: 1.39 g (60% based on Mo). $\mathrm{C_{54}H_{112}Mo_6N_6O_{20}}$ (1741.16): calcd. C 37.25, H 6.48, Mo 33.06, N 4.83; found C 37.14, H 6.34, N 4.79. UV/Vis (MeCN): λ_{max} (log ε) = 548 (3.76), 373 (3.88), 274 nm (4.4). IR (KBr): $\tilde{\nu}_{max}$ = 965 (s) 943 (s) [ν(Mo=O,Mo=N)], 790 (s), 762 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$p$-$\mathrm{NO}_2)]$ (11): Yield: 1.74 g (75% based on Mo). $\mathrm{C_{54}H_{112}Mo_6N_6O_{20}}$ (1741.16): calcd. C 37.25, H 6.48, Mo 33.06, N 4.83; found; C 37.62, H 6.81, Mo 32.80, N 5.04. UV/Vis (MeCN): λ_{max} (log ε) = 548 (4.59), 305 (sh, 4.25), 267 nm (4.50). IR (KBr): $\tilde{\nu}_{max}$ = 967 (m), 943 (s) [ν(Mo=O,Mo=N)], 791 (s), 762 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}\{\mathrm{N}_2\mathrm{C}_6\mathrm{H}_3$-$o,p$-$(\mathrm{NO}_2)_2\}]$ (12): Yield: 1.88 g (79% based on Mo). $\mathrm{C_{54}H_{111}Mo_6N_7O_{22}}$ (1786.16): calcd. C 36.31, H 6.26, Mo 32.22, N 5.48; found C 37.08, H 6.29, Mo 32.26, N 5.52. UV/Vis (MeCN): λ_{max} (log ε) = 525 (4.60) 300 (sh, 4.29), 258 nm (4.53). IR (KBr): $\tilde{\nu}_{max}$ = 969 (m), 946 (s) [ν(Mo=O,Mo=N)], 791 (s), 765 (s) cm^{-1} [ν(MoOMo)]. ^{95}Mo NMR: see Table 2. ^{17}O NMR: see Table 3.

$(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4$-$p$-$\mathrm{CO}_2\mathrm{H})]$ (13): Yield 0.74 g (32% based on Mo). $\mathrm{C_{55}H_{113}Mo_6N_5O_{20}}$ (1740.18): calcd. C 37.96, H 6.48, Mo 33.08, N 4.03; found C 37.67, H 6.68, Mo 32.92, N 3.89. UV/Vis (MeCN): λ_{max} (log ε) = 428 (4.16), 338 (sh, 3.86), 312 nm (3.94). IR (KBr): $\tilde{\nu}_{max}$ = 1701 (m), 1592 (s) [ν(C=O)], 966 (m), 943 (s) [ν(Mo=O,Mo=N)], 789 (s), 767 (s) cm^{-1} [ν(MoOMo)].

Crystal-Structure Analyses: Crystal-structure data are summarized in Table 4. Data were recorded at room temperature either with a

Table 4. Crystal data and structure refinement for **10** and **13**

Compound	**10**	**13**
Empirical formula	$C_{54}H_{112}Mo_6N_6O_{20}$	$C_{55}H_{113}Mo_6N_5O_{20}$
Formula mass	1741.15	1740.16
T [K]	295	295
a [Å]	17.396(2)	17.6789(25)
b [Å]	17.431(2)	17.7551(15)
c [Å]	24.052(4)	23.5582(23)
V [Å^3]	7294(2)	7394.7(9)
Z	4	4
Crystal system	orthorhombic	orthorhombic
Space group	Pmcn	$P2_1cn$
μ [mm^{-1}]	1.067	1.05
F(000)	3560	3560
$D_{\text{calcd.}}$ [Mg·m^{-3}]	1.59	1.56
Crystal size [mm]	0.30 × 0.40 × 0.50	0.25 × 0.30 × 0.32
Diffractometer	CAD4, Enraf−Nonius	Kappa-CCD, Bruker-AXS
λ [Å]	0.71073	0.71073
θ range [°]	1−25	1.6−27.5
Index ranges (h,k,l)	$0 \le h \le 20$, $0 \le k \le 20$, $0 \le l \le 28$	$-21 \le h \le 19$, $-22 \le k \le 22$, $-30 \le l \le 28$
Reflections collected	7062	30867
Independent reflections	6643	12296 [$R_{\text{int}} = 0.11$]
Data [$I > 3\sigma(I)$]/parameters	3020/383	6114/690
Final R_1/wR_2 [$I > 3\sigma(I)$]	0.0511/0.0623	0.0462/0.0523
Final wR_2 (all)	0.0642	0.145
GOF	1.13	1.108
Largest diff. peak/hole [e·Å^{-3}]	0.75/−0.50	1.11/−1.05

CAD4 Enraf−Nonius or a Kappa-CCD Bruker-AXS diffractometer with use of graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystals were mounted on glass fibres and sealed with an epoxy cement. Lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 automatically centred reflections in the range 15−15.2° for **10** (230 reflections between 4 and 21° for **13**). Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.[39] Only the reflections with $I > 3\sigma(I)$ were retained for calculations. Data processing was performed with the aid of the CRYSTALS program.[40] The structures were solved by direct methods[41] and subsequent Fourier synthesis. All atoms were refined anisotropically, except for one of the three tetrabutylammonium cations which was poorly defined in both structures. Hydrogen atoms were not included in the refinements. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[42] Molecular structures were drawn with the program CAMERON.[43] CCDC-204770 (**10**) and -204771 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

Financial support from the Université Pierre and Marie Curie, the CNRS and the CONICYT (PICS no. 929) and the FONDECYT (grant no. 1000437) is gratefully acknowledged.

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Received February 26, 2003