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Synthesis and characterization of Keggin derivatives containing an $[Mo(NO)]^{3+}$ unit: $(n\text{-}Bu_4N)_4[PM_{11}O_{39}\{Mo(NO)\}]$ (M = Mo, W)

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Abstract

The diamagnetic complexes $(n\text{-}Bu_4N)_4[PM_{11}O_{39}\{Mo(NO)\}]$ (M = Mo, W) have been synthesized in acetonitrile by reaction of the lacunary $[PM_{11}O_{39}]^{7-}$ species, generated *in situ* through degradation of the parent complete Keggin anions by $n\text{-}Bu_4NOH$, with either $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]$ 3MeOH or $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ acting as a source of the $[Mo(NO)]^{3+}$ unit. These new nitrosyl-oxometalates have been characterized by elemental analysis, infrared spectroscopy, electrochemistry, and ^{31}P and ^{183}W spectroscopy. Comparison of electrochemical and spectral data of the nitrosyl derivatives to those of the parent Keggin anions demonstrate that the electron-withdrawing effect of the nitrosyl ligand is opposed to the overall increase in charge of the heteropolymetalate framework arising from the replacement of an MO^{4+} unit by an $[Mo(NO)]^{3+}$ unit In the case of $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$, ^{183}W NMR data also support some delocalization of the Mo(II) d-electrons onto the polytungstate ligand

Key words. Molybdenum complexes, Polymolybdate complexes, Oxo complexes, Nitrosyl complexes

Introduction

The recent synthesis of Lindqvist-type oxo-nitrosyl polymolybdates [1, 2] and the observation that the replacement of a terminal oxo ligand by a nitrosyl ligand results in the activation of surface oxygen atoms [3] led us to search for analogous Keggin derivatives. Hydroxylamine is now known to react with a variety of polyoxomolybdates in methanol to give the lacunary $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion [1, 2], which transforms eventually into the complete $[Mo_6O_{18}(NO)]^{3-}$ anion [1, 3]. However, the reaction of NH_2OH with $[PMo_{12}O_{40}]^{3-}$ in CH_3OH results only in the formation of the one-electron reduced $[PMo_{12}O_{40}]^{4-}$ derivative. Thus, we have attempted to prepare nitrosyl Keggin anions by reacting lacunary Keggin anions with nitrosyl compounds containing the $[Mo(NO)]^{3+}$ unit. Such a strategy, which has been widely applied to the synthesis of substituted Keggin derivatives [4–17], was found to be convenient for the preparation of $[PM_{11}O_{39}\{Mo(NO)\}]^{4-}$ (M = Mo, W). The only previous reports of nitrosyl Keggin derivatives are those of $[XW_{11}O_{39}\{Fe(NO)\}]^{n-}$, which were prepared by reaction of NO with $[XW_{11}O_{39}\{Fe(H_2O)\}]^{n-}$ (X = P, $n = 5$; X = Si, $n = 6$) [18], and of nitrosylruthenate(II,III) heteropolyanions [19]

Experimental

Chemicals

The following chemicals were used as received from Aldrich: 1 M methanolic tetra-n-butylammonium hydroxide, $n\text{-}Bu_4NOH$, $NaBF_4$, $n\text{-}Bu_4NHSO_4$ and reagent grade solvents. Owing to difficulties in the recrystallization of commercial $n\text{-}Bu_4NBF_4$, this compound was synthesized from $NaBF_4$ and $n\text{-}Bu_4NHSO_4$.

$(n\text{-}Bu_4N)_3[PM_{12}O_{40}]$ (M = Mo or W) and $(n\text{-}Bu_4N)_4[XM_{12}O_{40}]$ (X = Si, M = Mo or W, X = Ge, M = Mo) were prepared according to the literature [20].

Preparation of $(n\text{-}Bu_4N)_4[PW_{11}O_{39}\{Mo(NO)\}]$ (3)

The lacunary Keggin $[PW_{11}O_{39}]^{7-}$ anion was generated *in situ* [11] by adding 5 ml of a solution of tetrabutylammonium hydroxide in methanol to $(n\text{-}Bu_4N)_3[PW_{12}O_{40}]$ (**1**) [20] (3.6 g, 1 mmol) in 10 ml of acetonitrile. $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]$ 3MeOH (**5**) [1] (0.67 g, 0.5 mmol) was then

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added in small portions. The red–purple solution turned slowly brown and a brown precipitate formed, which was filtered out after stirring for *c.* 3 h (yield: 0.9 g, 50% based on the nitrosyl precursor). Then, brown crystals of (n-$Bu_4N)_3[Mo_6O_{18}(NO)]$ [1, 3] deposited from the filtrate within a few days. *Anal.* Calc. for $C_{64}H_{144}N_5MoO_{40}PW_{11}$: C, 20.37; H, 3.85; N, 1.86; Mo, 2.54; P, 0.82; W, 53.60. Found: C, 20.58; H, 4.04; N, 1.72; Mo, 2.54; P, 1.15; W, 53.47%. ^{183}W NMR (DMF, 297 K, δ in ppm): 20.1 (2W), −38.7 (2W), −84.3 (2W), −90.2 (2W), −94.6 (1W), −101.4 (2W). ^{31}P NMR (CH_3CN, 293 K, δ in ppm): −13.44 (mult; $^2J(W–P) \approx 1.2$ Hz). IR (cm^{-1}, KBr): 1622(s) $\nu(NO)$, 1076, 1057 $\nu_{as}(P–O_a)$, 963(s) $\nu_{as}(M–O_d)$, 886(s) $\nu_{as}(M–O_bM)$, 800(s), $\nu_{as}(M–O_c–M)$, 390, 340(w) (O_a refers to an oxygen atom shared by 3 MO_6 octahedra and the PO_4 tetrahedron; O_b and O_c refer to oxygen atoms shared by two MO_6 octahedra belonging to two different M_3O_{13} units, and to the same M_3O_{13} unit, respectively, O_d refers to a terminal unshared oxygen atom). Recrystallization of **3** from dimethylformamide (DMF) at room temperature afforded solvated brown crystals, which slowly decay due to solvent loss. Crystal data for (n-$Bu_4N)_4[PW_{11}O_{39}\{Mo(NO)\}]$ DMF: $a = 14.205(6)$, $b = 17.415(6)$, $c = 22.84(1)$ Å, $\beta = 101.74(3)°$, $V = 5533$ Å^3.

Preparation of (n-$Bu_4N)_4[PMo_{12}O_{39}(NO)]$ (4)

Method 1. Compound **4** was similarly obtained from (n-$Bu_4N)_3[PMo_{12}O_{40}]$ (**2**) [20] (2 g, 0.7 mmol), n-Bu_4NOH (5 ml) and **5** (0.67 g, 0.5 mmol) in acetonitrile (10 ml). The resulting green solution was allowed to stand at room temperature for a few days, whereupon green crystals of **4** formed in low yield (*c.* 12%).

Method 2. A solution of tetrabutylammonium hydroxide in methanol (5 ml, 5 mmol) was added to a suspension of (n-$Bu_4N)_3[PMo_{12}O_{40}]$ (**2**) (1.27 g, 0.5 mmol) in acetonitrile (15 ml). $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ (**6**) [21] (0.15 g, 0.25 mmol) was then added in small portions and the mixture was stirred at room temperature for 4 h. Green crystals formed slowly from the solution and were separated after 4 days (yield: 0.13 g, 9% based on the nitrosyl precursor). *Anal.* Calc. for $C_{64}H_{144}N_5Mo_{12}O_{40}P$: C, 27.39; H, 5.17; N, 2.50; Mo, 41.03; P, 1.10. Found: C, 27.67, H, 5.39; N, 2.39; Mo, 41.01; P, 1.18%. ^{31}P NMR (CH_3CN, 293 K, δ in ppm): −3.12 (0.5 Hz). IR (cm^{-1}, KBr): 1613(s) $\nu(NO)$, 1063, 1040 $\nu_{as}(P–O_a)$, 941(s) $\nu_{as}(Mo–O_d)$, 865(s) $\nu_{as}(Mo–O_b–Mo)$, 795(s), $\nu_{as}(Mo–O_c–Mo)$, 385, 340(w).

Physical studies

Lattice parameters for **3** were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections in the range $11.0 \leqslant \theta \leqslant 11.2°$ with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Intensity data could not be obtained due to the fast decay of the crystal.

IR spectra (KBr pellets) were recorded with a Perkin-Elmer 597 spectrophotometer. ^{183}W ($I = 1/2$, natural abundance 14.4%) and ^{31}P ($I = 1/2$, natural abundance 100%) NMR spectra were registered on an AM 500 and an AC300 Bruker spectrometer at 20.8 and 121.5 MHz, respectively. Chemical shifts are given according to the IUPAC convention and are relative to aqueous alkaline Na_2WO_4 (^{183}W) and 85% H_3PO_4 (^{31}P) as external standards. Standard polarography at a dropping mercury electrode was conducted in DMF on a model PRG 3 Tacussel device. Cyclic voltammetry at a platinum or carbon electrode was carried out in DMF or CH_3CN on a PAR model 273 instrument. In any case, a standard three-electrode cell was used, which consisted of the working electrode, an auxiliary platinum electrode and an aqueous saturated calomel electrode (SCE) equipped with a double junction. Solution concentrations ranged from 0.2 to 1 mM for the compounds under study and were 0.1 M for the supporting electrolyte, n-Bu_4NBF_4. All potentials are relative to SCE.

Results and discussion

Syntheses

Synthetic routes to monosubstituted Keggin complexes have been reported for a long time [22–25]. There is now general agreement that the most convenient procedure in aqueous solution involves the metalation of the preformed monovacant form even if the one-pot synthesis of the substituted compound from acidified solutions of mononuclear components does work. Unlike $[PW_{11}O_{39}]^{7-}$ [26], $[PMo_{11}O_{39}]^{7-}$ [27] is hydrolytically unstable in aqueous solutions. However, these two monovacant Keggin derivatives are now available in the form of non-aqueous solvent-soluble tetrabutylammonium salts, (n-$Bu_4N)_4[H_3PM_{11}O_{39}]$ (M = W [28], M = Mo [17]). It has been otherwise reported that the synthesis of monosubstituted Keggin derivatives can be achieved in non-aqueous media by reaction of $[PM_{11}O_{39}]^{7-}$, generated *in situ* through basic degradation of $[PM_{12}O_{40}]^{3-}$, with the appropriate metal salt [11].

As the reductive nitrosylation of $[PM_{12}O_{40}]^{3-}$ by hydroxylamine failed to give the desired products, the most straightforward syntheses of $[PM_{11}O_{39}\{Mo(NO)\}]^{4-}$ would seem to be the reactions of the defect $[PM_{11}O_{39}]^{7-}$ anions with a nitrosyl molybdenum complex as a source of the $[Mo(NO)]^{3+}$ unit. On the other hand, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ the anion of **5**, which transforms spontaneously into $[Mo_6O_{18}(NO)]^{3-}$ in dichloromethane or acetonitrile [1], was assumed to be a potential source of the $[Mo(NO)]^{3+}$ unit. Unfortunately, the reaction of $(n\text{-}Bu_4N)_4[H_3PW_{11}O_{39}]$ with **5** in CH_3CN did not yield until now the desired product, the major product of the reaction being the parent Keggin species. Similarly, the expected organoimido Keggin derivative $[PW_{12}O_{39}(NR)]^{3-}$ could not be obtained by reaction of $[H_3PW_{11}O_{39}]^{4-}$ with $[W(NR)Cl_4]_2$ ($R = p\text{-}MeC_6H_4$) [29]. Fortunately, we have succeeded in synthesizing $[PM_{11}O_{39}\{Mo(NO)\}]^{4-}$ by reacting $[PM_{12}O_{40}]^{3-}$ with **5** in acetonitrile in the presence of $n\text{-}Bu_4NOH$. The maximum yield in **3** was 50%. Brown crystals of $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ also formed in the reaction, very likely through transformation of **5** [1]. So far as the synthesis of **3** is concerned, the formation of $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ could be avoided by using a pure nitrosyl Mo(II) complex, such as $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ (**6**), instead of **5**. However the reaction of this dinuclear Mo(II) complex with **1** gave **3** in an even lower yield than that obtained from **5**. This indicates that the formation of the nitrosyl Lindqvist derivative is not the only cause for the low yield of the nitrosyl Keggin derivative in the reaction of **1** with **5**. However the use of **6** in place of **5** has a definite advantage for the synthesis of **4**. Indeed, samples of **4** obtained from **5** sometimes proved to be contaminated by a yet unidentified impurity which showed up as a signal at 1.20 ppm in the ^{31}P NMR spectrum. Such a contamination was avoided by the use of **6** as the source of the $[Mo(NO)]^{3+}$ unit.

Infrared spectra

IR spectra of **3** and **4** display a strong band at 1622 and 1613 cm^{-1}, respectively, which is assigned to $\nu(NO)$. Otherwise, they closely resemble those of the parent Keggin compounds **1** and **2** [30]. In particular, they exhibit the pattern of two bands characteristic of the α form in the 300–400 cm^{-1} range [31]. The decrease in symmetry from T_d to C_s on going from $[PM_{12}O_{40}]^{3-}$ to $[PM_{11}O_{39}\{Mo(NO)\}]^{4-}$ does not produce the expected splitting, not even a significant broadening, in the M–O and M–O–M stretchings. However, a slight but definite decrease in the frequencies is observed, which has been interpreted as a charge effect and results in the weakening of the anion cohesion [32, 33]. Only the ν_3 vibration of the central PO_4 is split into two components as usually observed for the metallo derivatives of defect $[PM_{11}O_{39}]^{7-}$ anions [32, 34]. The value of the ν_3 splitting has been considered as a measure of the interaction of the phosphate oxygen with the substituent metal cation [32, 34]. The observed splittings in **3** (19 cm^{-1}) and **4** (23 cm^{-1}) are about half those of the corresponding defect anions (45 and 50 cm^{-1} for $[PW_{11}O_{39}]^{7-}$ and $[PMo_{11}O_{39}]^{7-}$, respectively, as neutral K^+ or NH_4^+ salts [32]). The lower interaction between the central oxygen atom and the $[Mo(NO)]^{3+}$ unit, in comparison with that between O_a and an MO^{4+} unit, might result from the higher radii of the low-spin d^4 Mo(II) center, compared to that of the d^0 M(VI) centers. As a heteropolyanion molybdenum–oxygen framework is likely to be more flexible than its tungsten analogue [33], the interaction between the $[Mo(NO)]^{3+}$ unit and the central PO_4 would be larger in **4** than in **3**, thus decreasing the splitting. That is not apparent from the observed splittings. It is worth pointing our that the observed splittings in **3** and **4** are similar. This contrasts to 3d transition metal phosphopolyanions, for which the splitting is usually smaller, and even zero, for molybdenum than for tungsten compounds [32]. This might indicate that the $[Mo(NO)]^{3+}$ unit has the proper dimension for the cavity of the $[PM_{11}O_{39}]^{7-}$ anions. The $\nu(NO)$ frequencies lie in the range usually observed for oxo-nitrosyl polymetalates [1–3] and the small difference between the values for **3** and **4** is hardly significant.

^{183}W NMR spectroscopy

The clean ^{183}W NMR spectrum of the $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ anion (Fig. 1) displays six lines with the relative intensities close to 2:2:2.2:1:2 in agreement with the expected C_s symmetry. The two lines at 20.1 and −38 7 ppm are well separated from the four other lines between −84.3 and −101.4 ppm. Because of the efficient chemical shift anisotropy relaxation in the dimethylformamide solution the tungsten resonances are relatively broad ($\Delta\nu_{1/2} \approx 5$ Hz); this precludes observation of the tungsten satellites and making a full assignment.

In a stick diagram presentation Rong and Pope [15] have summarized the ^{183}W chemical shifts for a number of diamagnetic $[PW_{11}O_{39}\{M^{II}(H_2O)\}]^{5-}$ anions. When data for monosubstituted Keggin anions containing a trivalent unit, such as $Ti(Cp)^{3+}$ [35], $TiCl^{3+}$ [6], VO^{3+} [36a] and $Mo(NO)^{3+}$ are included for comparison, it appears that all d^0 and d^{10} derivatives present very similar spectra, more or less spread around −100 ppm; for these species, the tungsten belonging to the same triad as the substituting d^0 or d^{10} M atom (double μ-oxo junction) gives generally the most deshielded ^{183}W resonance [6, 36], whereas the other tungsten adjacent (single μ-oxo junction) to M is among the most shielded one. Only the diamagnetic $d^6\text{-}[PW_{11}O_{39}Ru(L)]^{5-}$ and $d^4\text{-}[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ derivatives exhibit a distinct behavior: their ^{183}W NMR spectra display two groups of lines. For the former species, the two high-frequency lines have been assigned to the tungsten atoms adjacent to the ruthenium atom and this deshielding has been explained by a partial delocalization of Ru π-electron density onto the polytungstate ligand [15]. On the same basis, the two lines at 20.1 and −38.7 ppm of $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ could be attributed to the tung-

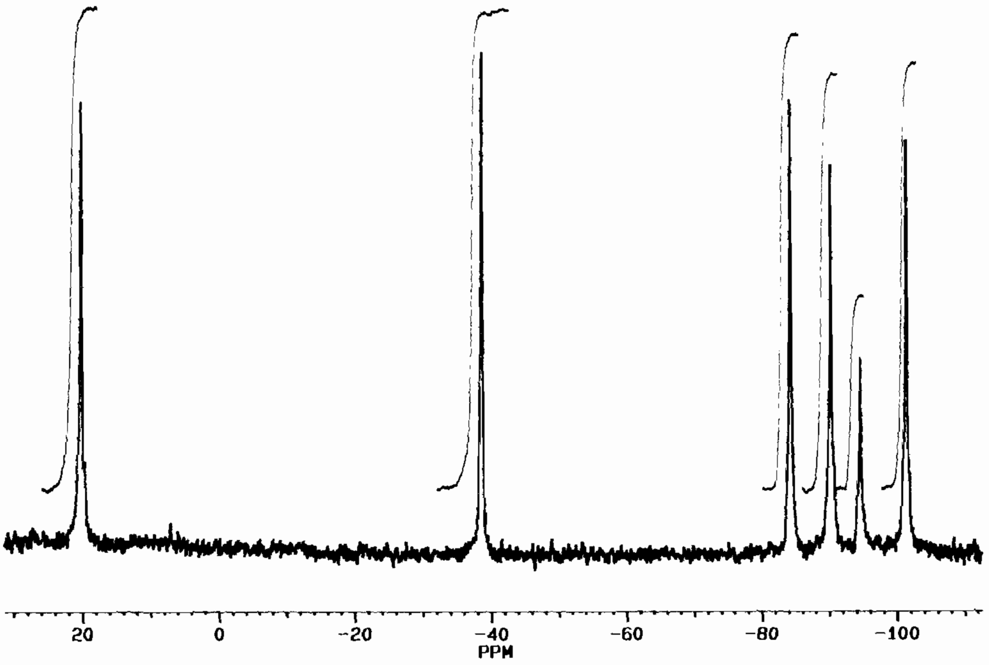

Fig. 1. 20.8 MHz ^{183}W NMR spectrum with computer integration of $(n\text{-}Bu_4N)_4[PW_{11}O_{39}\{Mo(NO)\}]$ (3) in DMF/d_6-acetone (90/10 vol./vol.) solution, measured at 297 K

sten atoms μ-oxo bound to the Mo(NO) group and it could be similarly argued that some delocalization of the Mo(II) d-electrons occurs in $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$. The resulting paramagnetic* contribution to the shielding of the ^{183}W resonances is however by far less important than in $[PW_{11}O_{39}Ru(L)]^{5-}$: the moderated effect could be due, not only to the smaller d-electron density of d^4 Mo(II) with respect to d^6 Ru(II) but also to an opposite flow of the electrons from the polyanion because of the strong π-accepting properties of the nitrosyl ligand.

^{31}P NMR spectroscopy

The ^{31}P chemical shifts for a number of phosphopolytungstates and phosphopolymolybdates are given in Table 1. The linewidths of the nitrosyl derivatives are similar to those of the corresponding oxo compounds; for the tungsten-containing anions, a multiplet is observed, which is due to the presence of different isotopomers with different numbers of magnetically active ^{183}W nuclei. The narrowness of the ^{31}P lines confirms that the nitrosyl derivatives are truly diamagnetic.

For chemical shifts mainly dictated by diamagnetic effects*, it could be anticipated that an increase in the overall charge of the heteropolyanion would result in a low-frequency shift of the P resonance. This is exactly what is observed, when we compare $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ with $[PW_{11}MoO_{40}]^{3-}$ and $[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$ with $[PMo_{12}O_{40}]^{3-}$; in both cases the substitution of $[Mo(NO)]^{3+}$ for $[MoO]^{4+}$ results in a shielding of the ^{31}P resonance. This shift is however very small for the tungsten anion (0.1 ppm) and comparatively larger for the molybdenum derivative (>0.5 ppm).

TABLE 1. ^{31}P NMR data of some Keggin phosphopolyanions

Compound	$\delta^{a,b}$	$\Delta\nu_{1/2}$ (Hz)	Reference
$[PMo_{12}O_{40}]^{3-}$	−2.58	0.5	this work
$[PMo_{12}O_{39}(NO)]^{4-}$	−3.12	0.5	this work
$[PW_{12}O_{40}]^{3-}$	−14.19	≈0.5[c]	this work
$[PW_{11}MoO_{40}]^{3-}$	−13.34	≈0.5[c]	this work
$[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$	−13.44	≈0.5[c]	this work
$[PW_{11}O_{39}\{Sn(OH)\}]^{4-}$	−13.1[d]		13
$[PW_{11}O_{39}\{Ru(H_2O)\}]^{4-}$	−8.7[e]	2.6	15

[a]Spectra recorded in CH_3CN/d_6-acetone (90/10 vol./vol.) at 297 K. [b] ^{31}P chemical shifts (in ppm) referred to external 85% H_3PO_4. [c]Complex multiplet due to coupling with ^{183}W ($^2J(W\text{–}P) \approx 1.2$ Hz). [d]Spectrum recorded in CD_3CN. [e]Spectrum recorded in H_2O

Electrochemical behavior

Cyclic voltammograms for $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ are shown in Fig. 2. This Keggin derivative is characterized by two reduction processes at −0.61 and −1.35 V (Fig. 2(a)) and by one oxidation process at +1.25 V (Fig. 2(b)). The three processes involve one electron

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*Note that the expression 'paramagnetic contribution to the shielding' refers to a deshielding of the nucleus but has nothing to do with any paramagnetic property of the compounds, which are diamagnetic.

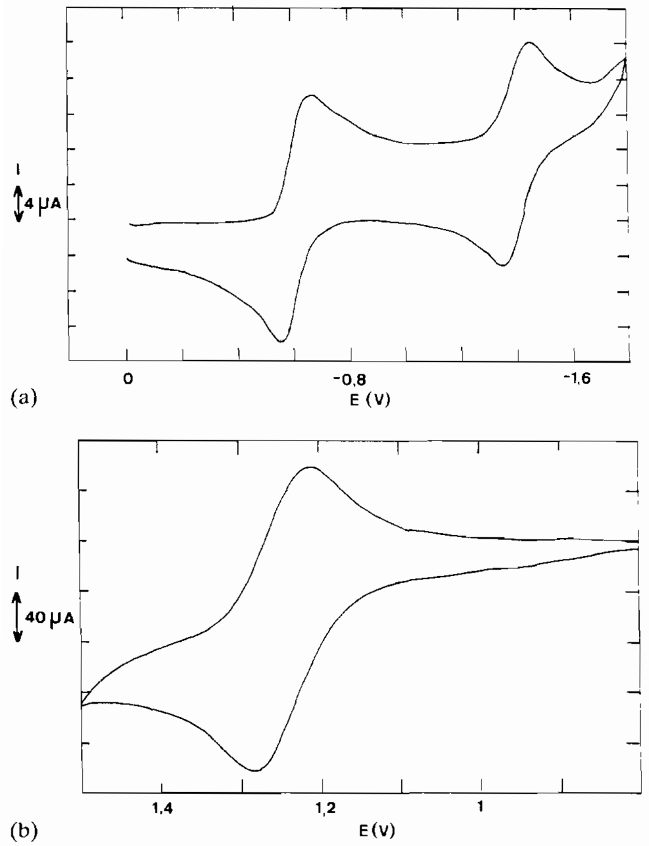

Fig 2 Cyclic voltammograms of (n-$Bu_4N)_4[PW_{11}O_{39}\{Mo(NO)\}]$ (**3**) (1 mmol l^{-1}) (a) in DMF at a carbon electrode, (b) in CH_3CN at a platinum electrode 0 1 mol l^{-1} n-Bu_4NBF_4, scan rate: 0.1 V s^{-1}; *E* vs SCE

TABLE 2 Half-wave reduction potentials[a,b] of some Keggin phosphopolyanions in DMF[c]

Compound[d]	$E_{1/2}$ (first process)	$E_{1/2}$ (second process)
α-$[SiMo_{12}O_{40}]^{4-}$	−0.45	−0.87
α-$[GeMo_{12}O_{40}]^{4-}$	−0.42	−0.84
α-$[PW_{12}O_{40}]^{3-}$	−0.26	−0.79
α-$[SiW_{12}O_{40}]^{4-}$	−0.83	−1.37
α-$[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$	−0.61	−1.35
α-$[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$	−0.40	

[a]Dropping mercury electrode [b]*E*, V vs SCE [c]0 1 M n-Bu_4NBF_4 [d]Tetrabutylammonium salts

and appear to be quasi-reversible ($\Delta E_p \sim 80$ mV). In aprotic media, Keggin compounds usually exhibit two one-electron reduction waves in the range 0 to −1 V and, eventually, a third reduction can be observed in the range −1.5 to −2 V. It appears that $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ is less easily reduced than $[PW_{12}O_{40}]^{3-}$, which displays two reduction waves at −0.26 and −0.79 V. It has been shown that Keggin polyanions are not solvated [37], so the reduction potentials become more negative as the anion charge increases, and comparison should be made between anions of the same charge, *e.g.* $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ and $[SiW_{12}O_{40}]^{4-}$, $[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$ and $[SiMo_{12}O_{40}]^{4-}$, $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ and $[PW_{12}O_{40}]^{4-}$ (one electron reduced form). Data of Table 2 show that the nitrosyl derivatives are more easily reduced than the underivatized Keggin anions. As the substitution of Si for P is not expected to produce a substantial change in the redox properties of the polyanion (see $[SiW_{12}O_{40}]^{4-}$ and $[PW_{12}O_{40}]^{4-}$), the observed effect is very likely associated with the electron-withdrawing properties of the nitrosyl ligand. It is worth pointing out that this effect is enhanced in Keggin derivatives in comparison with Lindqvist derivatives. Indeed, the reduction potential of $[Mo_6O_{17}(OCH_3)(NO)]^{2-}$ lies very close to that of $[Mo_6O_{19}]^{2-}$ [3]. It is also noteworthy that oxidation of $[PM_{11}O_{39}\{Mo(NO)\}]^{4-}$ occurs at more positive potentials than that of $[Mo_6O_{18}(NO)]^{3-}$ though the charge of the former is greater than that of the second. This reflects the enhanced stabilization of the Mo(II) state in $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ and $[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$ in comparison with $[Mo_6O_{18}(NO)]^{3-}$. Although a comparison between Keggin and Lindqvist compounds might be questionable, the anodic shift in the oxidation potential could arise from a greater π-delocalization of the Mo(II) d-electrons into the Keggin framework, in agreement with ^{183}W NMR data for $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$. This observation is also consistent with the fact that thermally activated electron hopping appears to be more easier in the Keggin structure than in the Lindqvist structure [38, 39].

Conclusions

(n-$Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]$ and $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ have proved to be suitable precursors for the synthesis of oxo-nitrosyl metalates. Two Keggin derivatives, e.g. $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$ and $[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$, have been synthesized by reaction with monolacunary polyanions, which were generated *in situ* by base degradation of the complete Keggin anions. Their properties reflect the electron-withdrawing effect of the nitrosyl substituent. Till now, all attempts to synthesize nitrosyl Keggin derivatives with a heteroatom other than P have failed.

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