Co-ordination chemistry of lacunary Lindqvist-type polyoxometalates: cubic *vs.* square-antiprismatic co-ordination

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In methanol, the sodium complex of the monovacant Lindqvist-type nitrosyl polyoxomethoxomolybdate $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ reacted with a number of divalent or trivalent cations, including Ca^{2+}, Sr^{2+}, Ba^{2+}, Ce^{3+}, Eu^{3+} and Bi^{3+}, to yield 2:1 complexes of the type $[X\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{n-}$ which have been isolated as tetrabutyl-ammonium salts. The crystal and molecular structures of $[NBu_4]_3[Bi\{Mo_5O_{13}(OMe)_4(NO)\}_2]\cdot3MeOH$, $[NBu_4]_3[Ce\{Mo_5O_{13}(OMe)_4(NO)\}_2]\cdot3MeOH$ and $[NBu_4]_4[Ba\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ have been determined by single-crystal X-ray diffraction. In these three compounds and most probably in all other members of the series, the tetradentate inorganic porphyrin-like $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anions provide an eight-co-ordination environment for the central cation. However, there are striking differences between the complexes. Indeed while the environment is square antiprismatic in the isomorphous compounds of Bi and Ce, it is square prismatic in that of Ba. Infrared spectroscopy also provides evidence for a square prismatic environment in the complexes of Ca^{2+} and Sr^{2+}. The related $[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ species has been obtained by controlled degradation of $[W_5O_{18}\{Mo(NO)\}]^{3-}$ in MeOH and isolated as $[NBu_4]_2[\{Na(MeOH)\}W_4O_{13}(OMe)_4\{Mo(NO)\}]$. Its bismuth(III) complex has been prepared and characterized. The molecular structure of $[Bi\{W_4O_{13}(OMe)_4Mo(NO)\}_2]^{3-}$ is quite similar to that of $[Bi\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{3-}$.

Polyoxometalate chemistry is widely controlled by acid–base equilibria and, among these reactions, partial base degradation of saturated species such as Keggin- and Dawson-type anions may lead to the formation of lacunary derivatives.[1,2] In a few cases it is possible to obtain highly vacant species, *e.g.* $[H_2P_2W_{12}O_{48}]^{12-}$,[3] but mono-, di- or tri-vacant complexes are more common. Some of them, *e.g.* α- and β-$[SiW_{11}O_{39}]^{8-}$,[4] $[PMo_{11}O_{39}]^{7-}$,[5] α1- and α2-$[X_2W_{17}O_{61}]^{10-}$,[6] γ-$[SiW_{10}O_{36}]^{10-}$,[4] α-A-$[SiW_9O_{34}]^{10-}$,[4] β-A-$[HSiW_9O_{34}H]^{9-}$,[4] are stable enough to be structurally characterized either in solution or in the solid state. These lacunary anions react with cations (notably transition metal cations) to give a large and varied class of complexes. Such ligands have unique properties: they contain π-donor atoms and are resistant to oxidation, thus they are able to stabilize high oxidation state cations such as Mn^{IV}.[7] In addition, they are π-acceptor ligands,[8] and indeed some of them are quite easily reduced.[1] Several transition metal-substituted polyoxometalates have proved to be efficient catalysts for the oxidation of organic substrates with different oxidants.[9] Moreover, owing to the structural analogy between polyoxometalates and extended oxides, polyoxometalate complexes may provide accurate structural and spectroscopic models for oxide-supported catalysts.[10]

Monovacant anions act either as pentadentate or tetradentate ligands and have been considered as analogues of metalloporphyrins.[11] Contrary to monovacant Keggin- and Dawson-type anions, free monovacant Lindqvist-type anions have not been characterized. A few substituted Lindqvist-type anions, *e.g.* $[M'M_5O_{19}]^{3-}$ (M = Mo, M' = V;[12] M = W, M' = V,[13,14] Nb[14,15] or Ta[16]), $[(MeO)M'W_5O_{18}]^{n-}$ (M' = Ti or Nb),[15] $[(Cp'Ti)M_5O_{18}]^{4-}$ (Cp' = Cp or Cp*, M = Mo or W),[17–20] are known, but can be hardly considered as complexes of the $\{M_5O_{18}\}^{6-}$ anions. The situation is quite different for lanthanide[21–31] and actinide[32,33] complexes of $\{W_5O_{18}\}^{6-}$ where the latter clearly acts as a tetradentate ligand. Complexes of the related $\{Mo_5O_{18}\}^{6-}$ anion have not yet been reported.

However, a derivatized Lindqvist-type $\{Mo_5\}$ unit, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$,[34,35] has been characterized, and its co-ordination chemistry has been investigated.[36–39] This ligand is able to co-ordinate to a metal ion either through the four terminal axial oxygen atoms surrounding the vacancy or two adjacent atoms of them.

We report herein the synthesis and characterization of a number of structurally related eight-co-ordinate complexes of alkaline earth metal (Ca^{II}, Sr^{II}, Ba^{II}), lanthanide (Ce^{III}, Eu^{III}) and bismuth(III) cations containing the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion, and of the sodium and bismuth(III) complexes of the related $[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ anion. The lanthanide complexes of monovacant polyoxometalates have recently been reviewed.[40] Current interest in lanthanide complexes of polyoxometalates comes from the potential use of polyoxometalates for separation of lanthanide and actinide cations in connection with radioactive waste treatment,[41] and from the relevance of solid-state photochemistry of polyoxometallolanthanates to material science.[42] The co-ordination chemistry of polyoxometalates with main-group cations has received less attention than with d- and f-block cations. Complexes of strontium and barium with $[PW_{11}O_{39}]^{7-}$ and $[P_2W_{17}O_{61}]^{10-}$ have been reported[43] and cryptates of the type $[BaAs_4W_{40}O_{140}]^{26-}$ and $[MSb_9W_{21}O_{86}]^{7-}$ (M = Ca or Sr) have been characterized.[44] On the other hand, the chemistry of bismuth(III) polyoxometalates has been developed slowly despite the role of mixed Bi^{III}/Mo^{VI} oxides in industrial oxidation processes.[45] All the bismuth(III) heteropolytungstates that have been fully characterized appear to contain BiW_9 subunits.[46–49]

Experimental

General

The oxonitrosyl complexes $[NBu_4]_2[\{Na(MeOH)\}Mo_5O_{13}(OMe)_4(NO)]\cdot3MeOH$ **1**[34] and $[NBu_4]_3[W_5O_{18}\{Mo(NO)\}]$[50]

were prepared according to the published procedures. Reagent grade methanol, diethyl ether, $BiCl_3$, $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $Ce(SO_4)_2$ were obtained from commercial sources (Merck, Aldrich, Strem Chemicals and Carlo Erba) and used as received. When necessary, methanol was distilled over magnesium methoxide. Elemental analyses were performed by the Service central de microanalyses of the CNRS, Vernaison, France.

The infrared spectra (4000–250 cm^{-1}) were recorded from KBr pellets on a Bio-Rad FT-IR 165 spectrophotometer; electronic spectra on a Shimadzu model UV-2101 spectrophotometer and ^1H (300 MHz) NMR spectra at 293 K in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead. The chemical shifts are given according to the IUPAC convention, with respect to $SiMe_4$. The ^{183}W (12.5 MHz) and ^{14}N (21.68 MHz) NMR spectra were recorded in 10 mm o.d. tubes on the same spectrometer equipped with a low-frequency special VSP probehead; ^{183}W chemical shifts are given with respect to an external 2 mol dm^{-3} Na_2WO_4 solution in alkaline D_2O, and ^{14}N chemical shifts with respect to NBu_4^+ as an internal reference.

Preparations

$[NBu_4]_3[Bi\{Mo_5O_{13}(OMe)_4(NO)\}_2] \cdot 3MeOH$ 2. Equimolar amounts of $[NBu_4]_2[\{Na(MeOH)\}Mo_5O_{13}(OMe)_4(NO)] \cdot 3MeOH$ **1** (0.34 g, 0.25 mmol) and $BiCl_3$ (0.079 g, 0.25 mmol) were mixed in 10 cm^3 of MeOH and the resulting violet solution was stirred for 4 h at room temperature. After separation of a fine white solid, the filtrate was placed at $-40 \,°C$. X-Ray quality violet crystals of $[NBu_4]_3[Bi\{Mo_5O_{13}(OMe)_4(NO)\}_2] \cdot 3MeOH$ **2** were collected by filtration after 3 d and washed with diethyl ether. Yield: 0.23 g (70%, based on **1**) (Found: C, 26.08; H, 5.07; Bi, 7.70; Mo, 35.63; N, 2.65. $C_{59}H_{144}BiMo_{10}N_5O_{39}$ requires C, 25.67; H, 5.08; Bi, 7.98; Mo, 36.62; N, 2.67%). $\tilde{v}_{max}/cm^{-1}$ 1635s, 1070 (sh), 1040s, 940s, 830s and 680s. δ_H (CD_3COCD_3, 293 K) 4.68 (s, 12 H, OCH_3). λ_{max}/nm (MeOH) 559 (ε/dm^3 mol^{-1} cm^{-1} 145).

$[NBu_4]_4[Ba\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ 3. This compound was similarly prepared from **1** (0.34 g, 0.25 mmol) and $BaCl_2 \cdot 2H_2O$ (0.060 g, 0.25 mmol) in 10 cm^3 of MeOH. The solution was stirred for 4 h at room temperature and then kept at $-40 \,°C$ for 24 h. X-Ray quality violet crystals were collected by filtration and washed with ether. Yield: 0.26 g (75%, based on **1**) (Found: C, 31.15; H, 6.10; Ba, 4.97; Mo, 34.12; N, 2.90. $C_{72}H_{168}BaMo_{10}N_6O_{36}$ requires C, 30.99; H, 6.07; Ba, 4.92; Mo, 34.83; N, 3.01%). $\tilde{v}_{max}/cm^{-1}$ 1625s, 1065 (sh), 1040s, 930s, 880 and 700s. λ_{max}/nm (MeOH) 540 (ε/dm^3 mol^{-1} cm^{-1} 155).

$[NBu_4]_4[Sr\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ 4. This compound was similarly prepared from **1** (0.34 g, 0.25 mmol) and $SrCl_2 \cdot 6H_2O$ (0.067 g, 0.25 mmol) in 10 cm^3 of MeOH. Yield 0.16 g (47% based on **1**) (Found: C, 31.18; H, 6.21; Mo, 34.27; N, 2.83; Sr, 3.20. $C_{72}H_{168}Mo_{10}N_6O_{36}Sr$ requires C, 31.55; H, 6.18; Mo, 35.00; N, 3.07; Sr, 3.20%). $\tilde{v}_{max}/cm^{-1}$ 1610s, 1067 (sh), 1040s, 925s, 885s and 695s.

$[NBu_4]_4[Ca\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ 5. A mixture of compound **1** (0.68 g, 0.5 mmol) and $Ca(NO_3)_2 \cdot 4H_2O$ (0.118 g, 0.5 mmol) in MeOH (10 cm^3) was refluxed for 0.5 h. Then the solution was cooled to room temperature and diethyl ether (100 cm^3) added under vigorous stirring, which led to the precipitation of **5** as a violet powder. Yield: 0.62 g (92% based on **1**). The crude product was recrystallized by slow diffusion of ether into a nearly saturated solution in MeOH (Found: C, 32.53; H, 6.51; Ca, 1.67; Mo, 34.83; N, 3.20. $C_{72}H_{168}CaMo_{10}N_6O_{36}$ requires C, 32.11; H, 6.29; Ca, 1.49; Mo, 35.62; N, 3.12%).

$[NBu_4]_3[Ce\{Mo_5O_{13}(OMe)_4(NO)\}_2] \cdot 3MeOH$ 6. The salt $Ce(SO_4)_2$ (0.167 g, 0.25 mol) was added to a sample of compound **1** (0.68 g, 0.5 mmol) dissolved in MeOH (10 cm^3). The mixture turned immediately dark orange. It was refluxed for 36 h after which a fine yellow solid, identified as $[NBu_4]_2[Mo_6O_{19}]$, was separated by filtration. Upon cooling, pink-violet crystals of **6** formed from the filtrate within a few minutes. Yield: 0.32 g (49%, based on **1**) (Found: C, 26.35; H, 5.14; Ce, 5.35; Mo, 36.84; N, 2.87. $C_{59}H_{144}CeMo_{10}N_5O_{39}$ requires C, 26.77; H, 5.48; Ce. 5.29; Mo, 36.24; N, 2.65%). $\tilde{v}_{max}/cm^{-1}$ 1630s, 1065 (sh), 1040s, 940s, 845s and 690s. λ_{max}/nm (MeOH) 555 (ε/dm^3 mol^{-1} cm^{-1} 115).

$[NBu_4]_3[Eu\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ 7. This compound was similarly prepared from **1** (0.68 g, 0.50 mmol) and $Eu(NO_3)_3 \cdot 6H_2O$ (0.11 g, 0.25 mmol) in 10 cm^3 of MeOH. After a 7 h reflux the resulting mauve solution was cooled to room temperature. Violet crystals of **7** formed within 1 d and were collected by filtration. Yield: 0.40 g (62.4%) (Found: C, 25.99; H, 5.23; Eu, 5.80; Mo, 37.31; N, 2.68. $C_{56}H_{132}EuMo_{10}N_5O_{36}$ requires C, 26.24; H, 5.19; Eu, 5.93; Mo, 37.47; N, 2.73%). $\tilde{v}_{max}/cm^{-1}$ 1625s, 1065 (sh), 1040s, 940s, 840s and 690s.

$[NBu_4]_2[\{Na(MeOH)\}W_4O_{13}(OMe)_4\{Mo(NO)\}]$ 8. A 1 mol dm^{-3} solution (2.5 cm^3) of NaOMe in MeOH (2.5 mmol) was added to a suspension of $[NBu_4]_3[W_5O_{18}\{Mo(NO)\}]$ (1.28 g, 0.62 mmol) in 10 cm^3 of freshly distilled MeOH. Upon reflux for 24 h the solution turned from green to bright violet while a fine white solid appeared. After centrifugation the resulting solution was concentrated to 3 cm^3 and kept at $-40 \,°C$. After 1 d a microcrystalline violet solid **8** was collected by filtration and washed with diethyl ether. Yield 0.29 g (27% based on $[NBu_4]_3[W_5O_{18}\{Mo(NO)\}]$) (Found: C, 10.97; H, 3.10; Mo, 6.92; N, 3.02; Na, 1.78; W, 51.47. $C_{37}H_{88}MoN_3NaO_{19}W_4$ requires C, 11.18; H, 3.10; Mo, 6.87; N, 3.01; Na, 1.65; W, 52.65%). $\tilde{v}_{max}/cm^{-1}$ 1645s, 1065m, 1035s, 960 (sh), 945s, 910s, 890s, 720s and 635m. λ_{max}/nm (MeOH) 545 (ε/dm^3 mol^{-1} cm^{-1} 68). δ_H (CD_3COCD_3, 293 K) 4.85 (s, 12H, OCH_3). δ_N (CH_3OH–CD_3OD) 320 (1N, NO). δ_W (CH_3OH–CD_3OD) -38 (s, 4W). Unit cell parameters: $a = 12.751(12)$, $b = 12.850(3)$, $c = 18.556(11)$ Å, $\alpha = 71.04(4)$, $\beta = 82.80(6)$, $\gamma = 87.41(4)°$

$[NBu_4]_3[Bi\{W_4O_{13}(OMe)_4Mo(NO)\}_2]$ 9. A sample of $[NBu_4]_2[\{Na(MeOH)\}W_4O_{13}(OMe)_4\{Mo(NO)\}]$ **8** (0.15 g, 0.087 mmol) and an equimolar amount of $BiCl_3$ (0.028 g, 0.09 mmol) were dissolved in MeOH (10 cm^3). The violet solution was stirred at room temperature for 4 h during which a fine white solid appeared. After centrifugation, the solution was kept at $-40 \,°C$. After 3 d violet crystals of compound **9** were collected by filtration and washed with diethyl ether. Yield: 0.045 g (16%, based on **8**) (Found: C, 20.82; H, 3.95; N, 2.11. $C_{56}H_{132}BiMo_2N_5O_{36}W_8$ requires C, 20.24; H, 4.00; N, 2.11%). $\tilde{v}_{max}/cm^{-1}$ 1650s, 1050 (sh), 1030s, 953s, 845s, 835 (sh) and 700s.

X-Ray crystallography

Relevant crystallographic data for compounds **2**, **3**, **6** and **9** are summarized in Table 1. The intensity data were collected at room temperature (293 K) either on a CAD4 Enraf-Nonius diffractometer (**2**, **6** and **9**) or on a Philips PW1100 diffractometer (**3**) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Crystals of **2** and **6** decayed when standing in air due to solvent loss. Consequently, they were coated with oil and introduced in Lindeman tubes, while crystals of **3** and **9** were mounted on glass fibers. The lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 automatically centred reflections in the range 12.7–12.9° for **2**, 17.1–17.3° for **3**, 14.7–15.0° for **6** and 11.8–12.3° for **9**. Standard reflections were periodically monitored for intensity

Table 1 Crystal data for compounds **2**, **3**, **6** and **9**

	2	3	6	9
Molecular formula	$C_{59}H_{144}BiMo_{10}N_5O_{39}$	$C_{72}H_{168}BaMo_{10}N_6O_{36}$	$C_{59}H_{144}CeMo_{10}N_5O_{39}$	$C_{56}H_{132}BiMo_2N_5O_{36}W_8$
M	2716.14	2790.82	2615.28	3323.33
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	24.820(5)	19.382(10)	24.75(1)	17.028(2)
b/Å	17.831(4)	18.182(4)	17.56(1)	17.376(3)
c/Å	24.998(8)	15.594(6)	24.94(3)	32.941(4)
β/°	114.65(2)	90.69(5)	114.62(7)	99.23(1)
V/Å^3	10055(98)	5495(25)	9853(3)	9620(3)
Z	4	2	4	4
μ(Mo-Kα)/cm^{-1}	29.856	14.695	17.304	118.636
D_c/g cm^{-3}	1.7943	1.687	1.763	2.294
Reflections measured	14749	10025	9688	18136
Observed reflections	7828	6392	3571	4034
No. parameters	1029	567	503	490
R	0.043	0.0505	0.0980	0.063
R'	0.048	0.0562	0.1163	0.075
Goodness of fit (S)	2.853	0.786	1.077	1.171
Minimum, maximum $\Delta\rho$/e Å^{-3}	-4.68, 2.18	-0.82, 0.84	-1.52, 1.96	-1.51, 1.68

and orientation control. Reorientation of the crystal and scale discontinuities were observed for **6**, which resulted in a data set of relatively poor quality. Intensities were corrected for Lorentz-polarization effects, for standard decay in the case of **6** and for absorption.[51] Only the reflections with $I > 3\sigma(I)$ were used in subsequent calculations. The structures were solved by direct methods[52] and subsequent Fourier syntheses. Only two of the three expected methanol molecules of crystallization could be determined for **6**. The C–N and C–C bond lengths were constrained respectively to 1.50 ± 0.05 and 1.55 ± 0.05 Å, the N–C–C and C–C–C angles to $109 \pm 2°$ for two of the cations in **6**. Hydrogen atoms in **2**, **3**, **6** or **9** were not included in the refinements. All the other atoms in **2** and **3**, but only the metal atoms in **6** and **9** were refined anisotropically. Refinements were carried out using large-block matrix least-squares procedures. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[53] All computations were performed using CRYSTALS, version for PC.[54] The CAMERON plots[55] of the anions in **2** and **3** are given in Figs. 1 and 2. Thermal ellipsoids are shown at the 10% level. The numbering scheme for the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion follows that previously adopted:[34,35] the molybdenum(II) centre is labeled Mo(1), the molybdenum(VI) centres from Mo(2) to Mo(5). Terminal oxygen atoms (O_t) are labeled $O(ii')$, where i is the number of the molybdenum atom and $i' = 1$ or 2 depending on whether the oxygen atom is axial or equatorial. Bridging oxygen atoms (O_b) are labeled $O(ij)$, where i and j are the indexes of the bridged molybdenum atoms. Finally, the central oxygen atom (O_c) is labeled $O(10)$. The numbering scheme for the $[W_4O_{13}(OMe)_4(Mo(NO))]^{3-}$ anion was modeled on that of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ by substituting W(i) for Mo(i) ($i = 2$ to 5). The numbering scheme for the second distinct {M$_5$} unit in **2**, **6** and **9** was obtained by adding 100 to each basic index. Selected bond lengths for **2**, **3**, **6** and **9** are given in Table 2.

CCDC reference number 186/1262.

See http://www.rsc.org/suppdata/dt/1999/421/ for crystallographic files in .cif format.

Results and discussion

Syntheses

The sodium complex $[NBu_4]_2[\{Na(MeOH)\}Mo_5O_{13}(OMe)_4(NO)]\cdot3MeOH$ **1** is a convenient starting material for the synthesis of other complexes of the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion. Indeed, the sodium cation is easily displaced by a number of cations. Most often, the reaction takes place in methanol at room temperature and the tetrabutylammonium salt of the

product crystallizes upon cooling. 1:2 Complexes are invariably obtained with cations of Ca^{II}, Sr^{II}, Ba^{II}, Ce^{III}, Eu^{III} and Bi^{III}, even when the reactants are mixed in equimolar amounts. Similar attempts to prepare the Mg^{2+} complex by treating either $MgCl_2\cdot6H_2O$ or $Mg(NO_3)_2\cdot6H_2O$ with **1** in MeOH were unsuccessful. The cerium(III) compound **6** was initially obtained from $Ce(SO_4)_2$, the solvent being likely the reductant, but can be alternatively prepared from $Ce(NO_3)_3\cdot6H_2O$.† The bismuth(III) compound **2** was obtained either from $BiCl_3$ as described in the Experimental section, or from $Bi(NO_3)_3\cdot3H_2O$ or from $BiPh_2I$.

The $[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ anion has been obtained by controlled degradation of the $[W_5O_{18}\{Mo(NO)\}]^{3-}$ anion in methanol. The reaction is more complex than indicated by eqn. (1). Indeed, the white solid formed in the course of the

$$[W_5O_{18}\{Mo(NO)\}]^{3-} + 2MeOH + 2MeO^- \longrightarrow$$
$$[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-} + [WO_4]^{2-} + H_2O \quad (1)$$
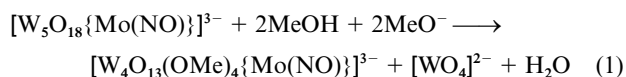
reaction is not merely sodium tungstate although it gives $Na_2WO_4\cdot2H_2O$ upon recrystallization from water. Moreover, complete transformation of $[W_5O_{18}\{Mo(NO)\}]^{3-}$ requires more than 2 equivalents of a base. A ^{14}N NMR analysis of the reaction mixture indicates the presence of at least one other product than $[W_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ but this was not identified. Degradation of $[W_5O_{18}\{Mo(NO)\}]^{3-}$ proceeds either with sodium hydroxide or sodium methoxide. The highest yield in **8** was obtained by using 4 equivalents of NaOMe per mol of $[NBu_4]_3[W_5O_{18}\{Mo(NO)\}]$ and did not exceed 30%. The reaction of $[Mo(NO)(acac)_2\{MeC(NH_2)NO\}]^{56}$ with $[NBu_4]_2[WO_4]$ in MeOH failed to give **8**. Only $[NBu_4]_3[W_5O_{18}\{Mo(NO)\}]$ was obtained, but in a lower yield than in MeCN.[50]

Infrared data

The infrared spectra of compounds **1**–**9** show similar patterns characteristic of the $[M_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ unit (M = Mo or W): these are five strong and relatively broad bands, one in the range 1610–1650 cm^{-1} assigned to ν(NO), one at *ca.* 1040 cm^{-1} assigned to ν(O–C), two (three for **8**) in the range 955–830 cm^{-1} characteristic of terminal oxo groups (O_t), and one at *ca.* 700 cm^{-1} assigned to ν(M–O_b–M). The band at *ca.* 1040 cm^{-1} usually displays a shoulder on its higher-frequency side and shoulders may also be observed on the bands assigned to MO

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† Complex **6** was incorrectly cited as a cerium(IV) complex in early accounts.[36,37]
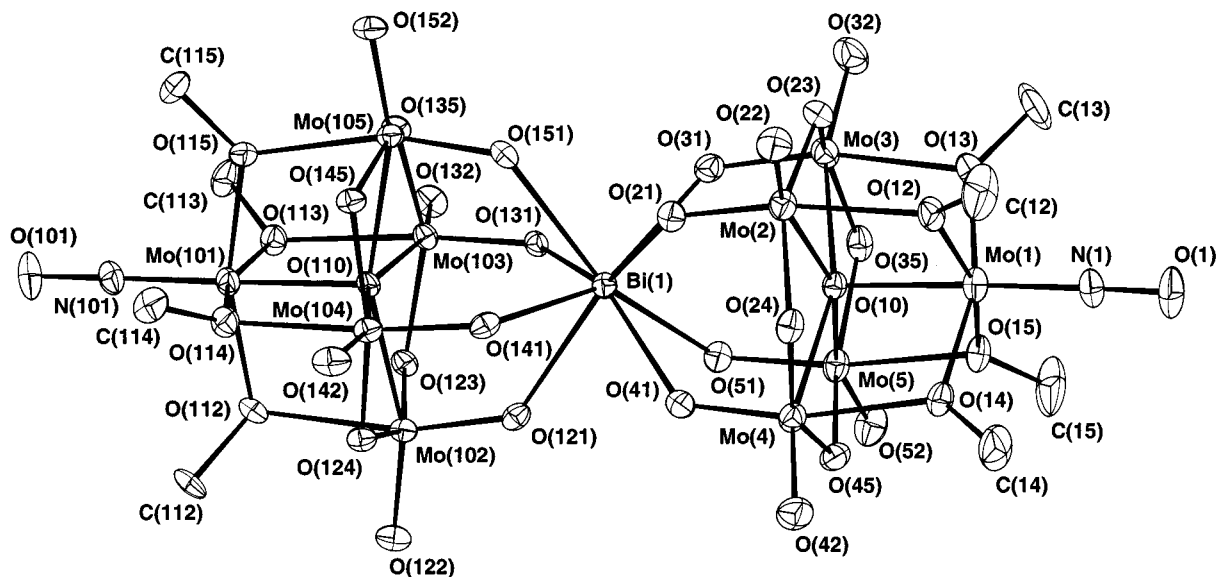
Fig. 1 Molecular structure of the anion [Bi{Mo$_5$O$_{13}$(OMe)$_4$(NO)}$_2$]$^{3-}$ in compound **2**.
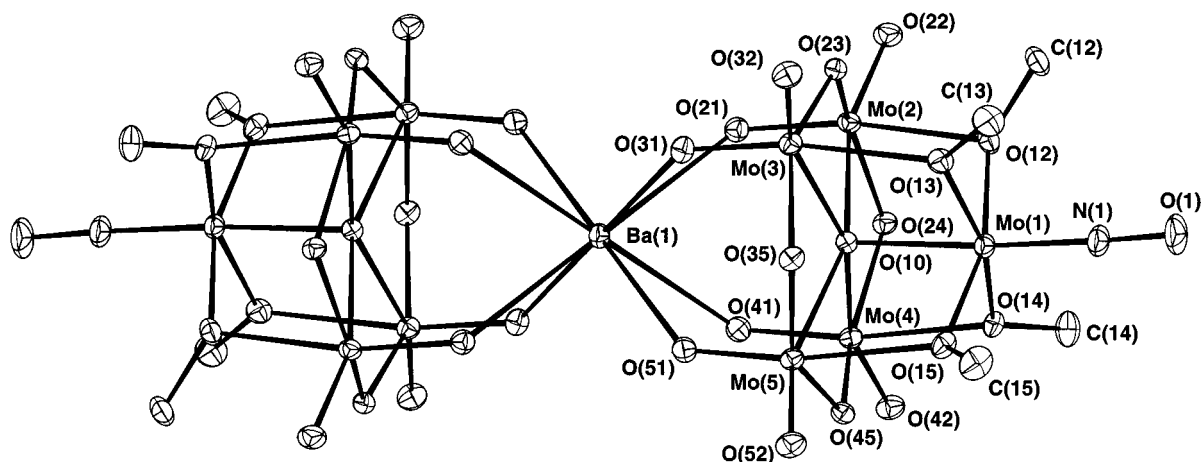
Fig. 2 Molecular structure of the anion [Ba{Mo$_5$O$_{13}$(OMe)$_4$(NO)}$_2$]$^{4-}$ in compound **3**.

stretching vibrations. Among these bands, those assigned to $v(MO_t)$ are the most sensitive to the intimate structure of the complex: (i) the expected shift to higher frequencies is observed for **8** and **9** with respect to their molybdenum analogues **1** and **2**; (ii) a low-frequency shift is observed on replacement of mono- by di- or tri-valent cations; and (iii) complexes with co-ordination number eight fall into two groups depending on the spacing between the two bands. The first group includes compounds **2**, **6**, **7** and **9** for which the spacing is *ca.* 100 cm^{-1} while the second comprises **3**, **4** and **5** for which the spacing is *ca.* 50 cm^{-1} (Table 3). As the geometry about the central cation is known to be square antiprismatic (*SAPR*) in **2**, **6** and **9** while it is square prismatic (*SPR*) in **3** (see below), it is tempting to use the value of the spacing as diagnostic of the geometry of the co-ordination polyhedron, *i.e.* all compounds in the first group are most probably *SAPR* while those in the second group are *SPR*.

Electronic spectroscopy

Compounds **1–9** are violet. This color results from an absorption band in the range 530–560 nm (ε *ca.* 140 dm^3 mol^{-1} cm^{-1} for 2:1 complexes in MeOH) which appears to be characteristic of the {Mo(NO)}$^{3+}$ chromophore in [M$_4$O$_{13}$(OMe)$_4${Mo-(NO)}]$^{3-}$ units (M = Mo or W). This band has been assigned to the d$_{xz}$,d$_{yz}$ $\longrightarrow$ d$_{xy}$ transition within the {Mo(NO)}$^{3+}$ unit.[35]

Single crystal X-ray analyses

The crystal structure determination of compound **1** has been previously reported.[34,35] Accurate structural parameters could not be obtained for **8** due to an insufficient number of observed data. However, a partial X-ray determination allowed the location of the metal atoms (W, Mo, Na), providing confirmation of the close relation between **1** and **8**. Thus it is presumed that **8** contains the sodium complex [{Na(MeOH)}-W$_4$O$_{13}$(OMe)$_4${Mo(NO)}]$^{2-}$.

In compounds **2**, **3**, **6** and **9** the central cation X (**2** and **9**, X = Bi^{III}; **3**, X = Ba^{II}; **6**, X = Ce^{III}) interacts with two [M$_4$O$_{13}$-(OMe)$_4${Mo(NO)}]$^{3-}$ units (**2**, **3** and **6**, M = Mo; **9**, M = W) acting as tetradentate inorganic porphyrin-like ligands and providing a eight-co-ordination environment (see Figs. 1 and 2, Table 2). Structural preferences in eight-co-ordinate complexes have been discussed.[57] With cyclic planar tetradentate ligands such as monovacant polyoxometalates the two sets of donor atoms are expected to lie in parallel planes. Depending on the rotation angle (2β) between the two units, the metal co-ordination polyhedron may be square prismatic (*SPR*, 2β = 0), square antiprismatic (*SAPR*, 2β = 45°) or intermediate between these two limiting geometries. Although the metal co-ordination polyhedra in compounds **2**, **3**, **6** and **9** are somewhat irregular (the anions in **2**, **6** and **9** have no crystallographically imposed symmetry, while the anion in **3** is centrosymmetrical)

Table 2 Selected intermolecular bond distances (Å) for compounds **2**, **3**, **6** and **9**

2		**3**		**6**		**9**	
Bi(1)–O(21)	2.42(1)	Ba(1)–O(21)	2.743(7)	Ce(1)–O(21)	2.50(2)	Bi(1)–O(21)	2.32(3)
Bi(1)–O(31)	2.45(1)	Ba(1)–O(31)	2.761(7)	Ce(1)–O(31)	2.54(3)	Bi(1)–O(31)	2.42(3)
Bi(1)–O(41)	2.47(1)	Ba(1)–O(41)	2.780(7)	Ce(1)–O(41)	2.49(2)	Bi(1)–O(41)	2.50(3)
Bi(1)–O(51)	2.44(1)	Ba(1)–O(51)	2.769(7)	Ce(1)–O(51)	2.57(3)	Bi(1)–O(51)	2.47(3)
Bi(1)–O(121)	2.50(1)	Mo(1)–N(1)	1.771(9)	Ce(1)–O(121)	2.58(2)	Bi(1)–O(121)	2.37(4)
Bi(1)–O(131)	2.519(9)	N(1)–O(1)	1.21(1)	Ce(1)–O(131)	2.52(2)	Bi(1)–O(131)	2.49(3)
Bi(1)–O(141)	2.48(1)	Mo(1)–O(10)	2.161(6)	Ce(1)–C(141)	2.65(2)	Bi(1)–O(141)	2.49(3)
Bi(1)–O(151)	2.464(9)	Mo(2)–O(21)	1.735(7)	Ce(1)–O(151)	2.59(2)	Bi(1)–O(151)	2.55(3)
Mo(1)–N(1)	1.75(1)	Mo(2)–O(22)	1.708(7)	Mo(1)–N(1)	1.54(4)	Mo(1)–N(1)	1.82(4)
N(1)–O(1)	1.20(2)	Mo(3)–O(31)	1.724(7)	N(1)–O(1)	1.34(5)	N(1)–O(1)	1.14(4)
Mo(1)–O(10)	2.131(9)	Mo(3)–O(32)	1.704(7)	Mo(1)–O(10)	2.03(3)	Mo(1)–O(10)	2.16(3)
Mo(101)–N(101)	1.75(1)	Mo(4)–O(41)	1.731(7)	Mo(101)–N(101)	1.60(4)	Mo(101)–N(101)	1.65(4)
N(101)–O(101)	1.21(1)	Mo(4)–O(42)	1.692(7)	N(101)–O(101)	1.33(4)	N(101)–O(101)	1.26(4)
Mo(101)–O(110)	2.110(9)	Mo(5)–O(51)	1.728(7)	Mo(101)–O(110)	1.99(2)	Mo(101)–O(110)	2.13(2)
Mo(2)–O(21)	1.746(9)	Mo(5)–O(52)	1.692(7)	Mo(2)–O(21)	1.70(3)	W(2)–O(21)	1.79(2)
Mo(2)–O(22)	1.67(1)			Mo(2)–O(22)	1.64(3)	W(2)–O(22)	1.72(4)
Mo(3)–O(31)	1.74(1)			Mo(3)–O(31)	1.69(3)	W(3)–O(31)	1.75(3)
Mo(3)–O(32)	1.70(1)			Mo(3)–O(32)	1.70(3)	W(3)–O(32)	1.75(3)
Mo(4)–O(41)	1.73(1)			Mo(4)–O(41)	1.70(3)	W(4)–O(41)	1.76(3)
Mo(4)–O(42)	1.68(1)			Mo(4)–O(42)	1.69(3)	W(4)–O(42)	1.61(3)
Mo(5)–O(51)	1.76(1)			Mo(5)–O(51)	1.65(3)	W(5)–O(51)	1.82(3)
Mo(5)–O(52)	1.69(1)			Mo(5)–O(52)	1.61(3)	W(5)–O(52)	1.69(3)
Mo(102)–O(121)	1.726(9)			Mo(102)–O(121)	1.66(3)	W(102)–O(121)	1.77(3)
Mo(102)–O(122)	1.69(1)			Mo(102)–O(122)	1.62(3)	W(102)–O(122)	1.71(3)
Mo(103)–O(131)	1.730(9)			Mo(103)–O(131)	1.68(2)	W(103)–O(131)	1.76(3)
Mo(103)–O(132)	1.695(9)			Mo(103)–O(132)	1.67(3)	W(103)–O(132)	1.78(3)
Mo(104)–O(141)	1.74(1)			Mo(104)–O(141)	1.59(2)	W(104)–O(141)	1.77(3)
Mo(104)–O(142)	1.697(9)			Mo(104)–O(142)	1.68(3)	W(104)–O(142)	1.62(4)
Mo(105)–O(151)	1.732(9)			Mo(105)–O(151)	1.65(2)	W(105)–O(151)	1.79(3)
Mo(105)–O(152)	1.687(9)			Mo(105)–O(152)	1.58(3)	W(105)–O(152)	1.74(3)

the geometry is clearly *SAPR* in **2**, **6** and **9**, while it is *SPR* in **3**. It is noteworthy that the lone pair on the Bi^{III} in **2** and **9** is not stereochemically active. The geometry of the metal co-ordination polyhedron can also be defined by the angle α between the C_4 axis and the metal–ligand bonds. The value of α in **3** indicates some elongation along the C_4 axis with respect to the cubic geometry (Table 4). The differences between the structures of complexes **2**, **6** and **9** on one hand and **3** on the other are striking. They possibly reflect changes in ionic radius. Indeed, a change from the *SPR* to the *SAPR* geometry is expected when the size of the metal centre decreases, as this minimizes ligand–ligand repulsions between the two polyoxometalate subunits. It remains that cubic co-ordination is very rare in discrete complexes and the reasons for its occurrence in **3** and possibly in **4** and **5** are not clear. As the radius of Ca^{2+}

is similar to that of Ce^{3+}, *SAPR* geometry would have been predicted for **5** instead of the *SPR* geometry inferred from IR data (see above). A change from cubic (before Gd) to square-antiprismatic co-ordination (after Gd) along the lanthanide series has been postulated for $[Ln(PW_{11}O_{39})_2]^{11-}$ on the basis of ^{183}W NMR data for aqueous solutions.[59] However, the results may reflect a smaller barrier to intramolecular rotation for the complexes of the larger lanthanides.[40] Indeed such a change has not been observed for complexes of the type $[Ln(W_5O_{18})_2]^{n-}$ where the lanthanide cation (Ln = Ce^{IV},[23,24] Ce^{III},[31] Pr^{III},[30] Nd^{III},[30] Eu^{III},[26] Sm^{III},[24,25,30] Gd^{III},[27,28,30] Tb^{III}[29,30] or Dy^{III}[30]) has an approximately square-antiprismatic co-ordination environment in any case. Considerations about the effect of ligand–ligand repulsions should take into account the relative flexibility of the $[M_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ units: the distance between two adjacent oxygen donors of the same subunit increases from 2.88 Å in **2** to 3.06 Å in **3** while the "normalized bite" defined as the ratio of the distance between the mean planes through the two sets of oxygen donors to the mean X–O bond length remains approximately constant (Table 4).

Although compounds **2** and **9** are not isomorphous their anions are isostructural. The mean Bi–O bond lengths are nearly equal [2.47(3) Å in **2**, 2.45(7) Å in **9**]. The most significant differences concern the geometrical parameters of

Table 3 Spacing between the two $\nu(MO_t)$ bands of compounds **2**–**7** and **9**

Compound	**2**	**6**	**7**	**9**	**3**	**4**	**5**
$\Delta\tilde{v}/cm^{-1}$	110	95	100	110	50	40	40
Geometry	*SAPR*	*SAPR*			*SPR*		

Table 4 Geometrical parameters of the eight-co-ordination environment of the central cation X in compounds **2**–**7** and **9**

Compound	X^{n+}	Effective ionic radius for X^a/Å	Geometry	Polar angle α/°	Rotation angle 2β/°	O···O$_{intra}$/Å	O···O$_{inter}$/Å	Mean X–O/Å	Normalized bite
2	Bi^{3+}	1.17	*SAPR*^{b}	55.7(6)	45	2.88(2)	3.19(6)	2.47(3)	1.29
3	Ba^{2+}	1.42	*SPR*^{b}	51.1(2)	0	3.06(3)	3.46(1)	2.76(1)	1.26
4	Sr^{2+}	1.26	*SPR*^{c}						
5	Ca^{2+}	1.12	*SPR*^{c}						
6	Ce^{3+}	1.14	*SAPR*^{b}	53.9(16)	45	2.93(3)	3.40(9)	2.55(5)	1.33
7	Eu^{3+}	1.07	*SAPR*^{c}						
9	Bi^{3+}	1.17	*SAPR*^{b}	56.7(4)	45	2.90(6)	3.11(9)	2.45(7)	1.27

^{a} From ref. 58. ^{b} Crystal structure determination. ^{c} On the basis of IR data.

the linear $\{Mo(NO)\}^{3+}$ unit. Despite the rather large standard deviations of bond lengths in **9**, there is a clear trend in the lengthening of the Mo–N bond and a concomitant shortening of the N–O bond on going from **2** to **9**. These variations are consistent with the increase in $\nu(NO)$ from **1** to **8** and from **2** to **9** and indicate that the net electron donation is less from the $[W_4O_{13}(OMe)_4]^{6-}$ core than from the molybdenum analogue. This is in keeping with the behaviour of the plenary Lindqvist-type species $[M_5O_{18}\{Mo(NO)\}]^{3-}$ (M = Mo or W).[50]

Despite the relatively low precision of the structure determination of compound **6**, notably the uncertainty in the number of the molecules of methanol, **2** and **6** appear isomorphous. The mean Ce–O distance of 2.55(5) Å in **6** is quite longer than that observed in the cerium(IV) complex $[Ce(W_5O_{18})_2]^{8-}$ (2.38 Å) but is similar to that observed in the cerium(III) derivative $[Ce(W_5O_{18})_2]^{9-}$.[31] The comparison of the molecular structures of $[Ce^{IV}(W_5O_{18})_2]^{8-}$, $[X^{III}\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{3-}$ (X = Bi or Ce) and $[Bi\{W_4O_{13}(OMe)_4Mo(NO)\}_2]^{3-}$ reveal some differences between the geometries of the $[M_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ and $[W_5O_{18}]^{6-}$ anions in their complexes. In the complexes of the $[M_4O_{13}(OMe)_4\{Mo(NO)\}]^{3-}$ (M = Mo or W) ligands the central oxygen atom is much more displaced from the mean plane through the four equatorial oxygen atoms than in $[Ce(W_5O_{18})_2]^{8-}$. Nevertheless, in all these complexes the M–O bonds that involve the oxygen atoms interacting with X retain significant double bond character. The X atom is placed over, rather than in, the lacunary site of the polyoxoanion unit and the complexes are clearly polyoxoanion supported.[60]

Conclusion

The monovacant Lindqvist-type nitrosyloxomethoxomolybdate $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ forms 2:1 complexes of the type $[X\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{n-}$ with a number of divalent or trivalent cations, including Ca^{2+}, Sr^{2+}, Ba^{2+}, Ce^{3+}, Eu^{3+} and Bi^{3+}. In all these complexes the tetradendate inorganic porphyrin-like $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anions provide a eight-co-ordination environment for the central cation. However, this environment is square prismatic for alkaline earth metal cations while it is square antiprismatic for rare earth metal cations and Bi^{III}. The complexes $[X\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ (X = Ba, Sr or Ca) provide examples for the rare cubic co-ordination.

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