Inorganica Chimica Acta 363 (2010) 4262–4268

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Aryldiazenido derivatives: A new entry to the functionalization of Keggin polyoxometalates

Carlos Bustos [a,b,*], Desmond Mac-Leod Carey [a], Kamal Boubekeur [b], René Thouvenot [b], Anna Proust [b,c,**], Pierre Gouzerh [b,***]

[a] *Instituto de Química, Universidad Austral de Chile, Casilla 567, Valdivia, Chile*
[b] *Institut Parisien de Chimie Moléculaire, UMR CNRS 7201, UPMC Univ Paris 06, Université Pierre et Marie Curie, Case courrier 42, 4 Place Jussieu, 75252 Paris Cedex 05, France*
[c] *Institut Universitaire de France, 103 Bd Saint-Michel, 75005 Paris, France*

ARTICLE INFO

Article history:
Available online 30 June 2010

Dedicated to Prof. Achim Müller for his invaluable contribution to chemistry.

Keywords:
Polyoxometalates
Lindqvist
Keggin
Functionalization
Diazenido ligands

ABSTRACT

A series of aryldiazenido polyoxomolybdates of the type $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNAr})\{\mathrm{Na(MeOH)}\}]$ (Ar = C_6F_5, **1**; Ar = O_2N-*o*-C_6H_4, **2**; Ar = O_2N-*m*-C_6H_4, **3**; Ar = O_2N-*p*-C_6H_4, **4a**; Ar = $(O_2N)_2$-*o*,*p*-C_6H_3, **5**) have been obtained by controlled degradation of the parent compounds $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{NNAr})]$ with NaOH in methanol. They have been characterized by elemental analysis and UV–Vis and IR spectroscopy. In addition, **4a** has been characterized by ^{95}Mo NMR spectroscopy and the crystal structure of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNC}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)\{\mathrm{Na(H_2O)}\}]\cdot\mathrm{H_2O}$ (**4b**) has been determined by X-ray diffraction. The molecular structure of the anion of **4b** features a lacunary Lindqvist-type anion $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNC}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)]^{3-}$ interacting with a sodium cation through the four terminal axial oxygen atoms. The 1:1 sodium complexes react with $BaCl_2$ and $BiCl_3$ to yield 2:1 complexes which have been isolated as $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Ba}\{\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNAr})\}_2]$ (Ar = C_6F_5, **6**; Ar = O_2N-*p*-C_6H_4, **7**) and $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Bi}\{\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNAr})\}_2]$ (Ar = C_6F_5, **8**; Ar = O_2N-*p*-C_6H_4, **9**). X-ray crystallography analysis of **9**·Me_2CO has shown that the tetradentate $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{N}_2\mathrm{C}_6\mathrm{H}_4\text{-}p\text{-}\mathrm{NO}_2)]^{3-}$ anions provide a square-antiprismatic environment for Bi. In contrast, IR spectroscopy provides evidence for a square-prismatic environment of Ba in **6** and **7**. In acetonitrile–methanol mixed solvent, $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNAr})]^{3-}$ and $[\mathrm{PW}_{11}\mathrm{O}_{39}]^{7-}$, generated *in situ* by alkaline degradation of their respective parents, $[\mathrm{Mo}_6\mathrm{O}_{18}(\mathrm{NNAr})]^{3-}$ and $[\mathrm{PW}_{12}\mathrm{O}_{40}]^{3-}$, react together to give the Keggin-type diazenido compounds $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{PW}_{11}\mathrm{O}_{39}(\mathrm{MoNNAr})]$ (Ar = O_2N-*o*-C_6H_4, **10**; Ar = O_2N-*m*-C_6H_4, **11**; Ar = O_2N-*p*-C_6H_4, **12**), which have been characterized by ^{31}P and ^{183}W NMR spectroscopy.

1. Introduction

The coordination chemistry of the lacunary Lindqvist-type oxonitrosyl molybdenum complex $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})]^{3-}$ has been studied extensively since its discovery in 1989 [1]. This ligand offers several coordination sites and can display various coordination modes: it can bind through its terminal axial oxo groups as a bidentate, tetradentate or bridging bisbidentate ligand [2,3]; in addition it can provide a triangle of three contiguous bridging oxygen atoms (one oxo and two methoxo groups), thus acting as a tridentate ligand. Interestingly, the $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})]^{3-}/\mathrm{Na}^+/\mathrm{Mn(CO)}_3^+$ system provides one of the very few examples of organometallic cation mobility on polyoxoanions [2]. In addition, $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})]^{3-}$ can rearrange under reaction with transition metal complexes. Its degradation, followed by reaggregation thus affords new polyoxoanions, such as $[\mathrm{Mo}_5\mathrm{O}_{16}(\mathrm{OMe})_2]^{4-}$ [2] or unexpected clusters such as $[\{\mathrm{Ni(MeOH)}_2\}_2\{\mathrm{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})\}_2]^{2-}$ [4]. In conclusion, the anion $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})]^{3-}$ anion displays a versatile coordination chemistry and it provides structural models for surface organometallic chemistry. In that sense, it has been considered as a soluble oxide analogue [2]. In view of these results we turned to the diazenido analogues $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNR})]^{3-}$ whose properties could be tuned though the substituent R. In addition, the latter could provide another functional group allowing for further derivatization and/or grafting on a support.

The analogy between the nitrosyl and diazenido ligands has been recognized for a long time [5]. These ligands are commonly considered as NO^+ and RNN^+, respectively, when they adopt terminal linear coordination modes as observed in $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NO})]^{3-}$ and expected in $[\mathrm{Mo}_5\mathrm{O}_{13}(\mathrm{OMe})_4(\mathrm{NNR})]^{3-}$. It follows that the $\mathrm{Mo(NO)}^{3+}$ and $\mathrm{Mo(NNR)}^{3+}$ units would contain d^4-Mo(II) centers. While there is some spectroscopic

---

* Corresponding author at: Instituto de Química, Universidad Austral de Chile, Casilla 567, Valdivia, Chile.
** Corresponding author at: Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France.
*** Corresponding author. Tel.: +33 1 44 27 55 53; fax: +33 1 44 27 38 41.
E-mail addresses: cbustos@uach.cl (C. Bustos), anna.proust@upmc.fr (A. Proust), pierre.gouzerh@upmc.fr (P. Gouzerh).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.06.044

evidence to support this view, DFT calculations suggest that the formal oxidation state of a linearly coordinated NNR ligand is −1, which leads to a Mo(NNR)$^{3+}$ unit as containing a d^2-Mo(IV) center [6]. Consequently it seems better to consider the "linear" Mo(NO)$^{3+}$ and Mo(NNR)$^{3+}$ units as {MoNO}^{4} and {MoNNR}^{4} following the formalism of Enemark and Feltham [7], where the exponent refers to the total number of electrons in the d_π and p_π orbitals whatever the formal oxidation states of the metal and the ligand.

While $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ is readily obtained by reductive nitrosylation of α-$[Mo_8O_{26}]^{4-}$ or other polyoxomolybdates in methanol, the use of arylhydrazines instead of hydroxylamine results most often in the formation of complexes containing $Mo(NNAr)_2{}^{2+}$ units [8,9]. In mild conditions, however, it has proved possible to isolate a range of compounds of the type $(nBu_4N)_3[Mo_6O_{18}(NNAr)]$ [10]. We show herein that controlled degradation of the latter with NaOH in methanol yields $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNAr)\{Na(MeOH)\}]$ which further reacts with $[PW_{11}O_{39}]^{7-}$ in acetonitrile to give $(nBu_4N)_4[PW_{11}O_{39}(MoNNAr)]$. We also report preliminary results of an ongoing study of the coordination chemistry of the polyanions $[Mo_5O_{13}(OMe)_4(NNR)]^{3-}$.

2. Experimental

2.1. General procedures and materials

All reactions were performed under dry nitrogen. Sodium molybdate dihydrate, hydrazines, hydrochloric acid, sodium hydroxide and nBu_4NCl were obtained from commercial sources and used as received. Methanol, acetonitrile and diethyl ether were purified and dried by standard procedures. $(nBu_4N)_3[PW_{12}O_{40}]$ [11], $(nBu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ [12] and $(nBu_4N)_3[Mo_6O_{18}(NNAr)]$ (Ar = C_6F_5, O_2N-*o*-C_6H_4, O_2N-*m*-C_6H_4, O_2N-*p*-C_6H_4 and $(O_2N)_2$-*o*,*p*-C_6H_3) [10] were prepared as previously reported. IR spectra were recorded in KBr pellets on a Nicolet Nexus FT-IR spectrophotometer. UV–Vis spectra were recorded in acetonitrile solutions on a Unicam UV 500 or JASCO V-670 spectrophotometer. The ^{95}Mo spectrum of **4a** was recorded at 50 °C on a Bruker DRX 500 spectrometer operating at a frequency of 32.6 MHz, from a solution in MeOH/Me_2CO in a 10 mm o.d. tube. Chemical shifts δ are reported in ppm with respect to external aqueous alkaline solution of 2 M Na_2MoO_4. The 121.5 MHz ^{31}P NMR spectra of compounds **10**–**12** were obtained at room temperature from *ca.* 30 mM CH_3CN/CD_3CN or DMF/CD_3COCD_3 solutions in 5 mm o.d. tubes on a Bruker AvanceII 300 spectrometer. Chemical shifts are referenced to external 85% H_3PO_4. The 20.8 MHz ^{183}W NMR spectra of compounds **10**–**12** were recorded at room temperature from nearly saturated (*ca.* 0.1 M) solutions in DMF/CD_3COCD_3 (90:10 v/v) in 10 mm o.d. tubes on a Bruker DRX 500 spectrometer equipped with a standard tunable BBO probehead. The 12.5 MHz $\{^{31}P\}^{183}W$ spectrum of **11** was further recorded at room temperature on the Bruker AvanceII 300 spectrometer equipped with a special low-frequency triple resonance VSP probehead. Chemical shifts are referenced to 2 M Na_2WO_4 in alkaline D_2O. They were measured by the substitution method, using a saturated solution of $H_4SiW_{12}O_{40}$ in D_2O as a secondary standard ($\delta = -103.8$ ppm [13]). All chemical shifts are reported 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 of the University Pierre et Marie Curie and by the Service central d'analyse of the CNRS (Solaize, France).

2.2. Syntheses

2.2.1. Synthesis of $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNR)\{Na(MeOH)\}]$

All these compounds were obtained according to the same procedure. To a suspension of $(nBu_4N)_3[Mo_6O_{18}(NNR)]$ (1 mmol) in methanol (15 mL) was added 5 mL of a 0.2 M solution of NaOH in methanol. The mixture was stirred and gently heated to about 60 °C for a time period ranging from half an hour to one hour and then allowed to cool at room temperature. When crystallization did not directly occur, the solution was exposed to diethyl ether by vapor diffusion until it became turbid, after which it was kept in a freezer at −28 °C for one day. The resulting solids were collected by filtration, washed with diethyl ether and dried in vacuo. The crude compounds were redissolved in methanol and recrystallized by slow diffusion of diethyl ether vapor. In the case of **5** (see below), the mother solution was evaporated to dryness and the residue was extracted with chloroform. After filtration, the filtrate was exposed to diethyl ether by vapor diffusion. The crystalline product was collected by filtration and recrystallized once more from chloroform by slow diffusion of diethyl ether vapor.

*2.2.1.1. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6F_5)\{Na(MeOH)\}]$, **1**.* Yellow-green crystals (yield: 76%). *Anal.* Calc. for $C_{43}H_{88}F_5Mo_5NaN_4O_{18}$ (1546.9): C, 33.39; H, 5.73; F, 6.14; Mo, 31.01; Na, 1.49; N, 3.62. Found: C, 33.17; H, 5.93; F, 6.17; Mo, 30.91; Na, 1.57; N, 3.89%. UV–Vis (CH_3CN): λ_{max}/nm (log ε): 376 (4.05). IR (KBr) ν/cm^{-1}: 1038 (m) [ν(O–C)], 926 (s), 896 (s) [ν(Mo=O)], 694 (s) [ν(MoOMo)].

*2.2.1.2. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6H_4\text{-}o\text{-}NO_2)\{Na(MeOH)\}]$, **2**.* Red crystals (yield: 69%). *Anal.* Calc. for $C_{43}H_{92}Mo_5NaN_5O_{20}$ (1501.9): C, 34.39; H, 6.17; Mo, 31.94; Na, 1.53; N, 4.66. Found: C, 33.83; H, 6.07; N, 4.75; Mo, 31.44; Na 1.56%. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 495 (3.62), 380 (3.84). IR (KBr) ν/cm^{-1}: 1039 (m) [ν(O–C)], 935 (s), 906 (s), 889 (s) [ν(Mo=O)], 701 (s) [ν(MoOMo)].

*2.2.1.3. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6H_4\text{-}m\text{-}NO_2)\{Na(MeOH)\}]$, **3**.* Brick red crystals (yield: 75%). *Anal.* Calc. for $C_{43}H_{92}Mo_5NaN_5O_{20}$ (1501.9): C, 34.39; H, 6.17; N, 4.66. Found: C, 34.89; H, 6.20; N, 4.32%. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 388 (4.10). IR (KBr) ν/cm^{-1}: 1039 (m) [ν(O–C)], 927 (s), 904 (s), 888 (s) [ν(Mo=O)], 693 (s) [ν(MoOMo)].

*2.2.1.4. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6H_4\text{-}p\text{-}NO_2)\{Na(MeOH)\}]$, **4a**.* Red crystals (yield: 89%). *Anal.* Calc. for $C_{43}H_{92}Mo_5NaN_5O_{20}$ (1501.9): C, 34.39; H, 6.17; Mo, 31.94; Na, 1.53; N, 4.66. Found: C, 34.27; H, 6.20; Mo, 32.42; Na, 1.65; N, 4.69%. UV/Vis (CH_3CN), λ_{max}/nm (log ε): 525(4.30). IR (KBr) ν/cm^{-1}: 1037 (m) [ν(O–C)], 926 (s), 905 (s), 888 (s) [ν(Mo=O)], 698 (s) [ν(MoOMo)]. ^{95}Mo NMR (MeOH/Me_2CO, 323 K, δ ppm): 54 (*Mo*=O), ~980 very broad (*Mo*N).

*2.2.1.5. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6H_4\text{-}p\text{-}NO_2)\{Na(H_2O)\}]\cdot H_2O$, **4b**.* Obtained by diffusion of diethyl ether vapor in a solution of **4a** (0.10 g) in MeOH/H_2O 90:10 (5 mL). Yield: 95%. *Anal.* Calc. for $C_{42}H_{92}Mo_5NaN_5O_{21}$ (1505.9): C, 33.50; H, 6.16; Mo, 31.85; Na, 1.53; N, 4.65. Found: C, 32.96; H, 6.19; Mo, 31.41; Na, 1.64; N, 4.58%.

*2.2.1.6. $(nBu_4N)_2[Mo_5O_{13}(OMe)_4(NNC_6H_3\text{-}o,p\text{-}(NO_2)_2)\{Na(MeOH)\}]$, **5**.* Red crystals (yield: 79%). *Anal.* Calc. for $C_{43}H_{91}Mo_5NaN_6O_{22}$ (1546.9): C, 33.93; H, 5.93; Mo, 31.01; Na, 1.49; N, 5.43. Found: C, 33.05; H, 5.76; Mo, 30.87; Na, 1.46; N, 5.44%. UV/Vis (MeOH), λ_{max}/nm (log ε): 519(3.06). IR (KBr) ν/cm^{-1}: 1037 (m) [ν(O–C)] 925 (s), 904 (s), 888 (s) [ν(Mo=O$_t$)], 708 (s) [ν(MoOMo)].