

A NEW LINDQVIST-TYPE HEXAMOLYBDATE CLUSTER FUNCTIONALIZED WITH THE π -DONOR LIGAND 4-BROMO-2,6-DIMETHYLPHENYLIMIDO. SPECTROSCOPIC, ELECTROCHEMICAL AND STRUCTURAL STUDIES

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ABSTRACT

A new ionic organic-inorganic hybrid complex of formula $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NR})] \cdot \frac{1}{2}\text{Me}_2\text{CO}$, $\text{R} = -\text{C}_6\text{H}_3-2,6\text{-Me}_2-4\text{-Br}$, $(n\text{-Bu}_4\text{N})_2[\text{I}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$, has been prepared in acetonitrile by reacting tetrabutylammonium α -octamolybdate, $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$, with 2,6-dimethyl-4-bromoaniline hydrochloride, 2,6-Me₂-4-Br-C₆H₃NH₂·HCl, using N,N'-dicyclohexylcarbodiimide, (C₆H₁₁)₂N=C=N(C₆H₁₁), as dehydrating agent. This complex, formulated as $(n\text{-Bu}_4\text{N})_2[\text{I}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$, contains a C-Br group which can be functionalized for constructing novel hybrid materials. The complex was fully characterized by IR, UV-Vis, ¹H- and ¹³C-NMR spectroscopies, and authenticated by single crystal X-ray diffraction analysis. The asymmetric unit contains two crystallographically independent anions, [I]²⁻, differing by the orientation of the phenyl ring relative to the hexamolybdate skeleton, and one molecule of acetone. Both molecules differ in the angles Mo(1)-N(1)-C(1) = 172.2(6)° and Mo(7)-N(2)-C(9) = 175.6(6)°. These angles, near to 180°, indicate the presence of a Mo≡N triple bond.

Keywords: areneimido-derivative, phenylimido-derivative, Lindqvist-type hexamolybdate, polyoxometalate, crystal structure, conformational isomers.

INTRODUCTION

Since the pioneering paper of Maatta *et al.*¹ describing the synthesis and X-ray structural determination of the first Lindqvist-type organoimido-derivative of hexamolybdate formulated as $[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{Me-p})]^{2-}$, a number of new organoimido-derivatives of hexamolybdate,²⁻¹⁹ hexatungstate,²⁰ and pentatungstenmolybdate,²¹ have been synthesized, spectroscopically characterized and, the majority, structurally authenticated by X-ray diffraction analysis. Very recently, the stability, bonding character, electronic properties, first hyperpolarizabilities of this type of complexes have also been studied by Density Functional Theory (DFT).²²⁻²⁴ Likewise, several topics concerning the progresses in polyoxometalate chemistry have been published^{25a} and, particularly, that dealing with derivatized polyoxometalates including organic and organometallic entities.^{25b} Among these complexes, the chloro-¹², bromo-^{12,18} and iodoareneimido hexamolybdates^{7-10,13-15} and iodoareneimido pentatungstenmolybdate²¹ seems to be of great importance considering their potential applications as precursors for the synthesis of new organic-inorganic hybrids containing additional organic^{7,8,10,14,15} or organometallic¹³ groups, or two similar clusters linked by an extended π -conjugated organic spacer.^{8-10,15} These halogenated precursors have successfully been applied for the synthesis of organoimido-hexamolybdates as polymer pendants⁵ and main-chain polymers.^{9,15} In this paper we report the synthesis, spectroscopic characterization, electrochemical studies and the X-ray crystal and molecular structure of the new organic-inorganic hybrid bearing the electron-withdrawal bromo group in a remote position: $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_3-2,6\text{-Me}_2-4\text{-Br})] \cdot \frac{1}{2}\text{Me}_2\text{CO}$, $(n\text{-Bu}_4\text{N})_2[\text{I}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$. The X-ray structure of a similar hybrid compound of formula $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4-4\text{-Br})]$, has previously been described in the literature¹⁸.

EXPERIMENTAL SECTION

General remarks

Solvents were dried and distilled under dinitrogen by standard methods prior to use. Reagents were purchased from commercial suppliers and used without further purification. $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$ was synthesized according to published procedures.²⁶ Microanalytical data were obtained on a Perkin Elmer model 2400 elemental analyzer. IR spectra were obtained as KBr disks on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range of 4000-450 cm⁻¹. Electronic spectra were recorded in MeCN and DMSO solutions with a Spectronic, Genesis 2, spectrophotometer. ¹H- and ¹³C-NMR spectra were acquired at 297 K on a multinuclear Bruker AC 400 spectrometer in acetone-*d*₆. All NMR spectra are reported in ppm (δ) relative to tetramethylsilane, with the residual solvent proton resonances and carbon resonances used as internal standards. Coupling constants (*J*) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: br=broad, s=singlet, d=doublet, t=triplet, m=multiplet. Electrochemical measurements were performed using a Radiometer Analytical model PGZ 100 all-in-one potentiostat, using a standard three-electrode setup

with a platinum electrode, platinum wire auxiliary electrode and Ag/AgCl as the reference electrode. DMF solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ with the voltage scan rate = 100 mV s⁻¹. Melting point was determined in evacuated capillary and was not corrected.

Synthesis of $(n\text{-Bu}_4\text{N})_2[\text{I}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$

A mixture of 6.45 g (3.0 mmol) of $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$, 1.42 g (6.0 mmol) of 2,6-dimethyl-4-bromoaniline hydrochloride, 2,6-Me₂-4-Br-C₆H₃NH₂·HCl, and 2.11 g (10.2 mmol) of N,N'-dicyclohexylcarbodiimide, (C₆H₁₁)₂N=C=N(C₆H₁₁)⁷, were dissolved in 50 mL of acetonitrile and refluxed for 12 h under N₂. Then, the reaction mixture was allowed to stand at room temperature. The white solid, corresponding to the dicyclohexylurea, was filtered off. The filtrate was concentrated under vacuum and the red colloidal residue was dissolved in acetone and then layered with ethanol and allowed to stand at -18°C. A red crystalline solid was deposited, which was filtered off, washed with diethyl ether, and dried under vacuum. Suitable single crystals were chosen of this crop for an X-ray diffraction structure determination. Yield 3.34 g (72% based on Mo), m. p. 236°C. Anal. Calcd C₈₃H₁₆₆Br₂Mo₁₂N₆O₃₇, Mr= 3151.32 g mol⁻¹: calcd C, 31.63; H, 5.31; N, 2.67. Found C, 31.54; H, 5.26; N, 2.54. UV/Vis (Me⁻): λ_{max} (log $\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$) = 254 (4.56), 274sh (4.47), 358 (4.37). IR (KBr): $\nu = 2961\text{s}, 2920\text{m}, 2874\text{m}$ (C-H); 975m (Mo-N); 950vs (Mo-O); 790vs (Mo-O-Mo) cm⁻¹. ¹H NMR (400 MHz, CD₃COCD₃): $\delta = 0.97$ (t, CH₃, 24H); 1.44 (m, CH₂, 16H); 1.80 (m, CH₂, 16H); 2.17 (s, CH₃, 6H); 3.43 (t, N-CH₂, 16H); 7.23 (s, ArH, 2H). ¹³C NMR (400 MHz, CD₃COCD₃): $\delta = 13.92$ (CH₃); 18.38 (CH₂); 20.38 (CH₂); 24.52 (Me₂-2,6); 59.36 (CH₂); 120.56 (C-4); 130.39 (C-3); 140.34 (C-2); 153.18 (C_{ipso}).

Structure determination of $(n\text{-Bu}_4\text{N})_2[\text{I}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$

Complete details of the crystal, X-ray data collection, and structure solution are provided as Supporting Information. Semi-empirical corrections, via ψ -scans, were applied for absorption. Intensity data were collected on a Bruker Smart Apex diffractometer equipped with a bidimensional CCD detector using graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The diffraction frames were integrated using the SAINT package²⁷, and corrected for absorption with SADABS²⁸. The structure was solved using XS in SHELXTL-PC²⁹ by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement was performed by the full-matrix least-squares method based on F^2 . Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms.

RESULT AND DISCUSSION

Synthesis and spectroscopic characterization

It is well known that the synthesis of organoimido-derivatives of polyoxometalates in reasonable yield using anilines containing an electron-

withdrawing group in the phenyl ring is very difficult. The presence of this type of group, *v. gr.*, chloro or bromo, provokes a deactivation of the amine group and, consequently, a diminution of its nucleophilic ability. Fortunately, Peng *et al.* have discovered that the addition of the dehydrating agent dicyclohexylcarbodiimide (DCC), facilitates the reaction of hexamolybdate with anilines, giving very good yields.⁷ Recently, this group has described two new organoimido-derivatives of hexamolybdate using 2-, 3- and 4-chloro-¹² and 4-bromoanilines.^{12,18} The reaction of 2,6-Me₂-4-Br-aniline as hydrochloride with tetra-butylammonium α -octamolybdate, (*n*-Bu₄N)₄[α -Mo₈O₂₆], and DCC in refluxing acetonitrile, has effectively allowed the synthesis of (*n*-Bu₄N)₂[1]^{1/2}Me₂CO in 72% yield. The role of the proton in the enhancement of the electrophilic ability of DCC toward the terminal oxo atom of the Mo=O group and in the conversion of the [α -Mo₈O₂₆]⁴⁻ into [Mo₆O₁₉]²⁻ through a degradation and re-assembly process, has recently been discussed.^{9,18}

Complex (*n*-Bu₄N)₂[1]^{1/2}Me₂CO was obtained as red and air stable crystalline solid, and was fully characterized by ¹H- and ¹³C-NMR, IR and UV-vis spectroscopy (see Experimental Section). The crystalline and molecular structure of this complex was determined by single crystal X-ray diffraction analysis (*vide infra*). The more salient features of the ¹H-NMR spectrum of this compound are (i) the singlet resonance in the at 2.17 ppm corresponding to the proton resonances of the methyl groups occupying the symmetrical 2,6-positions and the singlet at 7.23 ppm corresponding to the resonances of protons placed in the symmetrical 3,5-positions of the phenyl ring and (ii) the four groups of signals corresponding to the proton resonances of the two *n*-Bu₄N⁺ cations. Likewise, consistent with the proposed structure, the proton-decoupled ¹³C-NMR spectrum of complex (*n*-Bu₄N)₂[1]^{1/2}Me₂CO exhibits the expected characteristic sharp resonances of the phenyl ring carbon atoms and the resonances of the methyl carbon atoms placed in the 2,6-positions (see Experimental Section). On the other hand, the IR spectrum of (*n*-Bu₄N)₂[1]^{1/2}Me₂CO is characterized by the very strong absorption bands at 950 and 790 cm⁻¹ attributed to the Mo=O and Mo-O-Mo stretching modes,^{11,13,19} respectively. A strong shoulder near 975 cm⁻¹, attributed to the Mo≡N stretching mode,^{1,11-13,19,30} proves this complex to be the mono-organoimido substituted derivative. Finally, Figure 1 shows the UV-vis absorption spectrum of (*n*-Bu₄N)₂[1]^{1/2}Me₂CO in acetonitrile (a) and, for the sake of comparison, the spectrum of (*n*-Bu₄N)₂[Mo₆O₁₉] in the same solvent (b). The lowest-energy electronic transition at 325 nm in the precursor [Mo₆O₁₉]²⁻ has been attributed to a ligand-to-metal charge-transfer transition associated with the terminal oxygen non-bonding π -type HOMO to the molybdenum π -type LUMO.^{7,18} In complex [1]²⁻ the ligand-to-metal charge transfer transition band, observed at 358 nm, exhibits two important features relative to the spectrum of (*n*-Bu₄N)₂[Mo₆O₁₉]: (i) its intensity becomes nearly three times, and (ii) its wavelength is bathochromically shifted by 33 nm. These observations indicate that the N-Mo π -bonding is strongly delocalized through the organic conjugated backbone.^{7,13,18} The spectrum of (*n*-Bu₄N)₂[1]^{1/2}Me₂CO registered in DMSO does not exhibit hipso- or bathochromic effects.

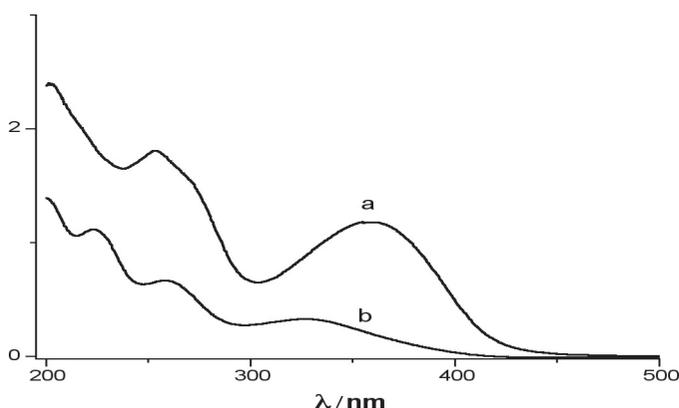


Figure 1. UV-vis absorption spectra of (*n*-Bu₄N)₂[1]^{1/2}Me₂CO (a) and (*n*-Bu₄N)₂[Mo₆O₁₉] (b), in acetonitrile.

Crystal structure

A summary of X-ray crystal data for (*n*-Bu₄N)₂[1]^{1/2}Me₂CO is presented in Table 1. Table 2 contains selected bond lengths and angles. The cluster crystallizes in the triclinic space group P-1. The asymmetric unit contains two conformational isomers A and B, generated by a different orientation

of the phenyl ring (see Figure 2). From the structural point of view, both crystallographically independent isomers differ by the rotation of the phenyl ring by 12.1(2)° relative to the plane including the Mo(1)-O(2)-Mo(2)-O(15)-Mo(6)-O(17)-Mo(4)-O(4) atoms in the case of the isomer A, and by 34.5(2)° relative to the plane including the Mo(7)-O(21)-Mo(9)-O(34)-Mo(12)-O(32)-Mo(11)-O(19) atoms in the case of the isomer B (see Figure 3). Similar examples have been described for the isoelectronic imido-hexamolybdate clusters [Mo₆O₁₈(NC₆H₂-2,6-Me₂-4-I)]²⁻ and [Mo₆O₁₈(NC₆H₂-2,6-Me₂-4-C≡CH)]²⁻.⁷ Although the majority of the molecular parameters of structures A and B are nearly the same, both structures differ in the angles Mo(1)-N(1)-C(1) and Mo(7)-N(2)-C(9) by 3.4°. These values, near to 180°, and the short Mo-N bond distances of 1.720(6) and 1.723(6) Å for the anions A and B, respectively, are in good accord with the presence of a triple bond in the Mo≡N fragment.³¹ On the other hand, the C-Br bond lengths of isomer A and B, 1.889(10) and 1.888(9) Å, respectively, are similar to the average bond length, 1.897 Å, calculated in aromatic bromine compounds. As distinguished from [Mo₆O₁₈(NC₆H₄-4-Br)]²⁻,¹⁸ complex [1]²⁻ does not exhibit dimerization.

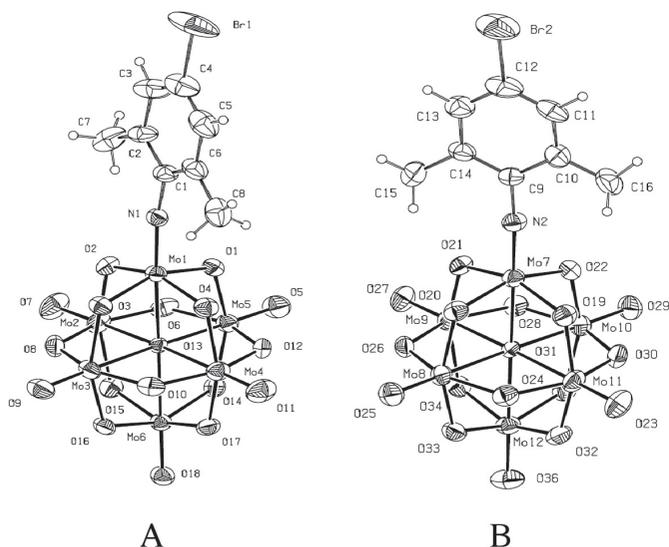
Table 1. Crystal data and structure refinement for (*n*-Bu₄N)₂[1]^{1/2}Me₂CO

Empirical formula	C ₈₃ H ₁₆₆ Br ₂ Mo ₁₂ N ₆ O ₃₇
Formula weight	3151.32
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	12.5861(15)
<i>b</i> (Å)	19.083(2)
<i>c</i> (Å)	25.456(3)
α (°)	103.313(2)
β (°)	91.074(2)
γ (°)	99.735(2)
Volume (Å ³)	2
<i>Z</i>	1.995
Absorption coefficient (mm ⁻¹)	0.369 x 0.238 x 0.184
Crystal size (mm ³)	1.64 to 28.11°
θ range for data collection	-16<= θ <=15,
Index ranges	-24<= <i>k</i> <=24,
	-33<= <i>l</i> <=32
Reflections collected	49891
Independent reflections [<i>R</i> _{int}]	25467 [0.0564]
Completeness to $\theta = 28.11^\circ$	89.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	25467 / 0 / 1283
Goodness-of-fit on <i>F</i> ²	0.930
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.1214
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1425, <i>wR</i> ₂ = 0.1513
Largest difference in peak and hole (e.Å ⁻³)	1.058 and -0.812

Table 2. Selected bond lengths (Å) and angles (°) for the two crystallographically independent anions A and B observed in complex $(n\text{-Bu}_4\text{N})_2[\text{1}]^{2-}$.

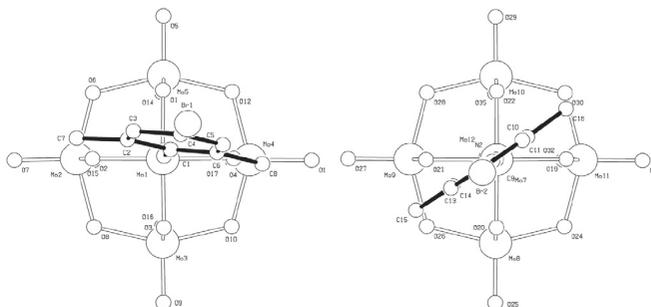
Anion A		Anion B	
Bond lengths			
Mo(1)-N(1)	1.720(6)	Mo(7)-N(2)	1.723(6)
Mo(1)-O _b (1)	1.959(5)	Mo(7)-O _b (19)	1.934(5)
Mo(1)-O _b (2)	1.924(5)	Mo(7)-O _b (20)	1.944(5)
Mo(1)-O _b (3)	1.945(5)	Mo(7)-O _b (21)	1.958(5)
Mo(1)-O _b (4)	1.959(5)	Mo(7)-O _b (22)	1.951(5)
Mo(1)-O _c (13)	2.209(4)	Mo(7)-O _c (31)	2.206(4)
Mo(6)-O _c (13)	2.364(4)	Mo(12)-O _c (31)	2.341(4)
Mo(6)-O _t (18)	1.669(5)	Mo(12)-O _t (36)	1.675(5)
Mo(6)-O _b (14-17)	1.915 ^a	Mo(12)-O _b (32-35)	1.908 ^a
Mo(2-6)-O _c (13)	2.330 ^a	Mo(8-11)-O _c (31)	2.330 ^a
Mo(2-5)-O _t	1.670 ^a	Mo(8-11)-O _t	1.670 ^a
Mo(2)-O _b	1.919 ^a	Mo(8)-O _b	1.920 ^a
Mo(3)-O _b	1.912 ^a	Mo(9)-O _b	1.914 ^a
Mo(4)-O _b	1.921 ^a	Mo(10)-O _b	1.918 ^a
Mo(5)-O _b	1.910 ^a	Mo(11)-O _b	1.915 ^a
N(1)-C(1)	1.384(8)	N(2)-C(9)	1.387(9)
C(4)-Br(1)	1.889(10)	C(12)-Br(2)	1.888(9)
Bond angles			
N(1)-Mo(1)-O(1-4)	101.9 ^a	N(2)-Mo(7)-O(19-22)	101.7 ^a
Mo(1)-N(1)-C(1)	172.2(6)	Mo(7)-N(2)-C(9)	175.6(6)
N(1)-C(1)-C(2)	117.4(8)	N(2)-C(9)-C(10)	119.0(8)
N(1)-C(1)-C(6)	120.8(8)	N(2)-C(9)-C(14)	119.3(7)

t = terminal; b = bridge; c = central; a = average

**Figure 2.** ORTEP drawings with the atom numbering scheme for the conformational isomers A and B of $[\text{1}]^{2-}$. Displacement ellipsoids are at 50% probability level.

Finally, as it has been observed in arylimido-derivatives of hexamolybdate, when the arylimido group substitutes an oxygen atom of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ precursor the bond lengths of Mo-O do not change significantly, however, the Mo(1)-O_b are lengthened and that of Mo(1)-O_c²² is shortened. On the other hand, the Mo(1)-O_c is always shorter than that of Mo(6)-O_c. In the case of complex $(n\text{-Bu}_4\text{N})_2[\text{1}]^{2-}$, the Mo(1)-O(13) bond length, in the conformational isomer A, is shorter than that of Mo(6)-O(13) by 0.155 Å, while

in the conformational isomer B this difference is 0.135 Å (see Tables 2). Table 3 compares the structural features of arylimido-derivatives of hexamolybdate. The influence of the substituent groups on the phenyl rings seems to be weak, so that a meaningful structural correlation between the bond lengths and the Hammett constants, σ_p -X, could not be established.

**Figure 3.** Spatial rotation of the phenyl rings in the structural isomers A and B of complex $[\text{1}]^{2-}$: A, 12.1(2)°; B, 34.5(2)°.

Electrochemistry

In DMF solution, Cyclic Voltammetry of $(n\text{-Bu}_4\text{N})_2[\text{1}]^{2-}$ Me₂CO exhibits two irreversible one-electron reduction processes at $E_p = -0.785$ and -0.890 V (vs Ag/AgCl). Corresponding values for $[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{-4-Me})]^{2-}$ are -0.52 and -1.09 V, whereas for the $[\text{Mo}_6\text{O}_{19}]^{2-}$ are -0.39 and -1.12 V.¹ The first process can be attributed to the reduction of the hexamolybdate fragment of the $[\text{1}]^{2-}$ complex to afford the reduced anionic species $[\text{1}]^{3-}$. This potential is more negative than those of $[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{-4-Me})]^{2-}$ and $[\text{Mo}_6\text{O}_{19}]^{2-}$ which indicates that the electron-accepting ability of the bromo group has been compensated by the two methyl groups. Under the same experimental conditions, ferrocene exhibits a reversible process at $E_{1/2} = +0.566$ V ($\Delta E = 68$ mV).

Table 3. Comparison of selected bond lengths (Å) and angles (°) of arylimido-hexamolybdates, $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$.

R=	Mo(1)-N	Mo(1)-O ^a	Mo(1)-O _c	Mo(6)-O _c	Mo(6)-O _b	Mo(1)-N-C	C-X	Ref
-C ₆ H ₄ -4-Cl	1.686(3)	1.927	2.237(1)	2.340(1)	1.685(4)	163.6(6)	1.656	12
-C ₆ H ₄ -4-Br	1.698(13)	1.934	2.234(8)	2.347(8)	1.659(10)	163.6(14)	1.854	18
-C ₆ H ₃ -2,6-Me ₂	1.723(7)	1.953	2.230(6)	2.337(6)	1.697(7)	178.4(7)		7
-C ₆ H ₃ -2,6-Me ₂ -4-Br [*]	1.720(6)	1.946	2.209(4)	2.364(4)	1.669(5)	172.2(6)	1.889(10) [#]	This work
	1.723(6)	1.946	2.206(4)	2.341(4)	1.675(5)	175.6(6)	1.888(9) [#]	This work
-C ₆ H ₃ -2,6-Me ₂ -4-I [*]	1.733(6)	1.947	2.222(4)	2.349(4)	1.690(5)	172.8(6)	2.093	7
	1.738(6)	1.936	2.249(4)	2.374(4)	1.702(5)	165.9(6)	2.086	7
-C ₆ H ₃ -2,6-Me ₂ -4-C≡CH [#]	1.729(5)	1.943	2.232(4)	2.353(4)	1.682(4)	172.8(6)		7
	1.727(5)	1.950	2.210(3)	2.342(3)	1.686(4)	165.9(6)		7
-C ₆ H ₃ -2,6-Me ₂ -4-C≡C-Tol- <i>p</i>	1.739(19)	1.936	2.193(14)	2.334(14)	1.68(2)	171.4(18)		8
-C ₆ H ₄ -4-CH=CH ₂	1.728(7)	1.944	2.223(5)	2.353(5)	1.689(6)	159.9(7)		5
-C ₆ H ₄ -4-Me	1.661(18)	1.960	2.202(11)	2.344(9)	n. r.	154.2(16)		1
-C ₆ H ₄ -2-Me	1.772(3)	1.933	2.205(1)	2.349(1)	1.700(2)	173.9(16)		12
-C ₆ H ₃ -2,6-Fr ₂	1.739(15)	1.954	2.254(10)	2.312(10)	1.649(14)	176.3(15)		6
-C ₆ H ₄ -4-OMe	1.733(4)	1.945	2.213(3)	2.355(3)	1.671(3)	163.3(4)		11
-C ₆ H ₄ -4-NMe ₂	1.730(4)	1.946	2.220(2)	2.354(3)	1.675(3)	160.3(4)		19
-C ₆ H ₃ -2,6-Me ₂ -4-C≡C-(η ⁵ -C ₅ H ₅)Pr(η ⁵ -Cp)	1.731(8)	1.953	2.205(5)	2.356(5)	1.676(6)	178.5(6)		13

*The asymmetric unit contains two crystallographically independent anions; ^aaverage; ^bbridge; ^ccentral; ^tterminal in *trans*-position; n. r.= not reported; X= Cl, Br, I; [#]average bond length for organic molecules = 1.897 Å.

CONCLUDING REMARKS

We have successfully prepared and characterized by spectroscopic methods and by X-ray diffraction analysis the new functionalized Lindqvist-type hexamolybdate cluster containing an arylimido moiety bearing two methyl substituent groups in the 2,6-positions and an electron-withdrawing bromo group in the remote 4-position of the phenyl group, $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_2\text{-2,6-Me}_2\text{-4-Br})]$. From the synthetic point of view, the C-Br moiety of this new precursor may be useful as an additional reaction site in this type of cluster for a further functionalization through a carbon-carbon coupling reaction,^{8-10,13} and,

potentially, with nucleophilic species to afford new molecular or polymeric hybrid materials.

From the structural point of view, both conformational isomers A and B observed in the asymmetric unit of $(n\text{-Bu}_4\text{N})_2[\text{1}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$ differ only by (i) the different rotation of the phenyl rings relative to the hexamolybdate skeleton, and (ii) the angles Mo(1)-N(1)-C(1)=172.2(6) and Mo(7)-N(2)-C(9)=175.6(6), which prove the presence of a Mo=N triple bond.

Supplementary materials

Crystallographic data (excluding structure factors) for the structure reported in this paper, $(n\text{-Bu}_4\text{N})_2[\text{1}] \cdot \frac{1}{2}\text{Me}_2\text{CO}$, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-631809. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Y. Du, A. L. Rheingold, E. A. Maatta, *J. Am. Chem. Soc.* **114**, 345 (1992).
2. B. J. B. Strong, R. Ostrander, A. L. Rheingold, E. A. Maatta, *J. Am. Chem. Soc.* **116**, 3601(1994).
3. W. Clegg, R. J. Errington, K. A. Fraser, S. A. Holmes, A. Schäfer, *J. Chem. Soc., Chem. Commun.* 455 (1995).
4. J. L. Stark, V. G. Young, E. A. Maatta, *Angew. Chem. Int. Ed. Engl.* **34**, 2547 (1995).
5. A. R. Moore, H. Kwen, A. M. Beatty, E. A. Maatta, *Chem. Commun.* 1793 (2000).
6. J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta, *J. Am. Chem. Soc.* **122**, 639 (2000).
7. Y. Wei, B. Xu, C. L. Barnes, Z. Peng, *J. Am. Chem. Soc.* **123**, 4083 (2001).
8. B. Xu, Y. Wei, C. L. Barnes, Z. Peng, *Angew. Chem. Int. Ed.* **40**, 2290 (2001).
9. L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng, D. R. Powell, *Angew. Chem. Int. Ed.* **41**, 4129 (2002).
10. M. Lu, Y. Wei, B. Xu, C. F. Cheung, Z. Peng, D. R. Powell, *Angew. Chem. Int. Ed.* **41**, 1566 (2002).
11. R. A. Roesner, S. C. McGrath, J. T. Brockman, J. D. Moll, D. X. West, J. K. Swearingen, A. Castineiras, *Inorg. Chim. Acta* **342**, 37 (2003).
12. P. Wu, Q. Li, N. Ge, Y. Wei, Y. Wang, P. Wang, H. Guo, *Eur. J. Inorg. Chem.* 2819 (2004).
13. J. Kang, J. A. Nelson, M. Lu, B. Xie, Z. Peng, D. R. Powell, *Inorg. Chem.* **43**, 6408 (2004).
14. M. Lu, J. Kang, D. Wang, Z. Peng, *Inorg. Chem.* **44**, 7711 (2005).
15. M. Lu, B. Xie, J. Kang, F.-C. Chen, Y. Yang, Z. Peng, *Chem. Mater.* **17**, 402 (2005).
16. Y. Xia, Y. Wei, Y. Wang, H. Guo, *Inorg. Chem.* **44**, 9823 (2005).
17. I. Bar-Nahum, K. V. Narasimhulu, L. Weiner, R. Neumann, *Inorg. Chem.* **44**, 4900 (2005).
18. Q. Li, P. Wu, Y. Xia, Y. Wei, H. Guo, *J. Organomet. Chem.* **691**, 1223 (2006).
19. Z. Xiao, Y. Zhu, Y. Wei, Y. Wang, *Inorg. Chem. Commun.* **9**, 400 (2006).
20. T. R. Mohs, G. P. A. Yap, A. L. Rheingold, E. A. Maatta, *Inorg. Chem.* **34**, 9 (1995).
21. Y. Wei, M. Lu, C. F. Cheung, C. L. Barnes, Z. Peng, *Inorg. Chem.* **40**, 5489 (2001).
22. L. Yan, Z.-M. Su, W. Guan, M. Zhang, G.-H. Chen, L. Xu, E.-B. Wang, *J. Phys. Chem.* **108** B, 17337 (2004).
23. L. Yan, G. Yang, W. Guan, Z. Su, R. Wang, *J. Phys. Chem.* **109** B, 22332 (2005).
24. D. Mac-Leod Carey, A. Muñoz-Castro, C. J. Bustos, J. M. Manríquez, R. Arratia-Pérez, *J. Phys. Chem.*, **111** B, 6563 (2007).
25. (a) Polyoxometalates, *Chem. Rev.* **98**, 3-387(1998). (b) P. Gouzerh, A. Proust, *Chem. Rev.* **98**, 77 (1998).
26. N. Hur, W. G. Klemperer, R.-C. Wang, *Inorg. Synth.* **27**, 78-79 (1990).
27. *SAINT-PLUS (version 6.02)*, Bruker Analytical X-ray Systems Inc., Madison, WI, USA (1999).
28. G. M. Sheldrick, *SADABS (Version 2.05): Empirical Absorption Program*, University of Göttingen, Germany.
29. *SHELXTL, Reference Manual (Version 6.14)*. Bruker Analytical X-Ray Systems Inc., Madison, WI, USA (1998).
30. A. Proust, R. Thouvenot, M. Chaussade, F. Robert, P. Gouzerh, *Inorg. Chim. Acta* **123** (2001) 4083.
31. D. E. Wigley, *Prog. Inorg. Chem.* **42** (1994) 239.