



Preliminary communication / Communication

A *p*-cyanophenylimido hexamolybdate: preparation and structure of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{18}(\text{N-}p\text{-C}_6\text{H}_4\text{CN})]^\dagger$

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Received 16 September 2004; accepted 6 December 2004

Available online 03 March 2005

† Dedicated with respect and good cheer to Professor Francis Sécheresse on the occasion of his 60th birthday

Abstract

The title compound has been prepared through reaction of the corresponding arylimino-triphenylphosphorane with $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Mo}_6\text{O}_{19}]$ in hot pyridine solution. The single crystal X-ray structure of the title compound has been determined.

To cite this article: H. Kwen et al., *C. R. Chimie* 8 (2005).

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Résumé

Ce composé a été préparé par réaction du dérivé arylimino-triphénylphosphorane avec $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Mo}_6\text{O}_{19}]$ dans la pyridine, à chaud. Sa structure a été résolue par diffraction des rayons X sur monocristal. **Pour citer cet article :** H. Kwen et al., *C.R. Chimie* 8 (2005).

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Keywords: Polyoxometalates; Organoimido ligands

Mots clés : Polyoxométales ; Ligands organoimido

1. Introduction

The first examples of organoimido-substituted hexamolybdates $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$ contained as their substituents simple aryl or alkyl groups [1–4]. Subsequent attention has focused on derivatives in which the spe-

cies' imido ligands bear modified substituents capable of either altering the complexes' electronic and physico-chemical properties or serving as sites for further elaboration and reactivity. Examples of substituents in such "second-generation" imido-hexamolybdates include a variety of *p*-X-substituted aryl groups (X = e.g. NH₂ [5], OMe, F, Cl, Br, CF₃, NO₂ [6], CH=CH₂ [7], I, C≡CH [8]), ferrocenyl [9], and terpyridyl [10]. Herein, we report the preparation and structure of an arylimido-

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hexamolybdate incorporating cyano functionality, namely $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{18}(\text{N-}p\text{-C}_6\text{H}_4\text{CN})]$, **1**.

2. Experimental section

2.1. General procedures

Syntheses and manipulations were carried out either in a nitrogen-filled glovebox or using standard Schlenk techniques. Commercially available reagents were used as received. $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ was prepared according to a literature method [11]. Anhydrous grade pyridine and acetonitrile (Aldrich) were used without further purification. ^1H NMR spectra were recorded using a Varian Unity Plus instrument operating at 400.1 MHz. Chemical shifts in ppm are referenced to residual protio impurities in the deuterated solvent. Electronic spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. Infrared spectra were recorded as Nujol mulls between KBr plates using a Perkin-Elmer 1330 spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.1.1. 4-Cyanophenyliminotriphenylphosphorane

4-Aminobenzonitrile (1.00 g; 8.5 mmol) and triethylamine (1.71 g; 17 mmol) were added to a suspension of dibromotriphenylphosphorane (3.57 g; 8.5 mmol) in 30 ml of benzene. The reaction mixture was stirred at room temperature overnight and then filtered through a sintered glass frit to remove the white precipitate of $[\text{Et}_3\text{NH}]\text{Br}$. The yellow filtrate was reduced to approximately one-half volume under vacuum, and diethyl ether was added to precipitate the product as a yellow powder, which was recovered by filtration and dried overnight under vacuum (0.82 g; 25%). IR, cm^{-1} : 2182 (ν_{CN}). ^1H NMR (CD_3CN ; 298 K): δ 7.79–7.74, 7.65–7.61, 7.56–7.51 (m, 15H, C_6H_5), 7.26, 7.24, 6.72, 6.69 (AA'BB', 4H, C_6H_4).

2.1.2. Compound **1**

4-Cyanophenyliminotriphenylphosphorane (0.30 g; 0.80 mmol) and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ (1.00 g; 0.73 mmol) were dissolved in 10 ml of pyridine. The reaction mixture was stirred under nitrogen at 85 °C for 12 days. The dark red–brown solution was filtered through a medium porosity sintered glass frit and sol-

vent was removed under vacuum. The tacky residue was first washed with diethyl ether, and subsequently triturated with benzene (5×15 ml) until the washings showed no trace of triphenylphosphorane oxide. The dark orange solid product was dried under vacuum (0.86 g; 80%). Single crystals suitable for X-ray structural studies were grown by diffusion of diethyl ether vapor into a concentrated acetonitrile solution at room temperature. Elemental analysis calculated (found) % for $\text{C}_{39}\text{H}_{76}\text{N}_4\text{O}_{18}\text{Mo}_6$: C, 31.98 (31.73); H, 5.23 (5.20); N, 3.83 (3.81). ^1H NMR (CD_3CN ; 298 K): δ 7.74, 7.72, 7.27, 7.25 (AA'BB', 4H, C_6H_4), 3.09 (m, 16H, NCH_2), 1.60 (m, 16H, CH_2), 1.34 (m, 16H, CH_2), 0.96 (t, 24H, CH_3). IR, cm^{-1} : 2230 (m, ν_{CN}), 980 (w, sh), 960 (s, ν_{MoO}), 780 (br, s, ν_{MoOMo}). UV–Vis (CH_3CN ; 298 K; 1.36×10^{-5} M): λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 333 (1.23×10^4), 266 (2.15×10^4).

2.2. X-ray structural determination

Data were collected using a Bruker P4 diffractometer on an irregular orange block of **1** with dimensions $0.30 \times 0.28 \times 0.10$ mm^3 : $M = 1464.68$, monoclinic, $P2_1/n$, $a = 17.2423(19)$, $b = 18.023(2)$, $c = 19.034(3)$ Å, $\beta = 114.268(8)^\circ$, $V = 5392.3(12)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.804$ g cm^{-3} , $T = 173(2)$ K, $\mu = 1.421$ mm^{-1} , $\lambda = 0.71073$ Å; 7189 reflections (6928 independent) were collected ($2\theta_{\text{max}} = 43.0^\circ$). The structure was solved by direct methods and refined by full-matrix least-squares (on F^2) and difference Fourier cycles. A semi-empirical absorption correction was applied ($T_{\text{min}}/T_{\text{max}} = 0.8246$). Final residuals were: (all data) $R1 = 0.0690$ and $wR2 = 0.0917$ for 6928 data and 604 parameters; $[I > 2\sigma(I)]$ $R1 = 0.0408$ and $wR2 = 0.0818$. Largest difference in peak and hole = 0.799 and -0.565 e Å^{-3} . GOF (F^2) = 1.057.

3. Results and discussion

The reaction of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ with $\text{Ph}_3\text{P}=\text{N-}p\text{-C}_6\text{H}_4\text{CN}$ to produce **1** and $\text{Ph}_3\text{P}=\text{O}$ proceeds smoothly, albeit slowly, in warm pyridine solution. The corresponding reaction of the hexamolybdate with the alternative imido delivery reagent $p\text{-OCN-}C_6\text{H}_4\text{CN}$ can also be used in the synthesis of **1** under identical conditions, but this reaction too is slow.

The solid state IR spectrum of **1** displays ν_{CN} at 2230 cm^{-1} and in the ν_{MoO} region, a distinct band

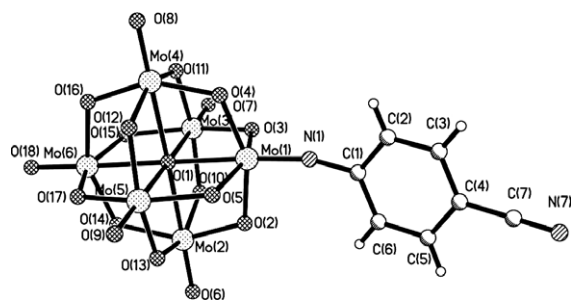


Fig. 1. Structure of the *p*-cyanophenylimido-hexamolybdate dianion within **1**.

at 980 cm^{-1} appears as a shoulder on the main feature at 960 cm^{-1} : such a ‘doublet’ pattern is a characteristic feature of the IR spectra of monosubstituted-hexamolybdate systems. In CH_3CN solution, the lowest-energy absorption in the electronic spectrum of **1** is observed at 333 nm; both the position and intensity of this band are in agreement with those observed previously for various mono-substituted arylimido-hexamolybdates [12].

The structure of the *p*-cyanophenylimido hexamolybdate dianion within **1** is shown in Fig. 1 and selected metrical parameters are collected in Table 1. The cyanophenylimido ligand is bound with an Mo(1)–N(1) distance of 1.720(6) Å, and with an angle Mo(1)–N(1)–C(1) of 164.1(7); both of these values are within the range expected for a formal $[\text{Mo}\equiv\text{NAr}]$ bonding description. The environment around the central μ_6 -oxygen O(1) is decidedly asymmetric: its distance to the substituted Mo(1) atom (2.220(4) Å) is substantially shorter than its distance to any of the other five Mo atoms (2.335(4) Å avg.). Other general features of the structure are typical of those observed in other mono-substituted arylimido-hexamolybdates.

4. Conclusions

Nitrile functionality can be incorporated into an arylimido ligand bound to the hexamolybdate core, as demonstrated by the preparation and structure of **1**. Given the broad utility of organonitriles as ligands in transition metal complexes, and given that other suitably functionalized organoimido systems have been shown to act as ‘metalloligands’ capable of binding exogenous metal complexes [13], we plan to explore the use of **1** and related systems in such applications.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Mo(1)–N(1)	1.720(6)
Mo(1)–O(3)	1.902(5)
Mo(1)–O(4)	1.909(5)
Mo(1)–O(2)	1.967(5)
Mo(1)–O(5)	1.969(5)
Mo(1)–O(1)	2.220(4)
Mo(2)–O(6)	1.679(5)
Mo(2)–O(13)	1.884(4)
Mo(2)–O(2)	1.899(5)
Mo(2)–O(14)	1.951(5)
Mo(2)–O(10)	1.983(5)
Mo(2)–O(1)	2.348(4)
Mo(3)–O(7)	1.674(5)
Mo(3)–O(10)	1.879(5)
Mo(3)–O(15)	1.903(5)
Mo(3)–O(3)	1.948(5)
Mo(3)–O(11)	1.987(5)
Mo(3)–O(1)	2.317(4)
Mo(4)–O(8)	1.679(5)
Mo(4)–O(11)	1.880(4)
Mo(4)–O(16)	1.909(4)
Mo(4)–O(4)	1.916(5)
Mo(4)–O(12)	1.977(4)
Mo(4)–O(1)	2.333(4)
Mo(5)–O(9)	1.686(5)
Mo(5)–O(5)	1.869(5)
Mo(5)–O(12)	1.887(4)
Mo(5)–O(17)	1.940(5)
Mo(5)–O(13)	1.980(4)
Mo(5)–O(1)	2.326(4)
Mo(6)–O(18)	1.685(5)
Mo(6)–O(17)	1.888(5)
Mo(6)–O(14)	1.906(4)
Mo(6)–O(15)	1.932(5)
Mo(6)–O(16)	1.942(4)
Mo(6)–O(1)	2.351(4)
N(1)–C(1)	1.398(10)
C(1)–C(6)	1.392(11)
C(1)–C(2)	1.401(11)
C(2)–C(3)	1.364(11)
C(3)–C(4)	1.369(12)
C(4)–C(5)	1.390(12)
C(4)–C(7)	1.403(13)
C(7)–N(7)	1.167(13)
C(5)–C(6)	1.384(12)

Supplementary crystallographic material for this paper may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12, Union

Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033, referring to deposit CCDC 246155.

Acknowledgements

We are grateful to the US Department of Energy, Office of Basic Energy Sciences for support of this research.

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