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Synthesis and Spectroscopic Characterization of $[Mo_2(\mu\text{-}O)_2(\mu\text{-}NO)_2(PPh_3)_4]$

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Abstract

Starting from $[MoOCl_3(PPh_3)_2]$ (I) in reaction with NO we synthesized, via $[Mo_2O_2Cl_4(\mu\text{-}NO)(PPh_3)_4]$ (II), new binuclear complex $[Mo_2(\mu\text{-}O)_2(\mu\text{-}NO)_2(PPh_3)_4]$ (III). The product was identified and its spectroscopic characteristics were presented. On the basis of the electronic spectra the energy terms and the crystal field parameters of the central ion were determined

Introduction

We have recently examined [1] the absorption bands of $[MoOCl_3(PPh_3)_2]$ in the UV–Vis region. In the same paper the rate constant of the Mo(V) complex reaction with solvated electron was calculated and the mechanism of its reduction was discussed in detail.

Since the reduction was connected with the elimination of the Cl ligands from the coordination sphere of Mo(V) we found it interesting to carry out the process of Mo(V) ion reduction using nitrogen oxide as the reducing agent. The possible replacement of Cl ligands by NO might easily lead to a nitrosyl complex of Mo(II) with triphenylphosphine in the coordination sphere. On the other hand, nitrosyl complexes with oxygen ligands have been relatively rarely described [2, 3]. In addition, the explanation of the electronic configuration of the central ion as well as the calculation of the crystal field parameters in such a compound would be of interest. It is worth adding that the method of synthesis, although sometimes applied, see for example ref. 15, differs from those usually described in the literature [4], and could easily lead to an important group of compounds with the bridging nitrogen oxide. For example, $[MoOCl(dppe)_2]^+$ – the catalyst in a radiation-catalytic reduction of molecular nitrogen [5], forms the nitrosyl bridged dimer and free dppe is liberated simultaneously [6].

Some analogies between nitrosyl complexes of the transition metal ions and their molecular nitrogen complexes together with the catalytic activities of the nitrosyl complexes in many important processes [7] are the reasons for the great interest in this subject.

Experimental

$[MoOCl_3(PPh_3)_2]$ was synthesized according to the literature [8]. Gaseous NO, purified by passing through a concentrated solution of KOH and then over NaOH pellets, was bubbled through a solution of the Mo(V) complex in CH_2Cl_2. When the reaction was completed, the tested solution was saturated for a moment with argon, after that the liberated Cl^- ions were extracted to the water layer and determined by titration with $AgNO_3$ solution. The organic, transparent yellow solution was evaporated under vacuum and the residue was dissolved in absolute ethanol. After a few hours bright yellow rod crystals appeared. Unfortunately, the crystals were not suitable for X-ray diffraction.

The standard methods of elemental analysis were applied; molybdenum was determined by the 8-hydroxyquinoline method. The absorption bands were recorded with a Beckman 5240 spectrophotometer; the NMR (^1H, ^{13}C, ^{31}P) spectra were made using a Varian VXR-300 spectrometer. IR measurements in KBr pellets were taken with the help of a Specord 75 IR spectrophotometer. For some additional measurements the following equipment was used: the IR spectra in the 400–200 cm^{-1} region were recorded with a Specord M-80 spectrophotometer, magnetic susceptibility was measured with a Gouy's balance. The Raman spectra were recorded with a monochromator GDN-100 (Ar laser, $\lambda = 688$ nm); the ESR signals were recorded with a UNIPAM spectrometer.

Results and Discussion

Several attempts were made to catch the moment when only one Cl ligand was removed from the

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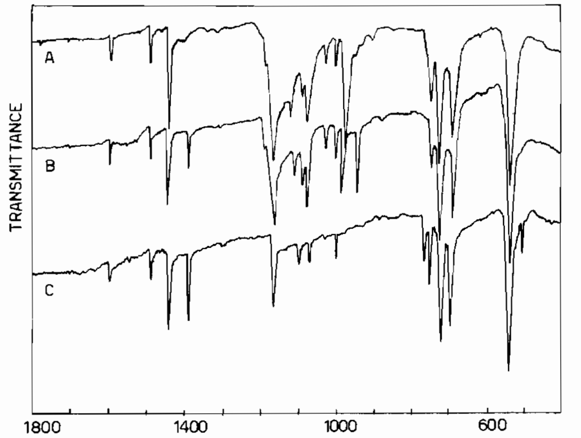


Fig. 1. IR spectra of: A, $[MoOCl_3(PPh_3)_2]$ (I); B, $[Mo_2O_2Cl_4(NO)(PPh_3)_4]$ (II); C, $Mo_2O_2(NO)_2(PPh_3)_4]$ (III).

coordination sphere of the central ion. Eventually we were successful using the above mentioned procedure of the Cl^- ions determination. Thus, one Cl ligand was liberated from one molecule of the Mo(V) complex and, consequently, Mo(V) was reduced to Mo(IV).

The isolated compound II was examined. Its IR spectrum shows (see Fig. 1 and Table 1) the stretching vibrations of the Mo=O modes at 940 and 970 cm^{-1} in comparison with ν(Mo=O) at 960 cm^{-1} in I. It can be assumed that these two bands of identical intensities derive from the two, sterically non-equivalent, Mo=O groups [9, 10]. Another new band appears at 1380 cm^{-1} and it seems to derive from the bridged NO($\nu(NO_b)$) vibrations [11]. The formation of the Mo(IV) nitrosyl complex, II, was also supported by the absorption bands of this compound (see Fig. 2). Two bands at 730 and 450 nm, attributed to d–d transitions in I, disappear in II.

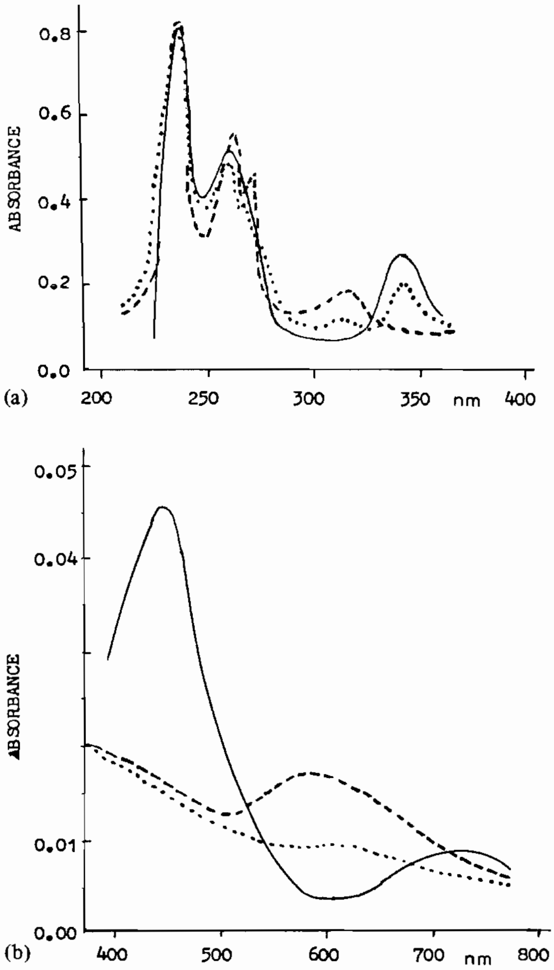
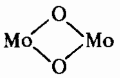
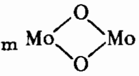


Fig. 2. Absorption spectra in (a) UV and (b) visible region of: A, $[MoOCl_3(PPh_3)_2]$ (I); B, $[Mo_2O_2Cl_4(NO)(PPh_3)_4]$ (II); C, $[Mo_2O_2(NO)_2(PPh_3)_4]$ (III); in CH_2Cl_2 solution, conc. = 5 × 10^{-4} M (a) and 5 × 10^{-3} M (b).

TABLE 1. The main vibrations in the IR spectra of the complexes I, II and III

Band (cm^{-1})	Assignment		
	$[MoOCl_3(PPh_3)_2]$ (I)	$[Mo_2O_2Cl_4(NO)(PPh_3)_4]$ (II)	$[Mo_2O_2(NO)_2(PPh_3)_4]$ (III)
510			ν_{sym} 
770			ν_{asym} 
940 970		ν(Mo=O)	
960	ν(Mo=O)		
1380		$\nu(NO_b)$	$\nu(NO_b)$

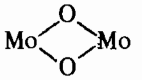
Instead, two new bands of low intensities at 320 and 600 nm appear. This third new band at 270 nm, attributed to the charge transfer Mo → NO (see Table 3), can also be regarded as an evidence of the coordination of NO.

While the removal of one Cl ligand took about 1 min, all the Cl ligands were liberated from the coordination sphere of the complex after about 30 min of bubbling NO through the test solution.

The obtained complex **III** in the form of bright yellow crystals was carefully examined. *Anal.* Found: Mo, 14.30; C, 64.52; H, 4.40; P, 9.33; N, 2.15; Cl, not found. Calc. for $[Mo_2O_2(NO)_2(PPh_3)_4]$: Mo, 14.48; C, 64.83; H, 4.50; P, 9.30; N, 2.10; Cl, 0.00%.

The nitrosyl complex of Mo(II) thus obtained shows no ESR signal and is diamagnetic ($\mu_{eff.}$ = 0 BM). Its ^1H, ^{13}C and ^{31}P NMR signals are presented in Table 2.

The NMR results and the chromatographic tests confirm the homogeneity of the formed substance and show clearly that the coordinated triphenylphosphine is not oxidized [12–16].

The IR spectrum of the obtained complex **III**, $[(PPh_3)_2Mo(\mu\text{-}O)_2(\mu\text{-}NO)_2Mo(PPh_3)_2]$, (see Fig. 1 and Table 1) shows no bands in the 900–1000 cm^{-1} region (ν(Mo=O)) or around 340 cm^{-1} (ν(Mo–Cl)). The strong band at 1380 cm^{-1} which appeared in the intermediate complex **II** ($\nu(NO_b)$) is still present and its intensity is increased. The new bands appear at 510 and 770 cm^{-1}. These bands can be assigned as ν_{sym} and ν_{asym} of a  group [17, 18]. Further support for this assignment comes from the fact that the possible existence of the Mo--Mo multiple (quadrupole) bond was excluded due to the lack of any vibrations in the 345–425 cm^{-1} region in the Raman spectra [19]. Some examples of similar nitrosyl complexes with bridging oxygen have been described in the literature [20, 21].

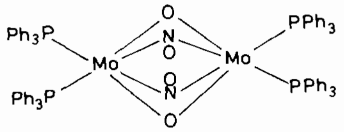
Taking into account the diamagnetism of the formed complex **III** and its electronic configuration d^4 one can assume that the energy terms in comparison with those of **I** should be reversed to assure the low spin configuration. Thus, the $(d_{xy})(d_{xz}, d_{yz})$ sequence, as in **I** [1], turns into $(d_{xz}, d_{yz})(d_{xy})$ with four electrons occupying the d_{xz} and d_{yz} orbitals. A similar situation was described in the case of the oxalate complex of Mo [22].

The electronic spectrum of complex **III** (see Fig. 2) shows three well-distinguished bands at 600, 320 and 270 nm. This latter band, which appeared in complex **II**, is well-recognized in **III**. It is due to the fact that the more NO molecules are in the coordination sphere of the complex the more likely is the electron transfer from $(d_{xz}, d_{yz})^4$ orbitals to π*NO. This band, however, is partially covered by the higher energy band at 260 nm. The band at 340 nm, attributed to the charge transfer π(Cl) → 4d(Mo) in **I**, completely disappeared in **III**. All the bands and their assignments are presented in Table 3.

TABLE 2. Chemical shifts and selected coupling constants of NMR signals of the complex III

75 MHz ^{13}C, TMS – internal reference		
Carbon atom	^{13}C (ppm)	^1J(P=C) (Hz)
1	131.8 d	105.4
2	133.1 d	10.2
3	129.6 d	12.3
4	133.4 d	2.9
300 MHz ^1H, TMS – internal reference		
Proton signal	^1H (ppm)	^1J(P=H) (Hz)
ortho	7.67	12.3
meta	7.48	
para	7.55	
121 MHz ^{31}P, 85% H_3PO_4 – external reference		
Phosphorous signal	^{31}P (ppm)	
	32.05 s	

From the presented data the ligand field parameters of the complex $[Mo_2O_2(NO)_2(PPh_3)_4]$ were determined to be as follows: Dq = 3125 cm^{-1}, Ds = 3736 cm^{-1} and D_T = –1060 cm^{-1}. Assuming a local symmetry of the obtained Mo(II) complex as C_{2v} the energy terms were calculated and are presented in Fig. 3. Thus, we can assume the obtained Mo(II) complex **III** to have the following dimeric structure.

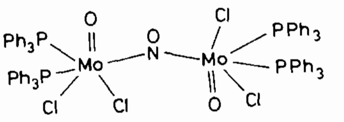


This complex is formed in the reaction

$$2MoOCl_3(PPh_3)_2 + 8NO \longrightarrow Mo_2O_2(NO)_2(PPh_3)_4 + 6NOCl$$

$$6NOCl + 6H_2O \longrightarrow 6HCl + 6HNO_2$$

The intermediate Mo(IV) complex **II** has the following structure



Similar complexes have been described in the literature [23, 24].

The relatively low frequency of the coordinated NO group vibrations is due to the effectiveness of the π-bond Mo → NO. Since the effective electron

TABLE 3. Absorption bands positions and their assignments of the complexes I, II and III

Band (nm)			Assignment
$[MoCl_3(PPh_3)_2]$ (I)	$[Mo_2O_2Cl_4(NO)(PPh_3)_4]$ (II)	$[Mo_2O_2(NO)_2(PPh_3)_4]$ (III)	
235			$\pi_O \rightarrow d_{xz}, d_{yz}$
	235	235	$\pi_O \rightarrow d_{xy}$
260	260	260	$\pi_{phen} \rightarrow 3dp$
	270	270	$d_{xz}, d_{yz} \rightarrow \pi^*_{NO}$
	320		${}^3E \rightarrow {}^2A_1$
		320	${}^1A_1 \rightarrow {}^3B_1$
340			$\pi_{Cl} \rightarrow d_{xy}$
	340		$\pi_{Cl} \rightarrow d_{xz}, d_{yz}$
450			${}^2B_2 \rightarrow {}^2B_1$
	600		${}^3E \rightarrow {}^3B_2$
		600	${}^1A_1 \rightarrow {}^3B_2$
730			${}^2B_2 \rightarrow {}^2E$

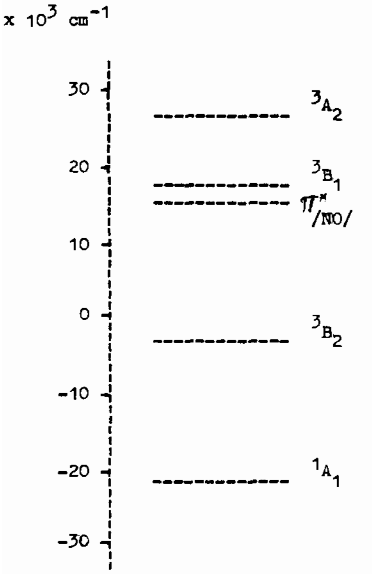


Fig. 3. The energy level diagram of the central atom orbitals for the complex $[Mo_2O_2(NO)_2(PPh_3)_4]$.

density of the π^* orbital of NO is the same in the case of complexes **II** and **III** (i.e. 2 electrons from each Mo atom per one molecule of NO in **II**, 4 electrons from each Mo atom per two molecules of NO in **III**) the frequencies of $\nu(NO_b)$ are equal in both cases. The delocalization of the oxygen electrons to the d_{xy} orbitals of Mo makes the donor abilities of the central ions more effective.

It is of interest that in the presented reaction between the oxochlorocomplex of Mo and nitrogen oxide, bridged complexes are formed and there are no terminal nitrosyl groups therein. In the case of the reactions of $MoCl_6{}^{3-}$, $Mo_2Cl_8{}^{4-}$ and $Mo_2Cl_8H^{3-}$ ions with gaseous NO (i.e. by continuous saturation) similar bridges are formed [25]. Thus, one can regard the procedure of the process, i.e. the NO bubbling through the solution or the permanent contact of NO with the solid reagents and, as a consequence, the sufficient concentration of NO, as the important factor in such a reaction.

Moreover, the reaction of $[MoOCl_3(OPPh_3)_2]$ (oxochloro bistriphenylphosphine oxide molybdenum(V)) with gaseous NO, which was made in the atmosphere of NO, without excess, was not successful [26]; this supports our conclusion. Besides, the high reactivity of the Mo(V) complex towards the redox reagents leads to the considerable concentration of the coordinatively unsaturated complex during the reaction. Therefore, the formation of the bridges, in the absence of other ligands (e.g. triphenylphosphine) as reagents, seems to be well-founded.

The reaction of complex **III** with gaseous NO in CH_2Cl_2 solution saturated with oxygen was also carried out. The isolated product revealed new strong vibrations at 1020, 850 cm^{-1} and a medium one at 1280 cm^{-1}, while the bands at 1380, 780 and 510 cm^{-1} almost disappeared. Hence, it can be attributed to a complex with the NO_2 group in the coordination sphere [27, 28]. Similar transformations connected with the catalytic abilities of the nitrosyl complexes have been described for other complexes [29, 30]. Our work in this area is in progress.

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