

Thiocyanatodioxomolybdenum(VI) complexes as efficient oxidizing agents

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Abstract

The reaction of $[(\text{SCN})_4\text{Mo}^{\text{VI}}\text{O}_2][\text{PPh}_4]_2$ with bipyridine leads to neutralization of the complex by loss of two moles of $[\text{SCN}][\text{PPh}_4]$ and complexation of bipyridine, but was immediately followed by oxo-ligand redistribution resulting in the formation of oligomeric products. The use of 4,4'-di-*t*-butyl-2,2'-bipyridine slows down significantly this redistribution reaction and allows the isolation of the desired complex dioxodithiocyanato-4,4'-di-*t*-butyl-2,2'-bipyridylmolybdenum(VI) (**6**). Compound (**6**) crystallizes in the orthorhombic group PNMA (#32) with $a = 15.793(2)$ Å, $b = 13.914(2)$ Å, $c = 10.658(3)$ Å. Full-matrix least-squares refinement converged at $R = 4.8\%$ and $R_w = 5.5\%$. The reactivity of (**6**) was studied as an oxygen atom transfer agent towards phosphines, alcohols and arylalkanes under stoichiometric and catalytic conditions, using DMSO as the oxo-donor reactant.

1. Introduction

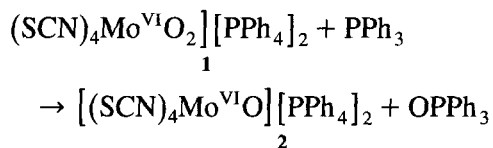
In the important field of transition metal–oxo chemistry, molybdenum is of particular interest since it is found in a wide range of catalytic systems going from molybdoenzymes to solid state reactions on metal oxides [1–3]. Although different roles can be attributed to this function [4–7], molybdenum–oxo complexes have been widely studied in oxygen atom transfer processes, especially as models of hydroxylases or oxotransferases [1,3]. In the great majority of these systems the molybdenum–oxo species

bore electron donating sulfur ligands; it was, thus, somewhat unexpected when a molybdenum dioxo anion bearing electron attracting cyano groups was found to be also capable of transferring an oxo group to a phosphine substrate. This was rationalized in terms of a ‘proximity effect’ by a neighboring second molecule of molybdenum dioxo playing the role of an electron donating entity [8].

An additional way to increase this oxygen atom transfer capability was thought, a priori, to replace cyano groups by sulfur bearing thiocyanato groups [1,3]. The thiocyanatodioxomolybdate(VI) anion was synthesized and characterized; but it exhibited N-bound thiocyanate groups. Despite its anionic character and the absence of any S-bound ligand this complex was found to be, nevertheless, an oxo transfer

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agent superior to any other known molybdenum–oxo complex [9].



A further way to improve the oxidizing power of this anion would be, a priori, to render it neutral, since this has been shown to the case for similar anions [10]. The work presented here concerns this aspect.

2. Experimental section

2.1. General materials and procedures

All materials were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use by repeated evacuation followed by admission of dry, oxygen free, nitrogen or argon. Tetraphenylphosphonium tetrathiocyanatodioxomolybdate(VI) (1) [11] and dithiocyanatodioxo-4,4'-di-*t*-butyl-2,2' bipyridyl molybdenum(VI) (6) [12] were prepared as reported. Triphenylphosphine was recrystallized prior to use and checked by ^{31}P NMR for purity. All oxidation products were compared with authentic samples. Kinetic measurements were done spectrophotometrically under conditions given in Table 4. NMR spectra were recorded on a Bruker WH 200 and a Bruker AMX 400 spectrometer. IR spectra were recorded on a Perkin-Elmer 1720 XFT spectrometer. UV spectra were recorded on an UV spectrophotometer HP 8542A diode array spectrometer with 89531A operating software and a Varian Lambda 12 spectrophotometer equipped with a thermostated cell compartment.

2.2. Crystal structure determination

A yellow thin plate crystal having approximate dimensions of $0.40 \times 0.30 \times 0.10$ mm was

mounted on a glass fiber with its long axis roughly parallel to the phi axis of the goniometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10 < q < 14$, measured by the computer controlled diagonal slit method of centering. The orthorhombic cell parameters and calculated volume are: $a = 15.793(1)$ Å $b = 13.914(2)$ Å, $c = 10.658(3)$ Å, $V = 2342.0(1)$ Å³. For $Z = 4$ AND F.W. = 474.48, the calculated density is 1.35 g/cm³. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.35 with a take-off angle of 3.0, indicating moderate crystal quality. From the systematic absences of $hk0$ $h = 2n$, $0kl$ $k + l = 2n$ and from subsequent least-squares refinement, the space group was determined to be PNMA.

The data were collected at a temperature of 23°C using the $w - 2q$ scan technique. The scan rate varied from 1 to 4/min (in omega). Data were collected to a maximum $2q$ of 48.0°. The scan range (in deg) was determined as a function of q to correct for the separation of the Ka doublet [13]; the scan width was calculated as follows: w scan width = $1.0 + 0.350 \tan q$. Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of q . The horizontal aperture width ranged from 2.7 to 2.9 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 16.7.

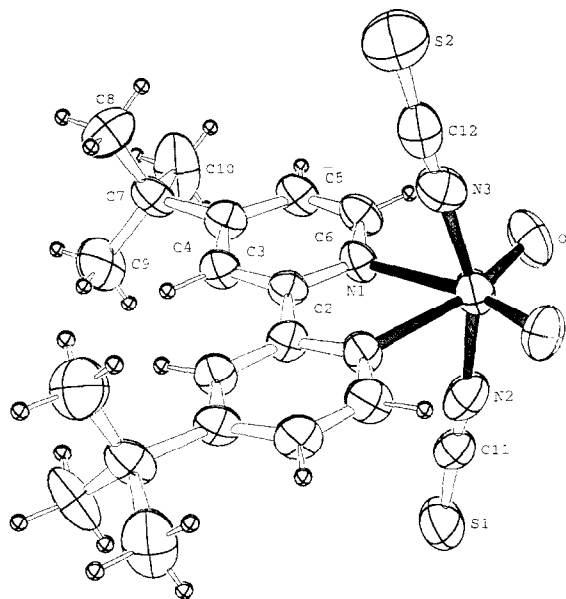
A total of 3152 reflections were collected, of which 1059 were unique and not systematically absent. As a check on crystal and electronic stability 2 representative reflections were measured every 120 min. The intensities of these

standards remained constant within experimental error throughout data collection. No decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.3 cm^{-1} for Mo K α radiation. No absorption correction was made. A secondary extinction correction was applied

[14]. Intensities of equivalent reflections were averaged. 89 reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 1916 observed and accepted reflections was 7.4%, based on intensity and 5.0% based on F_o .

Table 1
Experimental details of the crystal structure determination

A. Crystal data	
Empirical formula	$\text{C}_{18}\text{H}_{24}\text{MoN}_3\text{O}_2\text{S}_2$
F.W.	474.48 ($F(000) = 972$)
Crystal dimensions	$0.40 \times 0.30 \times 0.10 \text{ mm}^3$
Crystal color, habit	yellow, thin plate
Lattice type	primitive
No. of reflections used for unit cell determination (2θ range)	25 ($20\text{--}28^\circ$)
Omega scan peak width at half-height	0.35
Lattice parameters	$a = 15.793(1) \text{ \AA}$ $b = 13.914(2) \text{ \AA}$ $c = 10.658(3) \text{ \AA}$ $V = 2342.0 \text{ \AA}^3$ PNMA (#32)
Space group	
Z	4
D_{calc}	1.35 g/cm^3
$F(000)$	972
$\mu(\text{Mo K } \alpha)$	7.3 cm^{-1}
B. Intensity measurements	
Instrument	Enraf-Nonius CAD4 diffractometer
Radiation	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
Monochromator	graphite crystal, incident beam
Attenuator	Zr foil, factor 16.7
Take-off angle	3.0
Scan type	$\omega - 2\theta$
Scan rate	$1\text{--}4^\circ/\text{min}$ (in omega)
Scan width deg	$1.0 + 0.350 \tan \theta$
Maximum 2θ	48.0°
No. of refl. measured	3152 total, 1059 unique ($R_{\text{int}} = 0.074$)
Corrections	Lorentz polarization
C. Structure solution and refinement	
Anomalous dispersion	all non-hydrogen atoms
Reflections included	992 with $F_o^2 > 2.0\sigma(F_o^2)$
Parameters refined	83
Unweighted agreement factor	0.048
Weighted agreement factor	0.055
Factor including unobs. data	0.051
Esd of obs. of unit weight	0.99
Convergence, largest shift	0.04
High peak in final diff. map	$0.87(9) \text{ e/\AA}^3$
Low peak in final diff. map	$-.33(0) \text{ e/\AA}^3$
Computer hardware	VAX
Computer software	SDP/VAX (Enraf-Nonius & B.#A.#, Frenz & Associates, Inc.)

Fig. 1. ORTEP view of **6** showing the atom-labeling scheme.

coordinates for atoms of **6** are given in Table 2 and selected bond distances and angles are given in Table 3.

Table 2
Positional parameters and their estimated standard deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²) ^a
Mo	0.38275(6)	0.250	0.0318(1)	3.94(2)
S2	0.2222(2)	0.250	0.4111(4)	6.19(9)
S1	0.6265(2)	0.250	-0.2339(5)	7.5(1)
O	0.3377(3)	0.3477(4)	-0.0373(6)	5.7(1)
N3	0.3076(5)	0.250	0.192(1)	4.9(2)
N2	0.4877(6)	0.250	-0.081(1)	4.9(2)
N1	0.4670(3)	0.3432(3)	0.1573(6)	3.2(1)
C12	0.2732(6)	0.250	0.283(1)	3.8(2)
C11	0.5460(7)	0.250	-0.141(1)	4.5(3)
C2	0.5214(3)	0.3038(4)	0.2381(6)	3.0(1)
C3	0.5746(4)	0.3575(4)	0.3111(7)	3.3(1)
C4	0.5742(4)	0.4586(4)	0.3017(7)	3.3(1)
C5	0.5174(4)	0.4963(4)	0.2191(7)	3.7(2)
C6	0.4661(4)	0.4404(4)	0.1490(7)	3.8(2)
C7	0.6364(4)	0.5182(4)	0.3785(7)	3.8(2)
C9	0.6417(5)	0.4835(6)	0.5119(9)	6.2(2)
C8	0.7218(4)	0.5145(6)	0.319(1)	6.1(2)
C10	0.6064(5)	0.6243(5)	0.383(1)	7.6(2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(4/3)[a^2 b_{11} + b^2 b_{22} + c^2 b_{33} + ab(\cos \gamma)b_{12} + ac(\cos \beta)b_{13} + bc(\cos \alpha)b_{23}]$.

3.2. Oxidation of various substrates with **6**

3.2.1. Phosphines

It has been shown that the tetrathiocyanatodioxomolybdate(VI) anion (**1**) is about 2.5 times more efficient as an oxo transfer agent towards phosphines than the diethyldithiocarbamate molybdenum(VI) complex despite its anionic character and the fact that no Mo–S bonds were present [9]. Reducing its anionic character to give **6** was thus expected, a priori, to improve its oxidizing power even more. The reaction was followed spectroscopically and found to be faster by a factor greater than 10 [12]. The *k* values are given in Table 4.

As in the case of **1**, the reaction becomes catalytic in the presence of DMSO. Although the exact reason for this high oxidizing power is not clear, the mechanism can be expected to be a nucleophilic attack by the phosphine onto the molybdenum oxo group followed by the reduction of the metal and loss of phosphine oxide [21]. Similarly, the oxidation of the reduced

Table 3
Selected bond distances (Å) and angles (deg) for **6**^a

Mo–O	1.702(5)	N1–C6	1.354(7)
Mo–N3	2.07(1)	C2–C3	1.367(8)
Mo–N2	2.047(9)	C3–C4	1.410(8)
Mo–N1	2.290(5)	C4–C5	1.36(1)
S2–C12	1.58(1)	C4–C7	1.524(9)
S1–C11	1.61(1)	C5–C6	1.349(9)
N3–C12	1.12(2)	C7–C9	1.50(1)
N2–C11	1.12(1)	C7–C8	1.49(1)
N1–C2	1.335(8)	C7–C10	1.551(9)
O–Mo–N3	96.7(2)	C3–C4–C5	115.6(6)
O–Mo–N2	94.9(2)	C3–C4–C7	120.1(6)
O–Mo–N1	92.5(2)	C5–C4–C7	124.2(5)
N3–Mo–N2	160.8(4)	C4–C5–C6	122.1(6)
N3–Mo–N1	81.6(2)	N1–C6–C5	122.2(6)
N2–Mo–N1	82.6(3)	C4–C7–C9	111.7(5)
C2–N1–C6	117.3(5)	C4–C7–C8	109.6(6)
S2–C12–N3	179(1)	C4–C7–C10	109.8(6)
S1–C11–N2	177.1(1)	C9–C7–C8	109.9(6)
N1–C2–C3	122.6(5)	C9–C7–C10	107.0(7)
C2–C3–C4	120.1(6)	C8–C7–C10	108.9(6)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4
Kinetic data for the oxygen transfer reaction between $\text{Mo}^{\text{VI}}(\text{O})_2\text{L}$ complexes and PPh_3

L	$k \times 10^2 \text{ (s}^{-1} \text{ M}^{-1}\text{)}$	Reference
$(\text{NCS})_2(4,4'\text{-}t\text{-but-}2,2'\text{-bipy})$ (6)	220 ^a	[30]
$(\text{NCS})_4$ (1)	17 ^a	[30]
$(\text{S}_2\text{CNEt}_2)$	7.3 ^b	[31]

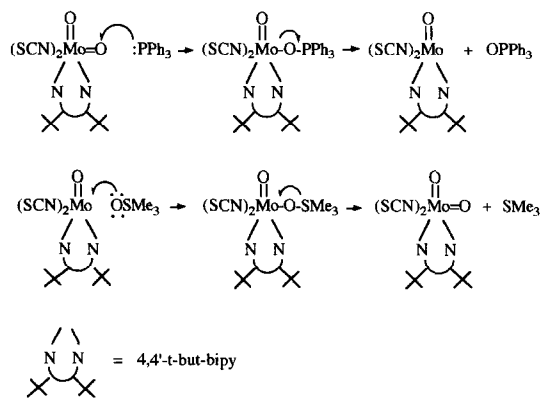
^a At 24°C in CH_2Cl_2 at pseudo first order conditions with PPh_3 ($\text{Mo}/\text{PPh}_3 = 1:100$). $[\text{PPh}_3] = 1.25 \times 10^{-2} \text{ M}$.

^b The values of k were measured at 23°C in dichloroethane.

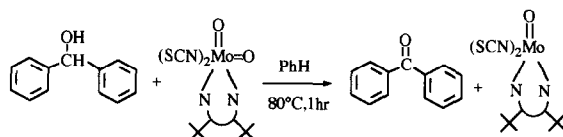
molybdenum species by DMSO can be pictured as a nucleophilic attack by the sulfoxide, transfer of the oxygen atom and loss of the sulfide **[3]** (Scheme 2).

3.2.2. Alcohols

The oxidation of alcohols into carbonyl compounds with metal–oxo complexes is a well known reaction specially with Cr(VI), Mn(VII), Ru(IV) and V(V) species [22–28]. Molybdenum–oxo compounds, on the other hand, believed to be much milder oxidants, have not been studied as oxidants for alcohols. Very recently, however, Osborn et al. reported such an oxidation in DMSO in the presence of $\text{MoO}_2(\text{acac})_2$ giving good yields of carbonyl compounds [29]. Among other molybdenum–oxo complexes it has also been shown [30,31] that the thiocyanatodioxomolybdate(VI) anion (**1**) was superior as an oxo transfer agent.



In our pursuit to investigate the reactivity of the neutral thiocyanatodioxo molybdenum(VI) complex (**6**), we tested it towards primary and secondary alcohols and found it to be an even more efficient oxidizing agent. In a typical experiment diphenyl carbinol is nearly quantitatively oxidized into benzophenone, in benzene, at 80°C in an hour.



The results obtained with other substrates are given in Table 5 and show that the rate of oxidation for secondary alcohols is slightly higher than for primary alcohols and that aliphatic alcohols are more difficult to oxidize. The formation of water during this reaction is certainly a hampering factor since when the rate of alcohol oxidation is low the rate of hydrolysis of the remaining dioxo complex becomes competitive and inhibits its activity. The use of molecular sieves lowers somewhat this effect, this was observed, for example, in the case of cyclohexanol.

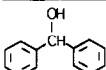
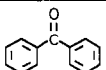
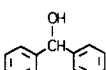
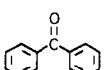
















As in the case of phosphine oxidation, this reaction becomes catalytic in the presence of DMSO. The results are given in Table 5.

3.2.3. Arylalkanes

Metal–oxo compounds are known to hydroxylate alkanes [1–4]. This property is well established in numerous enzymatic systems but also in many synthetic complexes. The metals of choice have been manganese and iron [1] when modelling enzymes whereas chromium [32], rhenium [33], ruthenium [34–36] and polytungstates [37] have been widely used as catalysts. Molybdenum–oxo species, on the other hand, had never been considered as potential agents for the oxidation of alkanes. It is the exceptional oxidizing character of **6** which prompted us to test this property towards arylalkanes [20].

When neat tetraline is treated with **6** at 80°C for 3 h the formation of a significant amount of α -tetralol and α -tetralone was observed. This constituted the very first example of an alkane functionalization with a molybdenum–oxo compound. This oxidation was further improved by performing the reaction under UV irradiation at room temperature yielding quantitatively α -tetralone, most probably through the formation of α -tetralol. In order to obtain the same result thermally the temperature was raised to 100°C

Table 5
Oxidation of alcohols with **6**

Alcohol	Conditions	Solvent	Oxidant	Product	Yield ^a
	80° / 1hr	PhH ^b	None		94
	80° / 1hr	PhH ^b	DMSO ^c		620
	80° / 1hr	PhH ^b	None		83
	80° / 1hr	PhH ^b	DMSO ^c		540
	80° / 1hr	Neat ^d	None		94
	80° / 1hr	Neat ^d	DMSO ^c		790
	80° / 1hr	Neat ^d	None		95
	80° / 1hr	Neat ^d	DMSO ^c		190
	80° / 3hrs	Neat ^d	None		50
	80° / 3hrs	Neat ^d	None		60 ^e

^a Based on **6** by GC analysis with an internal standard.

















^b Benzene solution (2 mL) containing 0.34 mmol of alcohol and 0.02 mmol of **6**.

^c 100 μ l (1.4 mmol).

^d Alcohol (2 mL) and 0.02 mmol of **6**.

^e Accompanied by dehydration.

Table 6
Oxidation of Arylalkanes with **6**

Alkane	Conditions ^a	Oxidant	Product	Yield ^b
	<i>h</i> ν , 25°C	None		50
	Dark, 100°C	None		50
	<i>h</i> ν , 25°C	DMSO ^c		310
	<i>h</i> ν , 25°C	None		70
	Dark, 80°C	None		42
	<i>h</i> ν , 25°C	DMSO ^c		196
	<i>h</i> ν , 25°C	None		22 ^d
	<i>h</i> ν , 25°C	DMSO ^c		236

^a Alkane, neat (2 mL) with 20 mg (0.038 mmol) of **6**, reaction time, 6 h, UV (Hg lamp, λ = 500 nm).

^b Based on **6** by GC analysis with an internal standard.

^c 100 μ L (1.4 mmol).

^d Some minor amount of alcohol and dehydration products were also detected.

for six hours. The results obtained with other substrates are given in Table 6.

As in the case of phosphines and alcohols this oxidation can be catalytic in the presence of DMSO. The results are given in Table 6.

Although the mechanism of the oxygen atom transfer from molybdenum to arylalkanes is not totally determined, some preliminary indications were given when adamantane was treated with **6**. The oxygen transfer could possibly occur either via a free radical two steps one electron process or via a non radical one step two electrons process. When adamantane is treated with **6** in benzene, oxidation occurs at a much lower rate than arylalkanes to give, in % selectivity, 1-adamantanol (52), 2-adamantanol (26) and 2-adamantanone (22). This corresponds to a ratio of secondary to tertiary of \sim 3, which could be indicative of a non radical process [38]. How-

ever, when the reaction was performed in the presence of CBrCl_3 , 1-bromoadamantane was the only observed product, suggesting in this case that a free radical intermediate could also be involved. Furthermore, a mechanism involving water as in the case of ruthenium(IV) [34,35] must a priori be excluded since the reaction is done under anhydrous conditions.

4. Conclusions

The high activity of **6** as an oxygen atom transfer agent to phosphine and alcohols has been shown. Its reactivity towards alkanes constitutes, furthermore, the first reported example of a molybdenum–oxo complex able to functionalize a C–H bond.

A more detailed study is under way to, hopefully, give a better insight to this enhanced ability of $\text{Mo}=\text{O}$ species to transfer oxygen atoms which can now be compared to group 7 and 8 transition metal–oxo complexes.

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