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Synthesis and X-ray Characterization of Tetraphenylphosphonium Tetrathiocyanatodioxomolybdate(VI): A Remarkable Oxo Transfer Agent

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The tetraphenylphosphonium salt of the anion $[Mo^{VI}(O)_2(NCS)_4]$ is prepared from sodium molybdate and potassium thiocyanate in acidic medium, followed by cation exchange under phase transfer conditions. The crystalline compound belongs to the tetragonal space group $P4_12_12$, with $a = b = 12.802(3)$ Å and $c = 31.820(4)$ Å. The volume of the unit cell is 5215 Å^3 with $Z = 4$. The structure was refined to $R = 8.9\%$. The title compound is found to catalyze the oxygen transfer from dimethyl sulfoxide to triphenylphosphine approximately 20 times more efficiently than the known dioxobis(*N,N'*-diethyldithiocarbamato)molybdenum(VI) complex.

Introduction

In the important field of oxo transfer chemistry, numerous molybdenum complexes have been studied, especially as models for the active site of oxo transfer molybdoenzymes.[1] Most of them contain sterically demanding sulfur ligands since two of the criteria for relevant models are the sulfur environment and hindrance to irreversible μ-oxo dimer formation. The presence of sulfur ligands appears indeed to be essential for an efficient oxo transfer process when these are compared with their oxygen analogs and found to have a significantly higher reactivity.[2] A third consideration for these stoichiometric or catalytic oxo transfer systems is the ability of the ligand to liberate reversibly a coordination site for potential binding of the substrate. This aspect is usually more easily attained with neutral complexes; it is thus not unexpected that, apart from isopoly- or heteropolymolybdate species,[3] very few ionic compounds of molybdenum are known to exhibit oxo transfer properties.

An oxoperoxomolybdate(VI) anion was reported[4] by us and could be considered as one such example. The oxo transfer step, in the absence of any sulfur-containing ligand, was rationalized in terms of electron donation by a close-by second molybdenum dioxo molecule. However, the presence of a peroxo ligand as well as the formation of a molybdenum(V) μ-oxo dimer made the clean observation of the oxo transfer process difficult.

We report here the synthesis and characterization of another ionic compound: a tetrathiocyanatodioxomolybdate(VI) complex anion and its remarkable ability to act as an oxo transfer agent.

Experimental Section

General Materials and Procedures. All materials were commercial products and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use. Dioxobis(*N,N'*-diethyldithiocarbamato)molybdenum (VI) (**3**) was prepared by the method described by Moore and Larson[5] and was recrystallized from benzene/diethyl ether. Triphenylphosphine (Fluka) was recrystallized prior to use and checked by ^{31}P NMR for purity. NMR spectra were recorded on a Bruker WH-100 and a Bruker AMX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer 1720 X FT spectrometer. UV spectra were recorded on a HP8452A diode array spectrometer with a 89531A operating software.

Crystal Structure Determination. Crystal data for compound **2**, together with details of the X-ray diffraction experiment, are reported in Table 1. Cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $22° < 2\theta < 28°$. A unique $^1/_{16}$th of the sphere of reflection was collected with Laue group *4/mmm*. Three intense reflections were recorded throughout the data collection every 3600 s and showed no change of intensity. Lorentz and polarization corrections were applied to the raw data since the value of μ is 6.05; absorption corrections were not necessary. The positions of Mo and P atoms were determined by combining Patterson and Multan calculations.[6] The remaining non-hydrogen atoms were located in successive difference Fourier syntheses. Although anomalous dispersion effects were small, they were included in the structure factor calculations. Space group determination seemed ambiguous since least-squares refinements in the two enantiomeric tetragonal space groups $P4_12_12$ and $P4_32_12$ converged to mainly the same *R* factor (0.089 and 0.091, respectively; identical weighting scheme and variable to reflection ratio). The latter ($P4_32_12$) was, however, rejected (at a 99.5% confidence level) using an *R* factor ratio test.[7] Hydrogen atoms were included in the structure factor calculation at the idealized positions and were not refined. Scattering factors were taken from ref 8. In the final cycle of refinement, all non-hydrogen atoms were refined anisotropically except atoms of CH_2Cl_2. The relatively large quality of fit indicators can be attributed to the highly agitated solvent molecule (CH_2Cl_2) present in the crystal with thermal agitation coefficients as high as 15–21. All calculations were performed on a VAX 2000 computer using SDP software.[9] The final atomic coordinates for the anion of **2** are given in Table 2, and selected bond distances and angles, in Table 3.

Synthesis of $[PPh_4]_2[Mo(O)_2(NCS)_4]\cdot CH_2Cl_2$ (2). To a 50-mL aqueous solution of Na_2MoO_4 (3.09 g, 15 mmol) and KSCN (6.31 g, 65 mmol) was slowly added, with stirring, 60 mL of 1 N HCl. The deep yellow mixture was stirred for 1 h and then mixed with a 70-mL CH_2Cl_2 solution containing PPh_4Cl (12.0 g, 32 mmol). Vigorous mixing for 5 min resulted in an orange organic phase which was isolated, dried over anhydrous $MgSO_4$, concentrated to 40 mL, and allowed to stand overnight at −20 °C. The orange-red crystalline precipitate was filtered off and recrystallized from CH_2Cl_2 to give 9.5 g (60% yield) of **2** (mp 230–232 °C). IR:

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(1) Holm, R. H. *Chem. Rev.* **1987**, 1401 and references cited therein.

(2) Topich, J.; Lyon, J. T., III. *Inorg. Chem.* **1984**, *23*, 3202.

(3) Hill, G. L., Ed. *Activation and Functionalization of Alkanes*; John Wiley & Sons: New York, 1988, see also references cited therein.

(4) Arzoumanian, H.; Petrignani, J. F.; Pierrot, M.; Ridouane, F.; Sanchez, J. *Inorg. Chem.* **1988**, *27*, 3377.

(5) Moore, F. W.; Larson, M. L. *Inorg. Chem.* **1967**, *6*, 998.

(6) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. N. Multan 80: A System of Computer Programs for the Automatic Solution of the Crystal Structures from X-Ray Diffraction Data. Universities of York, England, and Louvain, Belgium, 1980.

(7) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(8) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(9) Frenz, B. A. In *Computing in Crystallography*; Shenk, H., Olthof-Hazelkamp, R., Von Konigsveld, H., Bassi, B. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

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Table 1. Crystallographic Data, Data Collection Parameters, and Refinement Results

formula	$[PPh_4]_2[Mo(O)_2(NCS)_4]\cdot CH_2Cl_2$
fw	1124
space group	tetragonal $P4_12_12^a$
$a = b$ (Å)	12.802(3)
c (Å)	31.820(4)
$\alpha = \beta = \gamma$ (deg)	90
V (Å^3), F_{000}	5215, 2296
d_{calc} (g cm^{-3})	1.43
Z	4
cryst habit	irregular without indices for faces
cryst size (mm^3)	0.2 × 0.2 × 0.3
μ(Mo Kα) (cm^{-1})	
graphite monochromator	6.054
μr	0.12–0.18
data collecn instrument	Enraf-Nonius CAD-4
radiation	Mo Kα (λ 0.710 69 Å)
no. of orientation reflcns; 2θ range (deg)	25; 22–28
temp (°C)	20
scan method	θ–2θ
2θ scan range (deg)	2–58; $h_{max} = 14$, $k_{max} = 14$, $l_{max} = 36$
no. of measd data	3670
no. of unique data, $2\sigma(F_o^2)$	2884, 2423
no. of observns	1885
no. of params refined	300
R	0.089
R_w	0.098
quality of fit indicator	5.053
largest shift/esd, final cycle	0.30
largest peak (e/Å^3)	0.975

[a] The other enantiomeric space group $P4_32_12$, with an $R = 0.091$, was rejected on the basis of the R factor ratio test.[7] Using the reported tables, $R_{exp} = 1.02 > R_{calc} = 1.0026$, making the space group $P4_32_12$ improbable at a 99.5% confidence level. We thank one of the reviewers for pointing this out.

Table 2. Positional Parameters and Their Estimated Standard Deviations for $[Mo(O)_2(NCS)_4]^{2-}$ (Anion of **2**)

atom	x	y	z	B^a (Å^2)
Mo	0.5879(1)	0.588	0.000	4.21(3)
S_1	0.8088(4)	0.2948(4)	0.0335(2)	6.7(1)
S_2	0.4201(5)	0.3437(5)	−0.1009(2)	6.4(1)
O_1	0.626(1)	0.664(1)	0.0406(4)	6.0(3)
N_1	0.683(1)	0.462(1)	0.0157(5)	5.5(4)
N_2	0.509(1)	0.477(1)	−0.0438(4)	5.2(4)
C_1	0.733(1)	0.393(1)	0.0248(5)	4.5(4)
C_2	0.474(1)	0.422(1)	−0.0667(5)	4.0(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $^4/_3[a^2b_{11} + b^2b_{22} + c^2b_{33} + ab(\cos\gamma)b_{12} + ac(\cos\beta)b_{13} + bc(\cos\alpha)b_{23}]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**[a]

Mo–O_1	1.69(1)	N_1–C_1	1.13(2)
Mo–N_1	2.08(1)	N_2–C_2	1.10(2)
Mo–N_2	2.23(1)	C_1–S_1	1.61(2)
C_2–S_2	1.63(2)		
O_1–Mo–O'_1	104.2(5)	N_1–Mo–N'_1	164.7(4)
O_1–Mo–N_1	95.4(6)	N_1–Mo–N'_2	82.8(3)
O_1–Mo–N_2	167.3(5)	N_1–C_1–S_1	175.0(2)
O_1–Mo–N'_2	88.4(6)	N_2–C_2–S_2	178.0(2)
Mo–N_1–C_1	179.0(1)		

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

ν(–NCS) = 2099 (s), 2054 (s), 483 (w) cm^{-1}; ν(Mo=O) = 920 (s), 885 (s) cm^{-1}; $\nu(CH_2Cl_2)$ = 1261 cm^{-1}. Anal. Calcd for $C_{54}H_{42}N_4O_2P_2S_4Cl_2Mo$: C, 56.64; H, 3.77; N, 4.98; O, 2.85; P, 5.51; S, 11.41; Cl, 6.31; Mo, 8.54. Found: C, 55.35; H, 3.59; N, 5.21; P, 5.66; S, 11.36; Cl, 6.36; Mo, 8.44. Compound **2** is soluble in CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$, $(CH_3)_2CO$, and CH_3CN and insoluble in $(C_2H_5)_2O$ and aliphatic hydrocarbons.

Oxidation of Triphenylphosphine in DMSO in the Presence of 2 or 3. Into an NMR tube were placed 28.1 mg (0.025 mmol) of **2** and 65.5 mg (0.25 mmol) of triphenylphosphine. To the solid mixture was added at room temperature 0.5 mL of deuterated DMSO containing 200 μL of $CDCl_3$. This constituted time zero for the kinetic measurements. The tube was vigorously shaken until the solution was homogeneous and then placed in the NMR probe. The first kinetic point was taken at t = 3 min. The reaction was followed by integrating the signals corresponding to triphenylphosphine and triphenylphosphine oxide. Exact by the same procedure was followed for **3**.

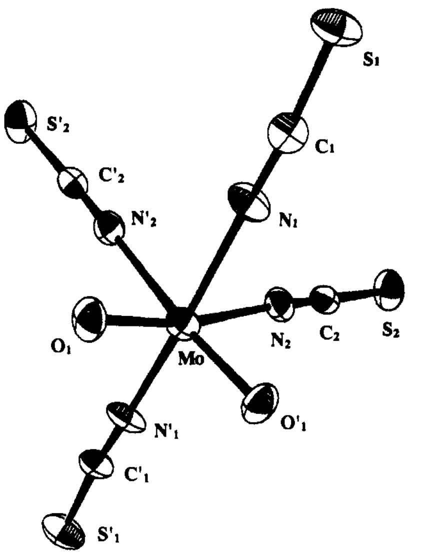

Figure 1. ORTEP view of **2** showing the atom-labeling scheme.

Results and Discussion

The thiocyanate function is ambidentate and can be bound to the metal through either the S or the N atom.[10] Although there is no strict rule, thiocyanates of heavier atoms are usually S-bound and constitute, a priori, a potentially efficient function for an oxo transfer process; however, the $[Mo^{III}(NCS)_6]^{3-}$ ion has been shown to be N-bound, and one might expect other molybdenum complexes to have analogous coordination modes.[11]

The tetrathiocyanatodixomolybdate(VI) anion has been reported[12] as an amorphous salt, but neither its S or N bond isomerism nor its oxo transfer properties were fully established. We undertook its synthesis as a tetraphenylphosphonium salt using a phase transfer catalysis technique and obtained a crystalline product in fairly good yield (60% of isolated crystals).

$$\begin{array}{l} Na_2MoO_4 + 4KSCN + 4HCl \rightarrow \\ \qquad\qquad Na_2[Mo(O)_2(NCS)_4] + 4KCl + 2H_2O \\ \qquad\qquad\qquad \mathbf{1} \\ [PPh_4]_2[Mo(O)_2(NCS)_4]\cdot CH_2Cl_2 \xleftarrow[H_2O/CH_2Cl_2]{PPh_4Cl} \\ \qquad\quad \mathbf{2} \end{array} \qquad (1)$$

The infrared spectrum of **2** exhibits two absorption bands at 920 and 885 cm^{-1} attributed to the oxo groups and three bands at 2099, 2054, and 483 cm^{-1} assigned to the thiocyanate ligand. The elemental analysis and the ^{1}H and ^{13}C NMR spectra indicated that 1 mol of solvated dichloromethane was present in the product. The nature of the thiocyanate bonding mode could be unambiguously established by an X-ray analysis. The experimental details for the analysis are given in the Table 1; the final atomic coordinates and selected bond distances and angles of the anion are presented respectively, in Tables 2 and 3.

The perspective drawing displayed in Figure 1 shows clearly

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[10] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; pp 324, 837.

[11] Bridson, B. J.; Edwards, D. A. *Inorg. Nucl. Chem Lett.* **1974**, *10*, 301.

[12] (a) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917. (b) Berg, J.M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925.

the thiocyanate ligands to be N-bound, in a somewhat distorted octahedra with *cis* dioxo atoms. The deviation from the ideal octahedral geometry is significant, for example, from an expansion from 90 to 104.2° for O_1–Mo–O'_1 to a contraction from 90 to 79.2° for N_2–Mo–N'_2. The molybdenum atom and the two oxo groups are coplanar with atoms N_2 and N'_2 within 0.001 Å, whereas the molybdenum atom is 0.203 Å (±0.001 Å) out of the plane $N'_1N_2O_1N_1$. This , together with the difference in bond length between Mo–N_1 or Mo–N'_1 (*cis* to the oxo) and Mo–N_2 or Mo–N'_2 (*trans* to the oxo), relates the structure to a trapezoidal based (O_1, O'_1, N_2, N'_2) bipyramid. The Mo–O distance (1.693 Å) is well within the range of those for other Mo(VI) dioxo compounds, and the four thiocyanate groups are nearly linear as expected.

This structurally well-defined and relatively simple molybdenum dioxo compound did not have all the criteria for a good model of molybdoenzymes,[12] but it was of interest to compare its oxo transfer properties with those of better known complexes such as dioxobis(*N*,*N'*-diethyldithiocarbamato)molybdenum(VI) (3).[13]

The anionic character and the absence of any sulfur-bound ligand in **2** were, a priori, hampering factors for an oxo transfer process although it was recently shown that polydentate nitrogen ligands can also induce such a transfer.[14] When **2** was reacted with triphenylphosphine in dimethyl sulfoxide, a fast reaction was observed transforming the substrate into the corresponding oxide in a catalytic manner[15]

$$PPh_3 + (CH_3)_2SO \xrightarrow{[PPh_4]_2[Mo(O)_2(NCS)_4]\cdot CH_2Cl_2} OPPh_3 + (CH_3)_2S \quad (2)$$

The same reaction was performed stoichiometrically in CH_2Cl_2, in the absence of DMSO, yielding cleanly 1 mol of triphenylphosphine oxide/mol of **2**.

$$PPh_3 + \underset{\mathbf{2}}{[PPh_4]_2[Mo^{VI}(O)_2(NCS)_4]} \xrightarrow{CH_2Cl_2} OPPh_3 + \underset{\mathbf{4}}{[PPh_4]_2[Mo^{IV}O(NCS)_4]} \quad (3)$$

Throughout the reaction, the color changed only slightly from yellow-brown to yellow-red; this is contrary to the case of (diethyldithiocarbamato)dioxomolybdenum (3), which immediately turns purple (Mo^V), indicating that the oxo transfer process with **2** does not involve a Mo^V μ-oxo intermediate.[16] At the end of the reaction a reddish solid, exhibiting a single IR absorption band at 956 cm^{-1} (attributed to an oxo group) and a UV band at 465 nm, was isolated and presumed to be **4**. This indicated clearly the absence of any comproportionation to a Mo^V species in the process and was supported by mixing, in CH_2Cl_2, under argon, equimolar amounts of **2** and **4** without any observable change over a period of days.

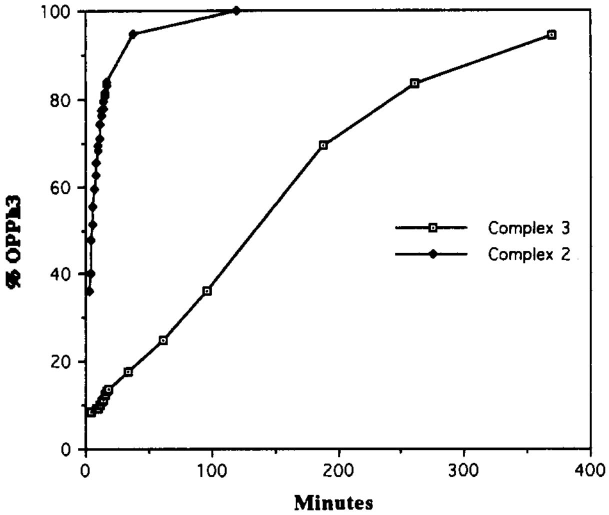

Figure 2. Plot of percent of triphenylphosphine oxide formed against time for **2** or **3** (0.025 mmol) and triphenylphosphine (0.25 mmol) in 0.5 mL of DMSO-d_6 at 25 °C.

The relatively fast stoichiometric oxo transfer reaction with **2** prompted us to compare, under identical experimental conditions, the oxidation of PPh_3 by DMSO as catalyzed by **2** and **3**. This was followed by the disappearance of PPh_3 and appearance of $OPPh_3$ by ^{31}P NMR (Figure 2) and indicated ***2** to be approximately 20 times more effective than **3**.*

Supplementary Material Available: Tables of full thermal and positional data and further distances and angles for **2** (10 pages). Ordering information is given on any current masthead page.

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[13] Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057.

[14] Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E.; Yamanouchi, K.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 3650.

[15] Compound **2** was reisolated at the end of the reaction, establishing the catalytic character of reaction 2.

[16] The potassium salt of (μ-oxo)bis[oxotetraisocyanatomolybdate(V)] tetrahydrate has been reported as dark purple crystals.[17]

[17] Bino, A.; Cohen, S.; Tsimering, L. *Inorg. Chim. Acta* **1983**, *77*, L79.