82090-98-0; Ni(4-MeBPI)$_2$, 78065-33-5; Ni(5-MeBPI)$_2$, 87802-48-0; Ni(4-*t*-BuBPI)$_2$, 87802-49-1; Fe(BPI)$_2$, 79062-05-8; Fe(3-MeBPI)$_2$, 79062-04-7; Fe(4-MeBPI)$_2$, 78065-31-3; Fe(5-MeBPI)$_2$, 87802-50-4; Fe(4-*t*-BuBPI)$_2$, 87802-51-5; Mn(3-MeBPI)$_2$·$^1/_2$CH$_2$Cl$_2$, 87802-52-6; Zn(BPI)$_2$, 87802-53-7; 4-*tert*-butylphthalic acid, 14236-13-6; 4-tert-butylphthalonitrile, 32703-80-3; 2-aminopyridine-d_4, 87802-54-8; phthalonitrile-d_4, 69299-71-4.

Supplementary Material Available: Details of the crystal structure analysis, space group, and unit cell data, listings of positional and thermal parameters and selected individual bond distances, angles, torsional angles, and least-squares planes, additional perspective and stereoscopic views of the molecules, and a table of structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

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^{95}Mo NMR Studies of Dioxo, Oxo–Sulfido, Oxo–Selenido, and Disulfido Complexes of Molybdenum(VI)

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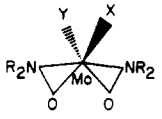
The ^{95}Mo NMR spectra of a number of Mo(VI) complexes with the general formula MoXY[ONHR]$_2$ and MoXY[ONR$_2$]$_2$ (X = O, S, Se; Y = O, S; R = CH$_3$, C$_2$H$_5$, C(CH$_3$)$_3$, CH$_2$C$_6$H$_5$; R$_2$ = C$_5$H$_{10}$) have been measured. Change of the terminal groups from oxygen to sulfur to selenium causes deshielding of the molybdenum nucleus in the order O < S < Se. A narrowing of the line width accompanies this deshielding. Bulky R groups also seem to have some deshielding effect. The quantitative conversion of the dioxo (MoO$_2$) complexes to the corresponding monooxo–monosulfido (MoOS) and disulfido (MoS$_2$) complexes by reaction with [(CH$_3$)$_3$Si]$_2$S was followed by ^{95}Mo NMR. Under similar conditions MoOSe[ONR$_2$]$_2$ was converted to MoOS[ONR$_2$]$_2$, MoS$_2$[ONR$_2$]$_2$, and several other species.

Introduction

Recently we have shown that low-symmetry, six-coordinate Mo(VI) complexes containing the $[MoO_2]^{2+}$ unit can be conveniently studied by ^{95}Mo NMR.[1,2] Another important group of $[MoO_2]^{2+}$ complexes are the Mo(VI) complexes of structure **1** that result from the reaction of substituted hydroxylamines with molybdate.[3] Our special interest in these complexes stems from the fact that their terminal oxo groups can be replaced by terminal sulfido and terminal selenido groups. Such complexes are relevant to understanding the molybdenum site of the oxidized form of xanthine oxidase. The molybdenum center of the active form of this enzyme is believed to contain a Mo(VI) atom with one terminal oxo and one terminal sulfido group (MoOS), whereas the inactive, cyanolyzed form of the enzyme is postulated to have two terminal oxo groups (MoO$_2$).[4] A ^{95}Mo NMR study of complexes of type **1** in which the terminal oxo groups can be replaced by sulfido groups is therefore an important prerequisite to future ^{95}Mo NMR studies of molybdenum in enzymes and their cofactors.[5] The ^{95}Mo NMR spectra for several type **1** complexes appeared while this work was in progress.[6] Here we present results for additional examples and show that the formation and the interconversions of the terminal O, S, and Se groups in type **1** complexes can be followed by ^{95}Mo NMR.



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Experimental Section

The complexes were synthesized as previously described.[3] The ^{95}Mo NMR data were obtained on a Bruker WM250 NMR spectrometer. A 10-mm molybdenum probe (16.3 MHz) was used. A delay of 200 μs prior to acquisition was used to reduce the effects of probe ringing.

Table I. ^{95}Mo NMR Data

compd	chem shift,[a] ppm	line width, Hz
MoO$_2$[ONH(CH$_3$)]$_2$	−219	200
MoO$_2$[ONH(C(CH$_3$)$_3$)]$_2$	−218	150
MoO$_2$[ON(CH$_3$)$_2$]$_2$	−165	120
MoO$_2$[ON(C$_2$H$_5$)$_2$]$_2$	−169	160
MoOS[ON(C$_2$H$_5$)$_2$]$_2$	+544	140
MoOSe[ON(C$_2$H$_5$)$_2$]$_2$	+865	120
MoS$_2$[ON(C$_2$H$_5$)$_2$]$_2$	+1234	100
MoO$_2$[ONC$_5$H$_{10}$]$_2$	−184	160
MoOS[ONC$_5$H$_{10}$]$_2$	+531	100
MoOSe[ONC$_5$H$_{10}$]$_2$	+855	70
MoS$_2$[ONC$_5$H$_{10}$]$_2$	+1219	70
MoO$_2$[ON(CH$_2$C$_6$H$_5$)$_2$]$_2$	−161	260

[a] Measured at room temperature in DMF, concentration 0.4 M; if less soluble, saturated; chemical shifts relative to 2 M Na$_2$MoO$_4$ in H$_2$O at pH 11. The estimated uncertainty of the chemical shifts is ±1 ppm.

A 2 M Na$_2$MoO$_4$ solution at pH 11 served as external standard. All solvents were dried prior to use. In the case of the oxo–selenido complexes the NMR spectra were measured in sealed 10-mm NMR tubes under nitrogen; in the other cases regular 10-mm NMR tubes were used.

In Situ Thiolation Reactions. MoO$_2$[ON(C$_2$H$_5$)$_2$]$_2$ (1.5 m Mol) was dissolved in 2.5 mL of dry DMF under nitrogen in a 10-mm sealed screw top NMR tube (Wilmad) and the ^{95}Mo NMR spectrum measured. An equimolar amount of [(CH$_3$)$_3$Si]$_2$S (Fluka Chemical

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Corp.) was added with a gastight syringe. (*Caution*: $[(CH_3)_3Si]_2S$ has a terrible stench: All manipulations must be carried out in an efficient hood. The NMR tubes must be tightly sealed before transfer to the NMR spectrometer.) The reaction was followed for 4 h by ^{95}Mo NMR after which a second equivalent of $[(CH_3)_3Si]_2S$ was added. The reaction was then checked periodically for 17 h and again after 1 week. A similar procedure was followed for $MoOSe[ONC_5H_{10}]_2$ except that the final solution resulted from a fourfold excess of the thiolating reagent. The identities of the products were inferred by comparison to the ^{95}Mo NMR spectra of known pure compounds.

Results and Discussion

These $MoXY[ONHR]_2$ and $MoXY[ONR_2]_2$ complexes (X = O, S, Se; Y = O, S; R = CH_3, C_2H_5, $C(CH_3)_3$, $CH_2C_6H_5$, R_2 = C_5H_{10}) are the only known six-coordinate Mo(VI) complexes where the terminal oxo groups can be replaced by terminal sulfido and selenido groups. Their geometry (**1**) is best described as a skew trapezoid bipyramid.[3]

The ^{95}Mo NMR signals of the dioxo species of these complexes occur around −200 ppm (Table I). As the R groups become bulkier, some deshielding of the ^{95}Mo NMR center is observed. The chemical shifts of these complexes are more negative than those of the pseudooctahedral Mo(VI) complexes with nitrogen and oxygen ligands.[1,6] When one terminal oxo group is replaced by a sulfido group, a deshielding of the Mo center of about 700 ppm is observed. The magnitude of this deshielding is somewhat larger than that observed in tetrahedral MoX_4^{2-} complexes (X = O or S)[7] when O is replaced by S. Replacement of the terminal oxygen by selenium causes deshielding of the molybdenum nucleus of over 1000 ppm, i.e. selenium causes more deshielding than sulfur as occurs for the tetrahedral MoX_4^{2-} complexes.[8] The ^{95}Mo NMR signals for the disulfido complexes occur around 1200 ppm, about another 700 ppm downfield from the monooxo–monosulfido complexes. The line widths decrease with the deshielding of the molybdenum center. The deshielding is accompanied by a bathochromic shift of the lowest energy electronic transition in the UV–Vis spectra (OS 413 nm, OSe 457 nm; SS 514 nm, for R_2 = C_5H_{10}[3]). While this study was in progress we received a preprint from Dr. A. Wedd, who independently studied several complexes of the same type.[6] The results for compounds common to both studies are in good agreement.

The large chemical shift differences among the type **1** complexes containing the MoO_2, MoOS, and MoS_2 groups prompted us to use ^{95}Mo NMR to investigate the reaction of $MoO_2[ONR_2]_2$ complexes with a thiolating reagent in aprotic media. Hexamethyldisilathiane, $[(CH_3)_3Si]_2S$, was added to $MoO_2[ON(C_2H_5)_2]_2$ in a 1:1 ratio in DMF at room temperature. After about 2 h the corresponding MoOS species appeared in the ^{95}Mo NMR spectrum, and the intensity of the MoO_2 peak decreased. When the ratio of hexamethyldisilathiane was increased to 2:1, the MoS_2 species began to appear. After 1 week no dioxo complex was left and the ratio of MoOS:MoS_2 was about 3:1.

The clean conversion of $MoO_2[ON(C_2H_5)_2]_2$ to the corresponding MoOS and MoS_2 complexes by $[(CH_3)_3Si]_2S$ led us to examine the reaction of $MoOSe[ONC_5H_{10}]_2$ with this reagent. Addition of an equimolar amount of hexamethyldisilathiane to the MoOSe complex resulted in formation of the MoOS complex after about 45 min. Increasing the ratio of disilthiane to complex to 4:1 produced the corresponding MoS_2 complex, two unidentified species at 1804 ppm and at 1840 ppm, and finally MoS_4^{2-}. After 7 h no MoOSe starting complex remained.

The facile thiolation reactions of the type **1** complexes in aprotic media raised the question as to whether these complexes exchange terminal O and S groups in the absence of thiolating reagents. No comproportionation to the MoOS complex was observed after 2 days when the MoO_2 and MoS_2 complexes were both present in the same solution at room temperature.

This work shows that six-coordinate MoO_2L_4, $MoOSL_4$, $MoOSeL_4$, and MoS_2L_4 complexes can be easily distinguished by ^{95}Mo NMR. In addition, ^{95}Mo NMR can be used to directly follow the formation and the interconversion of these complexes. The results also provide encouragement that ^{95}Mo NMR should be able to distinguish between the postulated six-coordinate Mo(VI) sites of the active (MoOS) and the inactive (MoO_2) forms of xanthine oxidase (or its cofactor) provided that the line widths are sufficiently narrow.

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Registry No. $MoO_2[ONH(CH_3)]_2$, 70631-31-1; $MoO_2[ONH(C(CH_3)_3)]_2$, 75701-12-1; $MoO_2[ON(CH_3)_2]_2$, 74081-85-9; $MoO_2[ON(C_2H_5)_2]_2$, 74081-86-0; $MoOS[ON(C_2H_5)_2]_2$, 76900-51-1; $MoOSe[ON(C_2H_5)_2]_2$, 84133-90-4; $MoS_2[ON(C_2H_5)_2]_2$, 76900-53-3; $MoO_2[ONC_5H_{10}]_2$, 84120-41-2; $MoOS[ONC_5H_{10}]_2$, 84133-89-1; $MoOSe[ONC_5H_{10}]_2$, 84133-41-5; $MoS_2[ONC_5H_{10}]_2$, 84146-55-4; $MoO_2[ON(CH_2C_6H_5)_2]_2$, 74081-87-1; ^{95}Mo, 14392-17-7.

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