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LETTER

Halido–Thiolate Complexes of Mo(III), Mo(IV) and Mo(V): Synthesis, Characterization and Crystal and Molecular Structures of $[MoCl_4\{SC_5H_2NH\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}_2]$, $(Ph_4P)[MoBr_4(SC_5H_3NH\text{-}3\text{-}SiMe_3)_2]$, $[MoBr_3(SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]$ and $(Ph_4P)[MoOBr_3(SC_5H_3N\text{-}3\text{-}SiMe_3)]$

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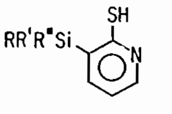
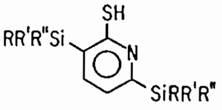
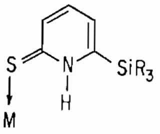
The coordination chemistry of mononuclear molybdenum thiolate complexes is relevant to the reduction of molecular nitrogen by nitrogenase, a metalloenzyme containing a sulfur and possibly nitrogen-ligated molybdenum center which is essential to N_2 fixation activity [1, 2]. Although molybdenum thiolate complexes capable of incorporating an inhibitor or substrate for nitrogenase (CO, RNC, acetylene, hydrazine) are of interest in this regard, comparatively few examples of complexes of the general class $[Mo(SR)_nX]$, where X is a substrate-type molecule, have been characterized [3–5]. By using a novel class of 2-pyridinethiols with bulky substituents [6], the monosilylated (**Ia**) and the disilylated (**IIb**) compounds, designated (HSNSi) and ($HSNSi_2$), respectively, we have isolated a number of mixed halido–thiol complexes of Mo(III), Mo(IV) and Mo(V): $(Ph_4P)[MoBr_4(SNHSi)_2]$ (**III**), $(Ph_4P)[MoOBr_3(SNSi)]$ (**IV**), $[MoBr_3(SNHSi)_3]$ (**V**) and $[MoCl_4(SNHSi_2)_2]\cdot(C_2H_5)_2O$ (**VII**). These complexes serve as synthetic precursors in ligand substitution reactions and redox coupled processes for the preparation of complexes incorporating hydrazido(2–), azido and other ligand types. The ability of the derivatized pyridine-2-thiol ligands to adopt the neutral 1*H*-pyridine-2-thiol form (**VIII**) or the anionic bidentate thiolate mode (**IX**) imbues the chemistry with a degree of structural diversity [7].



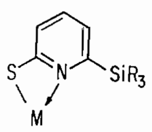
Ia R = R′ = R″ = Me
Ib R = R′ = Me, R″ = Ph
(HSNSi)



IIa R = R′ = R″ = Me
IIb R = R′ = Me, R″ = Bu^t
($HSNSi_2$)



VIII



IX

Experimental

Syntheses

$(Ph_4P)[MoBr_4(SC_5H_3NH\text{-}3\text{-}SiMe_3)_2]$ (III)

$[MoBr_2(CO)_4]$ (0.185 g, 0.5 mmol) was added to a solution of $HSC_5H_3N\text{-}3\text{-}SiMe_3$ (**Ia**) (0.366 g, 2.0 mmol) in acetonitrile (10 ml) to give immediately a deep red solution. After addition of Ph_4PBr (0.41 g, 1.0 mmol) and stirring for *c.* 24 h at room temperature, the solution was evaporated to dryness, yielding a red powder. Recrystallization from CH_3OH/diethyl ether yielded dark red crystals in 20% yield. Satisfactory elemental analysis was found.

$(Ph_4P)[MoOBr_3(SC_5H_3N\text{-}3\text{-}SiMe_3)]$ (IV)

The filtrate from the crystallization of **III** was treated with CH_2Cl_2 (5 ml) and allowed to stand for 2 weeks. Dark green crystals of $(Ph_4P)[MoOBr_3(SC_5H_3N\text{-}3\text{-}SiMe_3)]$ (**IV**) were collected in 20% yield. Satisfactory elemental analysis was found.

$[MoBr_3(SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]$ (V)

A solution of **Ia** (2.87 g, 15.67 mmol) in 15 ml of acetonitrile was added to $[MoBr_2(CO)_4]$ (1.45 g, 3.92 mmol) in 15 ml of acetonitrile. After stirring for 24 h, the resultant dark red solution was evaporated to an oil which was taken up in CH_2Cl_2/ether. After several days of standing at room temperature, red crystals of **V** were isolated in 25% yield. Satisfactory elemental analysis was found.

$[Mo_2O_3(SC_5H_3N\text{-}3\text{-}SiMe_3)_4]$ (VI)

Addition of $MoCl_5$ (0.60 g, 1.0 mmol) to **Ia** (0.74 g, 4.0 mmol) in CH_2Cl_2 (20 ml) resulted in a bright red solution, which was concentrated to *c.* 8 ml. After carefully layering with 12 ml of diethyl ether, the solution was allowed to stand for 5 days at room temperature and dark purple crystals of $[Mo_2O_3$-

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(SNSi)$_4$] (VI) were collected. The presence of characteristic infrared bands in the 800–950 cm^{-1} region confirmed the presence of the [Mo$_2$O$_3$]$^{4+}$ unit.

[MoCl$_4${SC$_5$H$_2$NH-3,6-(SiMe$_2$Bu^t)$_2$}$_2$] (VII)

MoCl$_5$ (0.5 g, 3.83 mmol) dissolved in CH$_2$Cl$_2$ (5 ml) was added to **IIb** (2.65 g, 7.80 mmol) in 20 ml of CH$_2$Cl$_2$. After stirring for 3 days, the resultant dark green solution was concentrated to 15 ml and 40 ml of n-hexane and 10 ml of diethyl ether were added. After standing for 3 weeks at 0 °C, dark green crystals of [MoCl$_4$SNHSi$_2$)$_2$]·(C$_2$H$_5$)$_2$O (VII) were collected in 32 % yield.

Crystal Data

Complex **III** gave triclinic space group $P\bar{1}$; a = 10.689(1), b = 14.511(3), c = 16.713(3) Å; α = 104.15(1)°, β = 103.58(1)°, γ = 95.46(1)°; V = 2411.6(8) Å^3, Z = 2, D_{calc} = 1.54 g cm^{-1}. Structure solution and refinement based on 3510 reflections with $F_o \geq 6\sigma(F_o)$ (in all cases Mo Kα, λ = 0.71073 Å, graphite monochromator) converged at a conventional residual of 0.0531. Complex **IV** gave monoclinic space group $C2/c$; a = 19.806(4), b = 12.271(3), c = 32.749(5) Å; β = 96.57(2)°, V = 7907.4(12) Å^3, D_{calc} = 1.46 g cm^{-3} for Z = 8. Structure solution and refinement based on 2440 reflections with $F_o \geq 6\sigma(F_o)$ converged at R = 0.0825. Complex **V** gave orthorhombic space group $Pbca$; a = 33.376(6), b = 18.751(4), c = 11.980(4) Å; V = 7494.6(14) Å^3, Z = 8, D_{calc} = 1.56 g cm^{-1}; 2863 reflections, R = 0.0316. Complex **VII** gave orthorhombic space group $Pbcn$; a = 16.245(4), b = 13.531(4), c = 23.739(6) Å; V = 5218.4(15) Å^3, Z = 4, D_{calc} = 1.25 g cm^{-1}; 1533 reflections, R = 0.0733.

Results and Discussion

The dark red, paramagnetic complex (Ph$_4$P)[MoBr$_4$(SNHSi)$_2$] (**III**) is prepared from the reaction of **Ia** with [MoBr$_2$(CO)$_4$], followed by treatment with Ph$_4$PBr. The infrared spectrum of **III** shows only absorptions assigned to the ligands, with the prominent feature at 840 cm^{-1} characteristic of ν(Si–C) and a medium intensity band at 3060 cm^{-1} assigned to ν(N–H) for the thione form of the ligand.

Treatment of the filtrate from the synthesis of **III** with wet CH$_2$Cl$_2$, followed by standing for 2 weeks, yielded (Ph$_4$P)[MoOBr$_3$(SNSi)] (**IV**). The infrared spectrum of **IV** is similar to that of **III** with an additional intense band appearing at 954 cm^{-1}, attributed to ν(Mo=O) and the disappearance of features above 3000 cm^{-1}.

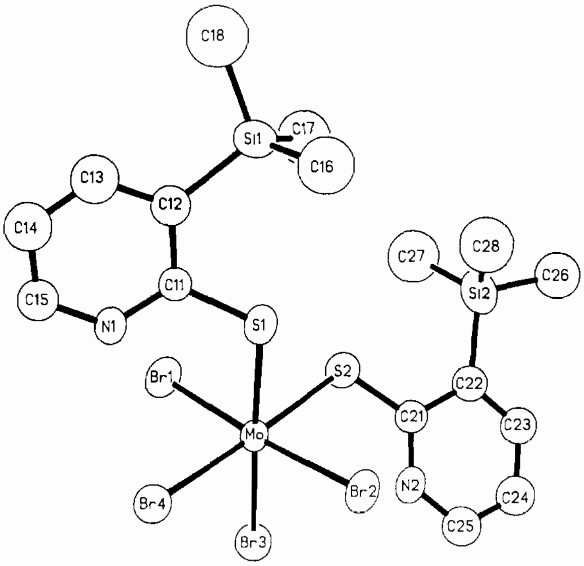

Fig. 1. Perspective view of the structure of (Ph$_4$P)[MoBr$_4$(SC$_5$H$_3$NH-3-SiMe$_3$)$_2$] (**III**) showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–Br(1), 2.566(2); Mo–Br(2), 2.605(2); Mo–Br(3), 2.616(2); Mo–Br(4), 2.611(2); Mo–S(1), 2.495(3); Mo–S(2), 2.509(3); Br(1)–Mo–Br(2), 175.0(1); Br(3)–Mo–S(1), 177.5(1); Br(4)–Mo–S(2), 176.3(1).

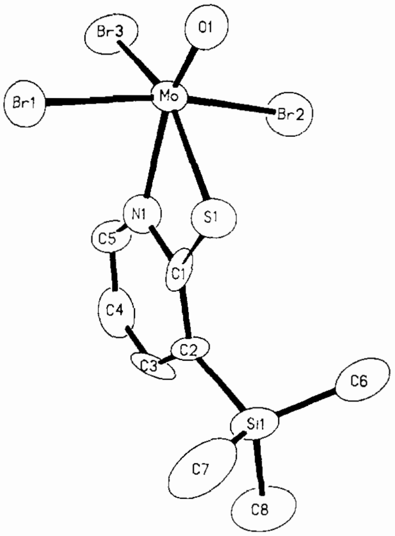

Fig. 2. ORTEP view of the molecular anion of (Ph$_4$P)[MoOBr$_3$(SC$_5$H$_3$N-3-SiMe$_3$)] (**IV**). Selected bond lengths (Å) and angles (°): Mo–O, 1.64(2); Mo–Br(1), 2.517(3); Mo–Br(2), 2.525(3); Mo–Br(3), 2.509(3); Mo–S, 2.467(7); Mo–N, 2.282(2); S–Mo–N, 64.0(5); O–Mo–N, 159.0(7).

The structure of the anion of **III**, shown in Fig. 1, consists of mononuclear Mo(III) centers coordinated in a pseudo-octahedral geometry to four bromide donors and two mutually *cis* thiol ligands. The pyridyl nitrogen atoms are non-coordinating, in contrast to complexes of 2-pyridinethiol which generally exhibit bidentate S,N-coordination [8]. However, the structure of the anion of **IV**, illustrated in Fig. 2, exhibits the (SNSi) ligand in the anionic bidentate coordination mode, such that the Mo

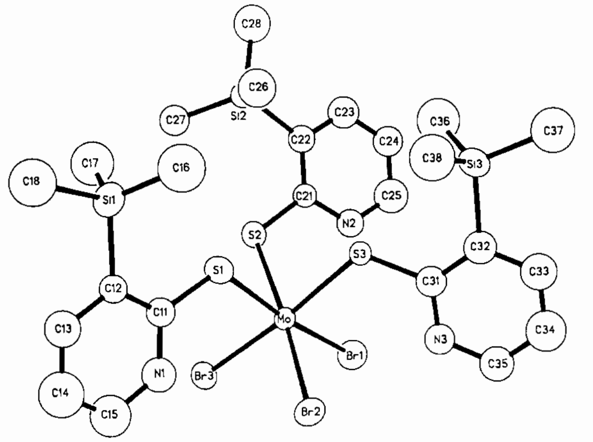

Fig. 3. ORTEP view of the structure of $[MoBr_3(SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]$ (V) showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–Br(1), 2.619(1); Mo–Br(2), 2.600(1); Mo–Br(3), 2.590(1); Mo–S(1), 2.502(2); Mo–S(2), 2.487(2); Mo–S(3), 2.492(2); S(1)–Mo–Br(1), 173.8(1); S(2)–Mo–Br(2), 172.8(1); S(3)–Mo–Br(3), 174.6(1).

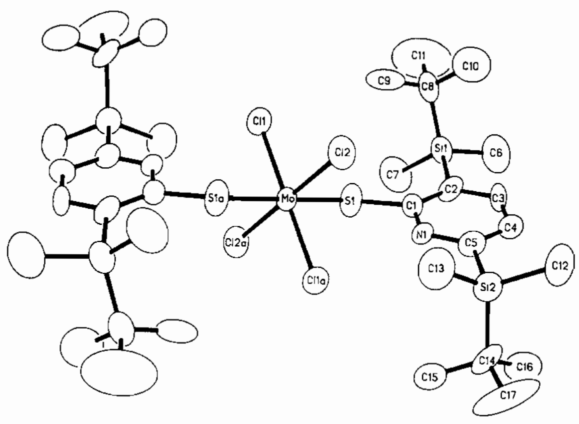

Fig. 4. ORTEP view of the structure of $[MoCl_4\{SC_5H_2NH\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}_2]$ (VII), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–Cl(2), 2.387(5), Mo–Cl(1), 2.404(5); Mo–S(1), 2.417(5); Cl(1)–Mo–Cl(2), 90.7(2); S(1)–Mo–Cl(1), 88.2(2); S(1)–Mo–Cl(2); 91.8(2).

center displays distorted octahedral $[MoOBr_3SN]$ coordination geometry. The bromide donors adopt a meridional geometry, and the pyridine N-donor occupies the position *trans* to the oxo group.

The reaction of **III** with **Ia** unexpectedly resulted in the Mo(III) species, $[MoBr_3(SNHSi)_3]$ (**V**), a complex which was also prepared directly from the reaction of $[MoBr_2(CO)_4]$ with excess **Ia**. The structure of **V**, illustrated in Fig. 3, consists of distorted octahedral mononuclear Mo(III) centers, with the thiol donors in the neutral 1*H*-pyridine-2-thione form and adopting a facial arrangement.

Reaction of $MoCl_5$ with **Ia** yields a bright red complex analyzing for $[MoCl_4(SNHSi)_2]$ which is extremely air- and moisture-sensitive. Attempts to recrystallize this species resulted in incorporation of oxygen to give dark purple crystals of $[Mo_2O_3(SNSi)_4]$, a complex exhibiting the characteristic $[Mo_2O_3]^{4+}$ core. On the other hand, by employing the more sterically encumbered ligand **IIb**, the complex $[MoCl_4(SNHSi_2)_2]$ (**VII**) was isolated as dark green paramagnetic crystals. The infrared spectrum of **VII** confirmed the absence of Mo=O units, exhibiting only characteristic ligand bands (ν(Si–C), 800 cm^{-1}; ν(N–H), 3150 cm^{-1}) and ν(Mo–Cl) at 298 cm^{-1}. As shown in Fig. 4, the structure of **VII** consists of discrete Mo(IV) monomers, with *trans* thiol donors. The nitrogen donors of **IIb** do not coordinate to the Mo center, a feature common to the structures of **III**, **V** and **VII** which all exhibit the ligand in the 1*H*-pyridine-2-thione form. The *trans* configuration of the thiolate donors is unusual in view of the tendency of weak π-donor ligands to adopt mutually *cis* orientations in order to maximize overlap with metal t_{2g} orbitals, as observed for **III**. However, the steric requirements of the ligand **IIb** appear to preclude the *cis* configuration, thus dictating the observed coordination geometry.

Complexes **III**, **IV**, **V** and **VII** provide unusual examples of mixed halido–thiol coordination to a molybdenum center. Other structurally characterized examples, $[MoCl_2(SC_6H_4SCH_2CH_2SC_6H_4S)]$ [9] and $[MoCl(TIPT)_4]$ [4]*, also rely upon steric or geometric characteristics of the thiol donors to retain halide coordination. The steric requirements of ligands of the class of which **Ia** and **IIb** are prototypes preclude exclusively thiolate ligation to satisfy the Mo coordination, thus necessitating halide ligation to complete the geometry. It remains problematical as to whether suitable modification of ligand substituents will permit isolation of a general series of halido–thiolate complexes $[Mo(SR)_{2+n}X_{4-n}]$ (X = halide).

As anticipated, the halide ligands of **III**, **IV**, **V** and **VII** are readily displaced by a variety of donors, including organohydrazine and pseudohalide ligands. Furthermore, **VII** reacts with NEt_3 to give $[Mo(SNSi_2)_3Cl_2]$, a species the reactions of which with alkylnitriles, alkylisonitriles and acetylenes are currently under investigation. In contrast, reduction of **VII** with hydrazine yields the binuclear Mo(III)–Mo(III) species $[Mo_2Cl_6(SNHSi_2)_3]$, a complex whose distinct Mo coordination environments allow one Mo center to act as a site for ligand substitution while the second Mo center functions as an electron sink. Further details of the chemistry of these species will be presented in future communications [10].

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*(TIPT) = $^{-}SC_6H_2\text{-}2,4,6\text{-}Pr^i_3$.

Supplementary Material

Atomic coordinates, bond lengths (Å), bond angles (°), anisotropic temperature factors, calculated hydrogen atom positions and observed and calculated structure factors for **III**, **IV**, **V** and **VII** are available from the authors on request.

Acknowledgements

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