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Molybdenum complexes with sterically-hindered thiolate ligands. The synthesis and structure of a seven coordinate complex with a molybdenum–diazenido core, $[Mo(NNC_6H_5)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$

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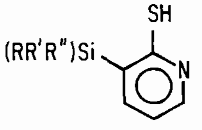
Abstract

The reaction of $[Mo_2Cl_4(\mu\text{-}S_2)(\mu\text{-}2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ with phenylhydrazine yields $[Mo(NNPh)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**1**). Complex **1** adopts a pentagonal bipyramidal geometry with the phenyldiazenido group occupying an axial position. The structural parameters exhibited by **1** are similar to those of other members of the class of seven coordinate Mo–hydrazido and Mo–diazenido species. Crystal data for $C_{30}H_{41}N_5Si_3S_3Mo$ (**1**): monoclinic space group $P2_1n$, $a = 11.600(2)$, $b = 14.880(3)$, $c = 21.681(3)$ Å, $\beta = 90.46(1)°$, $V = 3242.2(12)$ Å^3, $Z = 4$; 5690 reflections, $R = 0.049$.

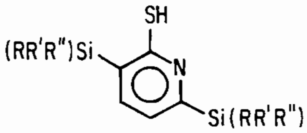
Introduction

Metal thiolate coordination chemistry has witnessed dramatic growth in the past decade because of the widespread occurrence of metal–cysteine coordination in metalloenzymes [1–3]. By introducing appropriate organic substituents into the thiolate ligand, complexes with unusual geometries [4–10] or oxidation states [11, 12] and displaying enhanced solubilities may be isolated. Variation of the degree of steric hindrance afforded by these substituents allows modification of the metal microenvironment, such that reactions with substrate molecules have been observed [13–20].

As part of our extensive investigations of the chemistry of sterically-hindered thiolate ligands [21–31], we have described a series of 3-(triorganosilyl)pyridine-2-thiols (**A**) and 3,6-bis(triorganosilyl)pyridine-2-thiols (**B**) and their coordination chemistry with molybdenum [29].



A



B

In the course of this investigation, the binuclear Mo(IV) complex $[Mo_2Cl_4(\mu\text{-}S_2)(\mu\text{-}2SC_5H_3NH\text{-}3\text{-}SiMe_3)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ (**C**) was observed to catalyze both disproportionation and reduction of hydrazine to produce ammonia. Since molybdenum–hydrazido complexes are often key intermediates in the formation of ammonia or amines [32–35], the reactions of **C** with various organohydrazine ligands were investigated. As part of this study, we report the synthesis and structural characterization of $[Mo(NNC_6H_5)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**1**).

Experimental

Materials and methods

The complex $[Mo_2Cl_4(\mu\text{-}S_2)(\mu\text{-}2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**C**) was synthesized as previously described [36]. Dichloromethane was technical grade and was distilled from P_4O_{10}. All manipulations were carried out under an atmosphere of argon. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Rigaku AFC-5S four-circle diffractometer; electrochemistry, BAS electroanalytical system.

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Preparation of compounds

[Mo(NNC$_6$H$_5$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$ (1)

To a solution of [Mo$_2$Cl$_4$(μ-S$_2$)(μ-2-SC$_5$H$_3$NH-3-SiMe$_3$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (**C**) (1.02 g, 1.0 mmol) in CH$_2$Cl$_2$ (20 ml) was added phenylhydrazine (0.11 g, 1.0 mmol). Upon stirring, the solution color changed from deep red to brown. The solution was concentrated to 10 ml and carefully layered with 15 ml of diethyl ether. After standing for 7 days, brilliant dark brown crystals of **1** were obtained in 55% yield. *Anal.* Calc. for C$_{30}$H$_{41}$N$_5$Si$_3$S$_3$Mo; C, 48.2; H, 5.52; N, 9.36. Found: C, 48.1; H, 5.48; N, 9.24%.

[Mo(NNHC$_6$H$_5$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$]BF$_4$ (2)

To a solution of **1** (0.374 g, 0.5 mmol) in CH$_2$Cl$_2$ (15 ml) was added an excess of HBF·(C$_2$H$_5$)$_2$O. After 1 h of vigorous stirring, the solution volume was concentrated to *c.* 10 ml and diethyl ether (2 ml) was added. After standing at 4 °C for several days, the brown microcrystalline precepitate of **2** was collected in 45% yield. *Anal.* Calc. for C$_{30}$H$_{42}$BN$_5$F$_4$Si$_3$S$_3$Mo: C, 43.1; H, 5.06; N, 8.38. Found: C, 42.8; H, 5.00; N, 8.22%.

Reactions of C with 1,1-disubstituted organohydrazines

To a solution of **C** (0.51 g, 0.5 mmol) in CH$_2$Cl$_2$ (15 ml) was added 1,1-methylphenylhydrazine (0.061 g, 0.5 mmol). Upon refluxing for 0.5 h, the solution became ruby red in color. The solution was concentrated to 8 ml and diethyl ether (10 ml) was added. Slow evaporation under argon gave red crystals of [MoCl$_2$(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$(NNMePh)]·(C$_2$H$_5$)$_2$O (**3**). *Anal.* Calc. for C$_{27}$H$_{42}$Cl$_2$MoN$_4$OS$_2$Si$_2$: C, 44.7; H, 5.79; N, 7.73. Found: C, 44.3; H, 5.63; N, 7.51%.

An excess of H$_2$NNMePh (0.183 g, 1.5 mmol) was added to a solution of **C** (0.51 g, 0.5 mmol) in methanol (15 ml). After stirring for 24 h at room temperature, diethyl ether (20 ml) was added to the solution. Upon slow evaporation under argon, orange–yellow crystals of [Mo(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$(NNMePh)$_2$] (**4**) were isolated in 35% yield. *Anal.* Calc. for C$_{30}$H$_{40}$MoN$_6$S$_2$Si$_2$: C, 51.4; H, 5.72; N, 12.1 Found: C, 50.9; H, 5.52; N, 12.2%.

X-ray structure determination

Full details of the crystallographic methodologies may be found in ref. 37. The crystal data and experimental conditions are summarized in Table 1.

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H distances set at 0.96 Å. All non-hydrogen atoms were refined anisotropically.

TABLE 1. Summary of the crystal data and experimental conditions for the structural determination of [Mo(NNPh)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$] (**1**)

Formula weight	748.08
a (Å)	11.600(2)
b (Å)	14.880(3)
c (Å)	21.681(3)
β (°)	90.46(1)
V (Å^3)	3742.2(12)
Z	4
Space group	$P2_1/n$
D_{calc} (g cm^{-3})	1.33
μ (Mo Kα) (cm^{-1})	6.23
No. reflections	5670
R	0.049
R_w	0.056
Goodness of fit	1.98

Results and discussion

Synthesis, spectroscopic and electrochemical properties

The complex [Mo$_2$Cl$_4$(μ-S$_2$)(μ-2-SC$_5$H$_3$NH-3-SiMe$_3$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (**C**) has been shown to effect the catalytic disproportionation of hydrazine to dinitrogen and ammonia. In contrast, reactions of **C** with mono- and disubstituted organohydrazines do not result in N–N bond cleavage to produce amines and ammonia, but rather yield mononuclear complexes with the molybdenum hydrazido(2−), MoNNR$_2$, or the molybdenum diazenido, MoNNR, cores. Thus, the reaction of **C** with an equivalent amount of H$_2$NNMePh yields [MoCl$_2$(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$(NNMePh)] (**3**), while the reaction of **C** with excess H$_2$NNMePh results in the formation of [Mo(NNMePh)$_2$(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (**4**). Both **3** and **4** have been prepared by alternative routes, and their structures have been reported [29]. The reaction of **C** with the monosubstituted hydrazine H$_2$NNHPh yields a complex whose analytic data is consistent with formulation as the seven coordinate [Mo(NNPh)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$] (**1**). The IR spectrum of **1** exhibits a strong band at 1490 cm^{-1}, assigned to ν(N=N), and prominent features in the 800–840 cm^{-1} region associated with ν(Si–C). The electronic spectrum exhibits a transition at 410 nm (ϵ, 6.0×10^3 M^{-1} cm^{-1}), assigned as a charge-transfer bond associated with the [MoNNPh] chromophore [38]. The structural identity of **1** has been confirmed by X-ray crystallography, *vide infra*.

The β-nitrogen of the Mo–diazenido core of **1** possesses a lone pair of electrons which may be susceptible to attack by electrophiles. Reaction of **1** with HBF$_4$·(C$_2$H$_5$)$_2$O yields the Mo–hydrazido(2−) complex [Mo(NNHPh)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$BF$_4$ (**2**). The IR spectrum of **2** exhibits a feature at 1520

$\mathrm{cm^{-1}}$ associated with $\nu(\mathrm{N{=}N})$ of the hydrazido(2−) moiety. Conductivity measurements in acetonitrile were consistent with a 1:1 electrolyte.

Complex **1** was examined by cyclic voltammetry at a platinum wire electrode in acetonitrile–0.1 M $(\mathrm{n\text{-}C_4H_9})_4\mathrm{NPF_6}$. The complex exhibited two successive one-electron oxidations at +0.31 and +0.96 V with respect to a saturated calomel electrode. The first oxidation process meets the criteria for a diffusion controlled reversible one-electron oxidation ($E_\mathrm{p}{}^\mathrm{ox} - E_\mathrm{p}{}^\mathrm{red} = 61$ mV; $i_\mathrm{p}{}^\mathrm{red}/i_\mathrm{p}{}^\mathrm{ox} = 1.0$), while the second electrode process is irreversible, even at scan rates of 50 V $\mathrm{s^{-1}}$. The oxidation processes may be summarized by the following equations:

$$[\mathrm{Mo(N_2Ph)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}] \underset{+1e}{\overset{-1e}{\rightleftharpoons}}$$

$$[\mathrm{Mo(N_2Ph)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]^+ \xrightarrow{-1e^-}$$

$$[\mathrm{Mo(N_2Ph)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]^{2+}$$

Controlled potential electrolysis carried out at +0.41 V resulted in a color change from brown to purple and a linear decay in current with charge passed. The charge passed corresponds to a 1 F $\mathrm{mol^{-1}}$ oxidation of the complex.

No reduction waves were observed at potentials up to −2.4 V versus saturated calomel. This observation indicates that the lowest unoccupied molecular orbital (LUMO) is at least 70 kcal higher in energy than the highest occupied molecular orbital (HOMO). This behavior seems to be characteristic of molybdenum–diazenido complexes, such as $[\mathrm{Mo(NNPh)(S_2CNR_2)_3}]$ [38] and $[\mathrm{MoBr(NNMe)(Ph_2PCH_2CH_2PPh_2)_2}]$ which are also electrochemically inactive toward reduction. The formation of the Mo–N multiple bond results in 18-electron complexes with no low-lying unoccupied orbitals, and the disruption of the d_π–p_π Mo–N bonding by reduction is not readily achieved.

Complex **2** is also electrochemically active. Cyclic voltammetry of **2** under conditions identical to those employed for **1** exhibits two successive one-electron reductions at −1.35 and −1.64 V, of which the first is reversible and the second irreversible at all scan rates. The electrode processes are consistent with the following scheme:

$$[\mathrm{Mo(N_2HPh)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]^+ \underset{-1e}{\overset{+1e^-}{\rightleftharpoons}}$$

$$[\mathrm{Mo(N_2HPh)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}] \xrightarrow{+1e^-}$$

$$[\mathrm{Mo(N_2HPh)(SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]^-$$

Similar electrochemical behavior has been reported for complexes of the type $[\mathrm{Mo(N_2R_2)(S_2CNR'_2)_3}]^+\mathrm{X}^-$, suggesting that **2** is a member of the class of seven coordinate Mo–hydrazido complexes of pentagonal bipyramidal geometry [39].

Description of the structure of 1

Atomic coordinates for the structure of $[\mathrm{Mo(NNPh)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$ (**1**) are given in Table 2, and selected bond lengths and angles are listed in Table 3. The crystallographic study revealed that the complex adopts a distorted pentagonal bipyramidal geometry with the sulfur and nitrogen donors of two of the derivatized pyridinethiolate ligands and the sulfur donor of the third pyridinethiolate chelate occupying the pentagonal plane

TABLE 2. Atomic positional parameters for **1**

Atom	*x*	*y*	*z*
Mo	0.75717(3)	0.13897(2)	0.83121(2)
S(1)	0.6591(1)	0.05122(8)	0.74806(5)
S(2)	0.6946(1)	0.26304(8)	0.90151(6)
S(3)	0.9258(1)	0.24524(8)	0.84128(5)
Si(1)	0.5622(1)	0.0931(1)	0.59637(6)
Si(2)	0.4998(1)	0.2826(1)	1.02465(8)
Si(3)	1.2031(1)	0.2714(1)	0.77738(7)
N(1)	0.6937(3)	0.2201(2)	0.7531(1)
N(2)	0.5877(3)	0.1220(2)	0.8749(2)
N(3)	0.9097(3)	0.1084(2)	0.7738(2)
N(4)	0.7980(3)	0.0554(2)	0.8882(1)
N(5)	0.8142(3)	−0.0073(2)	0.9232(2)
C(1)	0.8404(3)	0.0100(3)	0.9867(2)
C(2)	0.8336(4)	0.0945(4)	1.0131(2)
C(3)	0.8581(5)	0.1050(4)	1.0751(2)
C(4)	0.8877(5)	0.0322(5)	1.1107(2)
C(5)	0.8940(5)	−0.0514(5)	1.0850(3)
C(6)	0.8697(4)	−0.0632(3)	1.0226(2)
C(11)	0.6519(4)	0.1581(3)	0.7139(2)
C(12)	0.6109(4)	0.1798(3)	0.6544(2)
C(13)	0.6130(4)	0.2714(3)	0.6405(2)
C(14)	0.6539(5)	0.3355(3)	0.6820(2)
C(15)	0.6951(4)	0.3071(3)	0.7375(2)
C(16)	0.5364(6)	0.1522(5)	0.5221(3)
C(17)	0.4269(5)	0.0412(5)	0.6219(3)
C(18)	0.6756(6)	0.0066(4)	0.5873(3)
C(21)	0.5821(4)	0.1888(3)	0.9168(2)
C(22)	0.5042(4)	0.1907(4)	0.9660(2)
C(23)	0.4280(4)	0.1178(4)	0.9675(3)
C(24)	0.4319(5)	0.0506(4)	0.9239(3)
C(25)	0.5125(5)	0.0533(4)	0.8784(3)
C(26)	0.6412(6)	0.3076(7)	1.0579(3)
C(27)	0.4014(9)	0.2496(7)	1.0871(4)
C(28)	0.4469(9)	0.3844(6)	0.9852(5)
C(31)	0.9869(4)	0.1736(3)	0.7877(2)
C(32)	1.0984(4)	0.1767(3)	0.7627(2)
C(33)	1.1251(5)	0.1057(4)	0.7237(2)
C(34)	1.0453(5)	0.0391(4)	0.7092(2)
C(35)	0.9388(5)	0.0420(3)	0.7349(2)
C(36)	1.2247(5)	0.2904(5)	0.8612(3)
C(37)	1.3439(6)	0.2416(5)	0.7420(4)
C(38)	1.1447(6)	0.3728(4)	0.7383(3)

TABLE 3. Selected bond lengths (Å) and angles (°) for **1**

Mo–S1	2.493(1)	Mo–N4	1.814(3)
Mo–S2	2.505(1)	N4–N5	1.216(5)
Mo–S3	2.524(1)		
Mo–N1	2.201(3)		
Mo–N2	2.203(4)		
Mo–N3	2.218(4)		
S1–Mo–S2	133.88(5)	S3–Mo–N1	88.70(9)
S1–Mo–S3	137.70(4)	S3–Mo–N2	136.7(1)
S1–Mo–N1	65.37(9)	S3–Mo–N3	63.6(1)
S1–Mo–N2	81.2(1)	S3–Mo–N4	99.9(1)
S1–Mo–N3	81(3)1	N1–Mo–N2	95.7(1)
S1–Mo–N4	104.4(1)	N1–Mo–N3	86.8(1)
S2–Mo–S3	73.37(4)	N1–Mo–N4	169.8(1)
S2–Mo–N1	88.1(1)	N2–Mo–N3	159.4(1)
S2–Mo–N2	63.8(1)	N2–Mo–N4	81.8(1)
S2–Mo–N3	136.8(1)	N3–Mo–N4	92.1(1)
S2–Mo–N4	99.6(1)	Mo–N4–N5	171.7(3)

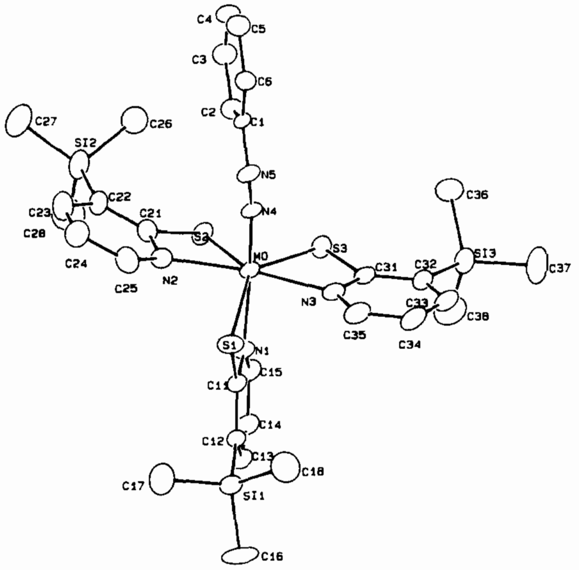

Fig. 1. ORTEP view of the structure of $[Mo(NNC_6H_5)(2\text{-}SC_5H_3\text{-}3\text{-}SiMe_3)_3]$ (**1**).

and the remaining pyridine nitrogen and the α-nitrogen of the phenyldiazenido group at the axial positions. An ORTEP view of **1** is given in Fig. 1.

The major distortions from regular pentagonal geometry for the [MoS1S2N2S3N3] grouping are consequences of non-bonding interactions of the in-plane donor groups and of the constraints imposed by the requirements of the four membered chelate rings. Thus, the S2–Mo–N2 and S3–Mo–N3 internal chelate angles are 63.8(1) and 63.6(1)(1)°, respectively, while the chelate ring which spans the pentagonal plane and one apex of the pentagonal bipyramid exhibits an expanded angle of 65.37(9)°.

TABLE 4. Selected bond lengths (Å) for pentagonal bipyramidal complexes with the Mo–N–N core

Complex	Mo–N	Donor groups in equatorial plane	Mo–L equatorial (L)	Mo–L apical (L)	Reference
$[Mo(N_2CO_2Et)(S_2CNEt_2)_3]$	1.732(5)	5×S	2.487–2.529(2) (S)	2.604(2) (S)	42
$[Mo(N_2Ph)(S_2CNMe_2)_3]$	1.781(4)	5×S	2.514(3) av. (S)	2.411(1) (S)	41
$[Mo(N_2MePh)Cl_2(SC_5H_3NSiMe_3)_2]$	1.75(1)	4×S, 1×Cl	2.416(4) (Cl)	2.451(4) (Cl)	29
$[Mo(N_2MePh)(SC_6H_4PPhC_6H_4S)_2]$	1.782(4)	3×S, 2×P	2.533(3) av. (S)	2.509(1) (S)	29
$[Mo(N_2Me_2)(SCH_2CH_2PPhCH_2CH_2S)_2]$	1.775(6)	3×S, 2×P	2.508(6) av. (S)	2.498(3) (S)	40
$[Mo\{Me_2CNNC(S)SMe\}\{N_2C(S)SMe\}\{MeSC(S)NNC(S)SMe\}]$	1.791(6)	3×S, 2×N	2.500(4) av. (S)	2.440(2) (S)	46
$[Mo\{N_2C(S)SEt\}\{H_2NNC(S)SEt\}\{S_2CNMe_2]$	1.77(1)	4×S, 1×N	2.464–2.526(4) (S)	2.562(4) (S)	45
$[Mo(N_2Ph)(SC_5H_3NSiMe_3)_3]$ (**1**)	1.814(3)	3×S, 2×N	2.203–2.218(4) (N)	2.201(3) (N)	This work

The phenyldiazenido group exhibits the common 'singly bent' geometry. The short Mo–N4 and N4–N5 distances, 1.814(3) and 1.216(5) Å, respectively, and the nearly linear Mo–N4–N5 linkage are consistent with considerable multiple bond delocalization throughout the Mo–N4–N5 moiety. Although the diazenido group is multiply bonded in the axial position, there is no apparent *trans* influence exerted on the *trans* nitrogen donor, Mo–N1 of 2.201(3) Å compared to Mo–N(equatorial) of 2.203(4) and 2.218(4) Å.

Seven coordinate Mo–hydrazido and Mo–diazenido complexes are well known, and the pentagonal bipyramidal geometry is ubiquitous for these species [40–46]. A common geometric feature shared by all structures of this class is the occupancy of one axial site by the hydrazido(2-) or diazenido ligand. A variety of donor groups may occupy the second axial site. In general, there does not appear to be a significant *trans* influence associated with the MoNN grouping, as there is no significant lengthening of the Mo–L distance of the other apical donor. Table 4 lists selected bonding parameters for some examples of pentagonal bipyramidal structures with the [MoNN] core. Complex **1** presents several unique features relative to other members of this class. The Mo–N axial distance is significantly longer than other examples cited in Table 4. The second axial donor is a neutral pyridine nitrogen, whereas all other examples of this class display an anionic ligand donor, most generally sulfur, in this site. The contribution of steric influences of the triorganosilyl substituents to these geometric anomalies is not obvious, and we are studying the influence of various substituents on the structures of complexes of the types $[Mo(N_2R)(SC_5H_3N\text{-}3\text{-}SiR'_3)_3]$ and $[Mo(N_2R)(SC_5H_2N\text{-}3,6\text{-}SiR''_3)_3]$.

Acknowledgement

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