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Molybdenum complexes with sterically-hindered thiolate ligands. The synthesis and structure of [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$]

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Abstract

The oxo–hydrazido(2−) molybdenum(VI) complex [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] was prepared either by the reaction of [Mo_2O_3(2-SC_5H_3N-3-$SiMe_3)_4$] with 1,1-methylphenylhydrazine or by the reaction of [$MoCl_2$(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] with atmospheric oxygen. The complex exhibits the *cis* oxo–hydrazido geometry, with the hydrazido (2−) ligand in the linear η^1 coordination mode. Crystal data: $C_{23}H_{32}N_4OSi_2S_2Mo$, triclinic space group $P\bar{1}$, $a=11.640(2)$, $b=17.206(3)$, $c=7.930(2)$ Å, $\alpha=102.92(1)$, $\beta=99.46(1)$, $\gamma=93.41(1)°$, $V=1519.3(9)$ Å^3, $Z=2$, $D_{calc}=1.30$ g cm^{-1}; structure solution and refinement based on 4746 reflections (Mo Kα, $\lambda=0.71073$ Å; $I_o \geqslant 3\sigma(I_o)$) converged at a conventional discrepancy value of 0.043.

Introduction

Metal thiolate coordination chemistry continues to attract considerable interest by virtue of its relevance to metal binding sites in metalloenzymes [1] and of the varied structural chemistry associated with this fundamental ligand type [2]. Recent work has demonstrated that sterically-hindered thiolate ligands afford complexes with unusual geometries [3–9] or oxidation states [10, 11] and enhanced solubilities and with the ability to bind small substrate molecules [12–18]. We have recently described the syntheses of a novel series of 3-(trioganosilyl)pyridine-2-thiols (**A**) and 3,6-bis(triorganosilyl)pyridine-2-thiols (**B**) and their coordination chemistry with Ag(I), Cu(I), Hg(II) and Mo(III)–Mo(V) [19–27].

Since hydrazido(2−) complexes are persistent intermediates in the formation of ammonia or ammines from molybdenum dinitrogen complexes [16, 17], we have made a systematic study of molybdenum–hydrazido(2−) coordination chemistry [18]. As part of this continuing investigation, we report the synthesis and structural characterization of [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$].

Experimental

Materials and methods

The complexes [Mo_2O_3(2-SC_5H_3N-3-$SiMe_3)_4$] and [$MoCl_2$(NNPhMe)(2-SC_5H_3N-3-$SiMe_3)_2$] were prepared as previously described [27]. Dichloromethane was technical grade and was distilled from $CaCl_2$ and P_4O_{10}. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Rigaku AFC-5S four-circle diffractometer.

Preparation of compounds

[MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$]

Method 1. To a solution of [Mo_2O_5(2-SC_5H_3N-3-$SiMe_3)_4$] (0.5 g, 0.5 mmol) in CH_2Cl_2 (20 ml) was added 1,1-methylphenylhydrazine (0.14 g, 1.1 mmol). Upon stirring for 4 h, the solution color turned from dark purple to red–brown. After concentrating the solution to 10 ml and carefully layering with 10 ml of diethyl ether, brilliant red crystals of [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] were obtained in 35% yield, *Anal.* Calc. for $C_{23}H_{32}N_4OSi_2S_2Mo$: C, 46.3; H, 5.37; N, 9.40. Found: C, 46.2; H, 5.38; N, 9.35%.

Method 2. Addition of moist CH_2Cl_2 to a solution of [$MoCl_2$(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] (0.245 g,

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0.7 mmol) in CH_2Cl (15 ml) under argon resulted in a rapid color change from red to brown. Addition of diethyl ether (15 ml) gave microcrystalline [MoO(NNMePh)(2-SC_5H_3N-3-$SiHe_3)_2$] in 55% yield.

Reaction with excess 1,1-methylphenylhydrazine

Addition of [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] (0.5 g) in CH_2Cl_2 (25 ml) to $H_2NNMePh$ (0.5 g) under argon, followed by overnight stirring and addition of diethyl ether, gives [Mo$(NNMePh)_2$-(2-SC_5H_3N-3-$SiMe_3)_2$] in 75% yield.

Reaction with HCl

The complex [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] (0.5 g) in CH_2Cl_2 (25 ml) was treated with a stream of HCl gas for 5 min. The resulting brown solution was evaporated to 5 ml and the complex precipitated as a brown solid by addition of diethyl ether (30 ml). The product was recrystallized as brown blocks from CH_2Cl_2–$(C_2H_5)_2O$ in 76% yield.

Reaction with 2-HSC_5H_3N-3-$SiMe_3$

The complex [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] (0.5 g) and 2-HSC_5H_3N-3-$SiMe_3$ (0.5 g) were heated under reflex in HCl saturated CH_2Cl_2 (50 ml) for 2 h to give a clear yellow solution. A solution of $NaBPh_4$ (0.5 g) in methanol (10 ml) was added to the cooled solution to precipitate the complex [Mo(NNMePh)$(SC_5H_3N$-3-$SiMe_3)_3$]BPh_4 as a pale yellow solid, recrystallized as microcrystalline blocks from CH_2Cl_2–CH_3OH. Yield: 65%. *Anal.* Calc. for $C_{55}H_{64}N_5BSi_3Mo$: C, 61.1; H, 5.92; N, 6.48. Found: C, 60.7; H, 5.63; N, 6.35%.

X-ray structure determination

Full details of the crystallographic methodologies may be found in ref. 28. 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 [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$]

Formula weight	596
a (Å)	11.640(2)
b (Å)	17.206(3)
c (Å)	7.930(2)
α (°)	102.92(1)
β (°)	99.46(1)
γ (°)	93.41(1)
V (Å^3)	1519.3(9)
Z	2
Space group	$P\bar{1}$
D_{calc} (g cm^{-3})	1.30
μ(Mo Kα) (cm^{-1})	6.50
No reflections	4746
R	0.043
R_w	0.049
Goodness of fit	1.77

Results and discussion

Synthesis and reactions of [MoO(NNMePh)-(2-SC_5H_3N-3-$SiMe_3)_2$]

The complex [MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] was synthesized from [Mo_2O_3(2-SC_5H_3N-3-$SiMe_3)_2$] by exploiting the condensation-type reaction characteristic of Mo-oxo groups with substituted hydrazine ligands [29]. Alternatively, the complex was prepared by the reaction of [$MoCl_2$(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$] with water.

$$[Mo_2O_3(SC_5H_3NSiMe_3)_4] + 2H_2NNMePh \xrightarrow{O_2} 2[MoO(NNMePh)(SC_5H_3NSiMe_3)_2] + 2H_2O$$

$$[MoCl_2(NNMePh)(SC_5H_3NSiMe_3)_2] + H_2O \longrightarrow [MoO(NNMePh)(SC_5H_3NSiMe_3)_2] + 2HCl$$

The infrared spectrum of [MoO(NNMePh)-$(SC_5H_3N$-3-$SiMe_3)_2$] shows bands at 1620 and 960 cm^{-1} characteristic of ν(N=N) of the hydrazido(2−) ligand and ν(Mo=O), respectively. This suggests a structural analogy to the [MoO$(NNR_2)(S_2CNR_2)_2$] class of compounds [30] and, indeed, the reaction chemistry of [MoO(NNMePh)$(SC_5H_3N$-3-$SiMe_3)_2$] parallels that of the dithiocarbamate species [31].

The complex [MoO(NNMePh)$(SC_5H_3N$-3-$SiMe_3)_2$] reacts with anhydrous halogen acids in organic solvents at room temperature to regenerate the seven coordinate [$MoCl_2$(NNMePh)$(SC_5H_3N$-3-$SiMe_3)_2$], illustrated in Fig. 1. In common with the complexes [MoO$(NNR_2)(S_2CNR_2)_2$], treatment of the the oxo-hydrazido(2−) complex with acid does not involve reactions at the hydrazido-nitrogens to give hydrazido(1−) or other protonated nitrogenous products.

The complex [MoO(NNMePh)$(SC_5H_3N$-3-$SiMe_3)_2$] reacts with 1,1-methylphenylhydrazine to replace the second oxo group to yield the bis[hydrazido(2−)] complex whose structure is also illustrated in Fig. 1.

$$[MoO(NNMePh)(SC_5H_3NSiMe_3)_2] + H_2NNMePh \longrightarrow [Mo(NNMePh)_2(SC_5H_3NSiMe_3)_2] + H_2O$$

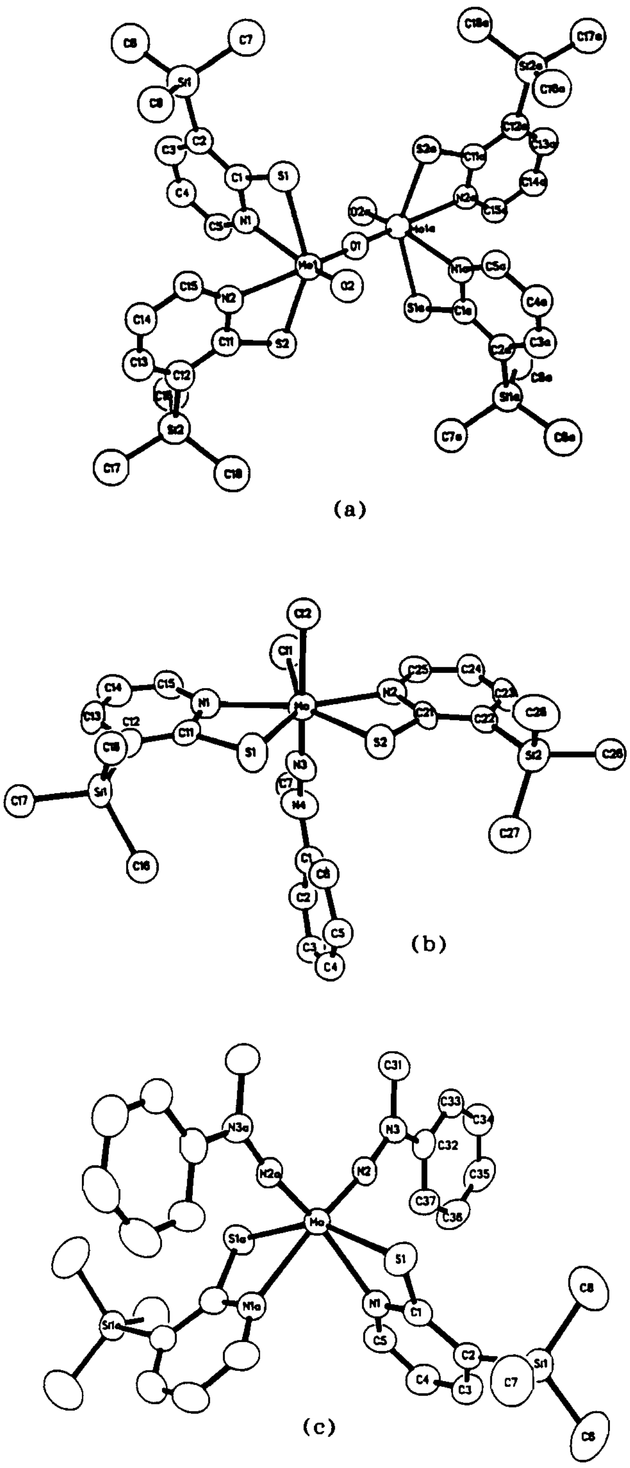

Fig. 1. Views of the structures of (a) $[Mo_2O_3(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_4]$, (b) $[MoCl_2(NNMePh)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$, (c) $[Mo(NNMePh)_2(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$.

In contrast, the oxohydrazido(2−) complex does not react with 1,1-dimethylhydrazine, even after prolonged refluxing, to give a bis[hydrazido(2−)] analogue. This indicates that the basicity of the hydrazine plays a crucial role in dictating the reaction pathway.

The cationic species $[Mo(NNMePh)(SC_5H_3NSiMe_3)_3]^+$, isolated as the tetraphenylborate salt, was prepared either by direct reaction of $[MoCl_2(NNMePh)(SC_5H_3N\text{-}SiMe_3)_2]$ with $HSC_5H_3N\text{-}3\text{-}SiMe_3$ or by reaction of $[MoO(NNMePh)(SC_5H_3NSiMe_3)_2]$ with excess ligand in HCl-saturated CH_2Cl_2. The structure of the analogous dithiocarbamate complex $[Mo(NNMePh)(S_2CNR_2)_3BPh_4$ has been reported [32], revealing the anticipated pentagonal bipyramidal structure with the hydrazido ligand in one of the axial sites.

Description of the structure

Atomic coordinates for the structure of $[MoO(NNMePh)(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ are given in Table 2, while Table 3 lists selected bond lengths and angles. The crystallographic study revealed that the structure consists of discrete mononuclear units with

TABLE 2. Atomic positions for $[MoO(NNMePh)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$

Atom	*x*	*y*	*z*
Mo(1)	0.00699(3)	0.24040(2)	0.16228(5)
S(1)	0.22578(9)	0.26163(7)	0.2571(1)
S(2)	−0.16078(9)	0.19482(7)	−0.0747(2)
Si(1)	0.4783(1)	0.3059(1)	0.1003(3)
Si(2)	−0.2694(1)	0.02213(8)	−0.4013(2)
O	−0.0152(3)	0.1929(2)	0.3229(4)
N(1)	0.1132(3)	0.2803(2)	−0.0328(4)
N(2)	0.0260(3)	0.1262(2)	−0.0289(4)
N(3)	−0.0382(3)	0.3382(2)	0.2315(4)
N(4)	−0.0831(3)	0.4055(2)	0.2740(4)
C(1)	−0.1369(3)	0.4221(2)	0.4234(4)
C(2)	−0.1718(3)	0.4969(2)	0.4843(5)
C(3)	−0.2251(4)	0.5116(3)	0.6309(6)
C(4)	−0.2455(4)	0.4517(3)	0.7138(6)
C(5)	0.2112(4)	0.3765(3)	0.6523(6)
C(6)	−0.1565(3)	0.3617(2)	0.5097(5)
C(7)	−0.0803(4)	0.4611(3)	0.1593(6)
C(11)	0.2241(3)	0.2840(2)	0.0521(5)
C(12)	0.3227(3)	0.3018(2)	−0.0197(6)
C(13)	0.2946(5)	0.3148(3)	−0.1886(6)
C(14)	0.1815(5)	0.3102(3)	−0.2769(6)
C(15)	0.0928(4)	0.2924(2)	−0.1955(5)
C(16)	0.5783(6)	0.3304(6)	−0.042(1)
C(17)	0.5061(6)	0.2076(5)	0.140(1)
C(18)	0.5038(5)	0.3820(5)	0.309(1)
C(21)	−0.0800(3)	0.1128(2)	−0.1364(5)
C(22)	−0.1158(3)	0.0441(2)	−0.2703(5)
C(23)	−0.0320(4)	−0.0105(2)	−0.2908(5)
C(24)	0.0773(4)	0.0030(2)	−0.1848(6)
C(25)	0.1042(3)	0.0720(2)	−0.0537(5)
C(26)	−0.2982(5)	0.1004(3)	−0.5266(7)
C(27)	−0.3707(4)	0.0209(4)	−0.2455(8)
C(28)	−0.2841(5)	−0.0790(3)	−0.5508(7)

TABLE 3. Selected bond lengths (Å) and angles (°) for [MoO(NNMePh)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$]

Mo–S1	2.514(1)	S1–Mo–S2	148.23(4)	O–Mo–N1	154.8(1)
Mo–S2	2.432(1)	S1–Mo–O	94.5(1)	O–Mo–N2	93.4(1)
Mo–O	1.704(3)	S1–Mo–N1	63.45(8)	O–Mo–N3	104.9(1)
Mo–N1	2.323(3)	S1–Mo–N2	89.39(8)	N1–Mo–N2	75.3(1)
Mo–N2	2.245(3)	S1–Mo–N3	103.5(1)	N1–Mo–N3	92.7(1)
Mo–N3	1.787(3)	S2–Mo–O	106.1(1)	N2–Mo–N3	156.4(1)
N3–N4	1.298(4)	S2–Mo–N1	90.04(8)	Mo–N3–N4	173.5(3)
N4–C1	1.412(4)	S2–Mo–N2	65.88(8)		
N4–C7	1.462(5)	S2–Mo–N3	94.4(1)		

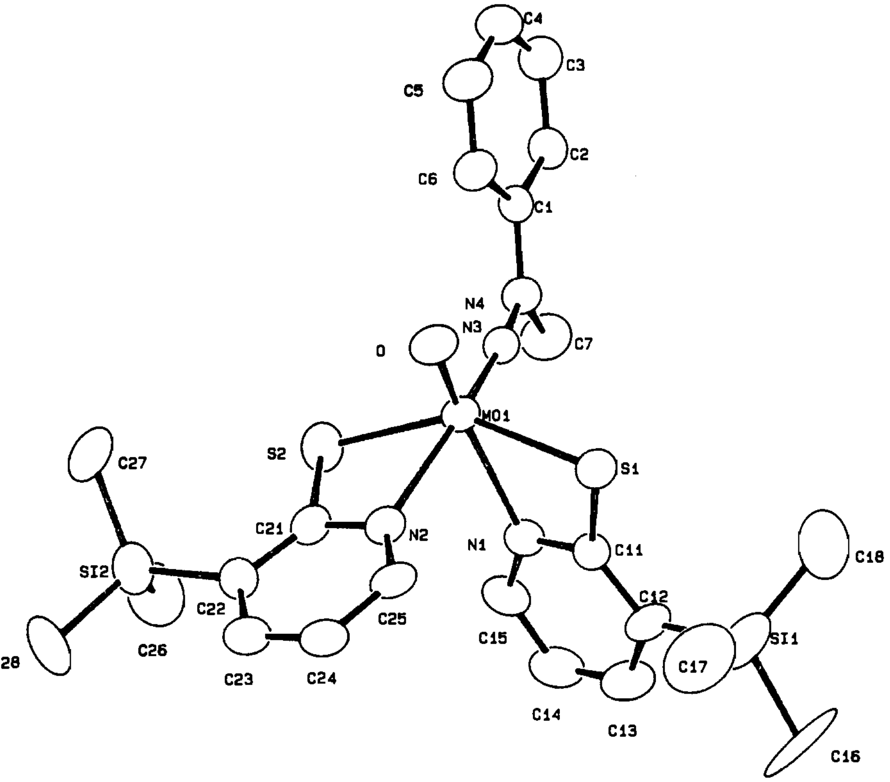

Fig. 2. ORTEP view of the structure of [MoO(NNMePh)(2-SC$_6$H$_3$N-3-SiMe$_3$)$_2$], showing the atom-labeling scheme.

distorted octahedral geometry about the Mo(VI) site, as shown in Fig. 2.

The structure exhibits the anticipated *cis* oxohydrazido(2−) geometry, maximizing the overlap of this strongly π-bonding group with the metal t_{2g} orbitals. The *trans* influence of the oxo group is apparent in the Mo–N1 distance of 2.323(3) Å, which is considerably longer than the Mo–N distance of 2.15 Å calculated for a Mo–N single bond unperturbed by a strongly π-bonding ligand in a *trans* position. The Mo–N2 distance of 2.245(3) Å suggests that the hydrazido(2−) ligand also exerts a significant *trans* influence, albeit a considerably weaker effect than that associated with the oxo group.

Further evidence for Mo–N3 multiple bonding may be drawn from the short Mo–N3 distance of 1.787(3) Å and the linear Mo–N3–N4 linkage. This overall linear geometry and the short N3–N4 distance of 1.298(4) Å indicate considerable multiple bonding between the nitrogens and delocalization throughout the Mo–N3–N4 moiety.

The distortions from idealized octahedral geometry are consequences of the varied ligand set, with both strongly π-bonding ligands and exclusively σ-bonding donors present, and of the constraints imposed by the five membered Mo–S–C–C–N chelate rings. Thus, the chelate bite angles for S1–Mo–N1 and S2–Mo–N2 are 63.45(8) and 65.88(8)°, respectively, considerably distorted from the octahedral limit of 90°. Furthermore, angles involving donors *cis* to the Mo–oxo and Mo–hydrazido moieties are forced to expand to values greater than 90° by the steric requirements of these π-bonding groups. These effects are reflected in the S1–Mo–S2 *'trans'* anlge of 148.23(4)°, a significant deviation from the idealized value of 180°. The overall low symmetry of the complex also finds expression in the inequivalent Mo–S1 and Mo–S2 distances of 2.514(1) and 2.432(1) Å, respectively.

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