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Dithiolate-hydrazido(2-) molybdenum complexes: synthesis and structure

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Dedicated in honor of Professor Pierre Braunstein

Abstract

Reaction of $[MoO_2(acac)_2]$ with an excess of $X(CH_2CH_2SH)_2$ where X = O, S leads to the formation of mononuclear complexes $[MoO_2\{X(CH_2CH_2S)_2\}]$: (1a) for X = O and (1b) for X = S. The complexes 1a and 1b react with organohydrazines in methanol, MeCN or THF to give the family of hydrazido(2-)-oxo-molybdenum compounds $[MoO(NNRR')\{X(CH_2CH_2S)_2\}]$: (2a) for R = R' = Me and X = O; (2b) for R = R' = Me and X = S; (2c) for R = Me, R' = Ph and X = O; (2d) for R = Me, R' = Ph and X = S. Similar reaction carried out in CH_2Cl_2 with an excess of NH_2NMe_2 leads to the formation of 2a and hydrazinium salt $[NH_2N(CH_2CI)Me_2]Cl$ consisting of tetrahedral cations bonded by hydrogen bonds to chloride ions as shown by X-ray studies. The X-ray crystal structures of 2a and 2b have been determined. These molecules have a distorted trigonal bipyramidal configuration with the hydrazido(2-) ligand bonded linearly in a *trans* position to either the ether oxygen or the thioether sulfur atoms of the dithiolate ligand. Me_3SiCl causes abstraction of the oxo group in 2a-2d to create the six-coordinate compounds $[Mo(Cl_2(NNRR')\{X(CH_2CH_2S)_2\}]$ (3a-3d), respectively. The chlorides in 3d can be easily substituted by oxygen and nitrogen donor ligands to give the new compounds $[Mo(di-t-Bu-cat)(NNRR')\{X(CH_2CH_2S)_2\}]$ (4) and $[Mo(NNRR')_2\{X(CH_2CH_2S)_2\}]$ (5), respectively.

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1. Introduction

Hydrazido(2-) complexes are plausible intermediates in the protonation of ligating dinitrogen to ammonia [1]. They may also be involved in the process catalysed by nitrogenase enzymes [2], in which the cofactor FeMco (M = Mo, V, Fe) has been considered the site responsible for the conversion of N₂ into NH₃ [3–5]. The X-ray crystallography showed FeMoco to contain an MoFe₇S₉ cluster with the Mo atom ligated by one histidine nitrogen, three sulfides and two oxygen atoms from homocitrate [6]. Research on the coordination chemistry of molybdenum complexes as models which mimic the molybdenum centre (MoS₃O₂N) in nitrogenase and are

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able to bind small molecules is of great importance in understanding the mode of action of this enzyme.

The interaction of complexes possessing а molybdenum-thiolate core with organohydrazine has been extensively investigated by Chatt, Zubieta, Dilworth and coworkers [7-15]. Recently a rich chemistry of the molybdenum [16] and vanadium [17,18] with the tripodal sulfur-donor ligand $N(CH_2CH_2S)_3^{3-}$ has been developed. It proved the ability of Mo and V carrying this ligand to bind species such as N₂H, N₂H₂ and N₂H₄ and their derivatives. Similar trend has been demonstrated for V with the tridentate dithiolate O(CH₂CH₂S)₂²⁻ [18].

As part of this continuing investigation, we report here the synthesis and reactivity of $[MoO_2{X(CH_2CH_2S)_2}]$ (X = O, S) towards organohydrazines. The crystal structures of $[MoO(N-NMe_2)({X(CH_2CH_2S)_2}]]$ (2a) for X = O and (2b) for

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X = S and the substitution reactions of the oxo group by chloride, catecholate and imide ligands are also described.

2. Experimental

2.1. General procedures

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds [MoO₂(acac)₂] [19] and [MoO(NNMePh)(acac)₂] [20] were prepared by literature methods. The sodium salt of 2,5-di-*tert*-butylcatechol Na₂(di-t-Bu-cat) was prepared by treating it with NaH in THF. All other starting materials were obtained from the Aldrich chemical Co. and used without further purification unless stated otherwise. Infrared spectra were recorded on a Perkin–Elmer 180 spectrophotometer in Nujol mulls. NMR spectra were performed on a Bruker ARX 300E spectrometer. Microanalysis were conducted with a ASA-1 (GDR, Karl-Zeiss-Jena) instrument (in-house).

2.2. Preparation of [MoO(NNMe₂)(acac)₂]

This compound was prepared by identical procedure to that reported in reference [20]. To a stirred suspension of $[MoO_2(acac)_2]$ (5.54 g, 17 mmol) in dry methanol (50 ml) was added NH₂NMe₂ (1.02 g, 17 mmol). The reaction mixture was stirred for 24 h at room temperature (r.t.). The resulting light orange precipitate was filtered off and washed with methanol and diethyl ether and dried in vacuum. Yield 97%. Elemental analysis: *Anal.* Found: C, 38.5; H, 5.3; N, 7.3. Calc. for C₁₂H₂₀N₂O₅Mo: C; 39.1; H, 5.5; N, 7.6%. IR (Nujol mulls, cm⁻¹): v(Mo=O) 942(s).

2.3. Preparation of $[MoO_2{O(CH_2CH_2S)_2}]$ (1a)

A suspension of $[MoO_2(acac)_2]$ (2.4 g, 7.37 mmol) and $O(CH_2CH_2SH)_2$ (1.02 g, 7.37 mmol) in methanol (30 ml) was stirred for approximately 10 h, during which time the brick-brown solid precipitated. It was filtered off, washed with methanol, diethyl ether and dried under vacuum. Yield 43%. Elemental analysis: *Anal.* Found: C, 18.2; H, 3.0; S, 23.7. Calc. for C₄H₈O₃S₂Mo: C; 18.2; H, 3.1; S, 24.3%. IR (Nujol mulls, cm⁻¹): v(Mo=O) 948(s), 912(s).

2.4. Preparation of $[MoO_2{S(CH_2CH_2S)_2}]$ (1b)

This compound was obtained in 39% yield as a burgundy-red solid from appropriate quantities of [MoO₂(acac)₂] and S(CH₂CH₂SH)₂ by a method similar

to that used to prepare **1a**. Elemental analysis: *Anal.* Found: C, 17.0; H, 2.8; S, 33.5. Calc. for $C_4H_8O_2S_3Mo$: C; 17.1; H, 2.9; S, 34.3%. IR (Nujol mulls, cm⁻¹): $\nu(Mo=O)$ 948(s), 912(s).

2.5. Preparation of $[MoO(NNMe_2) \{O(CH_2CH_2S)_2\}]$ (2a) and $[NH_2N(CH_2Cl)Me_2]Cl$

2.5.1. Method (a)

A suspension of **1a** (1.38 g, 5.2 mmol) and NH₂NMe₂ (0.31 g, 5.2 mmol) in MeCN (50 ml) was heated under refluxed for 6 h. The resulting mixture was filtered from a brown solid (which was characterised as the unreacted substrate), to give an orange–red solution. This was concentrated to about 10 ml in vacuum then allowed to stand overnight at r.t., whereupon yellow crystals suitable for X-ray analysis deposited. Yield 23%. Elemental analysis: *Anal.* Found: C, 23.2; H, 4.3; N, 9.0; S, 19.7. Calc. for C₆H₁₄O₂N₂S₂Mo: C; 23.5; H, 4.6; N, 9.2; S, 21.0%. IR (Nujol mulls, cm⁻¹): v(Mo=O) 920(s).

2.5.2. Method (b)

The compound NH_2NMe_2 (0.21 g, 3.5 mmol) was added dropwise to a stirred suspension of [MoO(N-NMe_2)(acac)_2] (1.29 g, 3.5 mmol) in MeOH (30 ml) and the mixture was stirred for 14 h. The resulting microcrystalline yellow solid was filtered off, washed with methanol, recrystallized from hot acetonitrile and dried in vacuum. Yield 96%.

2.5.3. Method (c)

To a stirred suspension of $[MoO_2{O(CH_2CH_2S)_2}]$ (3.29 g, 1.24 mmol) in CH_2Cl_2 (50 ml) was added NH₂NMe₂ (5 ml, 6.6 mmol). After stirring for 48 h at r.t. a light-brown crude $[NH_2N(CH_2Cl)Me_2]Cl$ precipitated from a dark brown solution. It was filtered off, washed with CH_2Cl_2 , recrystallized from hot MeCN and dried in vacuo. Yield 22%. Elemental analysis: *Anal.* Found: C, 24.5; H, 6.9; Cl, 48.0; N, 19.3. Calc. for $C_3H_{10}N_2Cl_2$: C; 24.8; H, 7.0; Cl, 48.9; N, 19.3%. IR (Nujol mulls, cm⁻¹): ν (N–H) 3258(s), 1582(m).

The dark brown filtrate was evaporated to dryness and washed with Et_2O to give, after recrystallisation, light yellow crystals of [MoO(NNMe₂){O(CH₂CH₂S)₂}] (2a). Yield 61.4%.

2.6. Preparation of [MoO(NNMe₂) {S(CH₂CH₂S)₂}] (2b), [MoO(NNMePh) {O(CH₂CH₂S)₂}] 2c, [MoO(NNMePh) {S(CH₂CH₂S)₂}] (2d)

These compounds were obtained by identical procedure to route 2.3(b) using appropriate quantities of $[MoO(NNMe_2)(acac)_2]$ or $[MoO(NNMePh)(acac)_2]$ and dithiol. Elemental analysis for: $[MoO(NNMe-Ph){O(CH_2CH_2S)_2}]$: *Anal.* Found: C, 35.2; H, 4.3; N, 7.2; S, 17.0. Calc. for $C_{11}H_{16}O_2N_2S_2Mo$: C; 35.9; H, 4.4; N, 7.6; S, 17.4%. IR (Nujol muls, cm⁻¹): ν (Mo=O) 922; [MoO(NNMe₂){S(CH₂CH₂S)₂}]: *Anal.* Found: C, 22.0; H, 4.3; N, 8.2; S, 29.0. Calc. for C₆H₁₄ON₂S₃Mo: C; 22.4; H, 4.4; N, 8.7; S, 29.8%. IR (Nujol muls, cm⁻¹): ν (Mo=O) 918; [MoO(NNMePh){S(CH₂CH₂S)₂}]: *Anal.* Found: C, 34.0; H, 4.3; N, 7.0; S, 24.2. Calc. for C₁₁H₁₆ON₂S₃Mo: C; 34.4; H, 4.2; N, 7.3; S, 25.0%. IR (Nujol muls, cm⁻¹): ν (Mo=O) 921.

2.7. Preparation of [MoCl₂(NNMe₂) {O(CH₂CH₂S)₂}] (**3a**), [MoCl₂(NNMePh) {O(CH₂CH₂S)₂}] (**3b**) and [MoCl₂(NNMePh) {S(CH₂CH₂S)₂}] (**3c**)

To a solution of **2a** (1.05 g, 3.4 mmol) in THF was added Me₃SiCl (0.74 g, 7.0 mmol) via a syringe to afford an intense green solution. The reaction mixture was stirred for 24 h during which time a dark-green solid precipitated. It was filtered off, washed with THF and dried under vacuum. Yield 87%. Elemental analysis for [MoCl₂(NNMe₂){O(CH₂CH₂S)₂}] (**3a**): *Anal.* Found: C, 19.8; H, 3.7; Cl, 19.2; N, 7.5; S, 17.2. Calc. for C₆H₁₄ON₂S₂Cl₂Mo: C; 20.0; H, 3.9; Cl, 19.6; N, 7.8; S, 17.8%. IR (Nujol mulls, cm⁻¹): ν (Mo–Cl) 366, 304.

 $[MoCl_2(NNMePh){O(CH_2CH_2S)_2}] (3b) and$ $[MoCl_2(NNMePh){S(CH_2CH_2S)_2}] (3c) were prepared$ by an identical procedure in approximately 80% yield. $Elemental analysis for [MoCl_2(NNMe-Ph){O(CH_2CH_2S)_2}] (3c): Anal. Found: C, 30.9; H,$ $3.78; Cl, 16.1; N, 6.4; S, 14.9. Calc. for C_{11}H_{16}ON_2-S_2Cl_2Mo: C; 31.2; H, 3.8; Cl, 16.8; N, 6.6; S, 15.5\%. IR$ $(Nujol mulls, cm⁻¹): <math>\nu$ (Mo-Cl) 364(m), 302(m).

 $[MoCl_2(NNMePh){S(CH_2CH_2S)_2}] (3d): Anal. Found: C, 30.0; H, 3.7; Cl, 15.9; N, 6.4; S, 19.9. Calc. for C_{11}H_{16}N_2S_3Cl_2Mo: C; 30.1; H, 3.7; Cl, 16.1; N, 6.4; S, 21.9\%. IR (Nujol mulls, cm⁻¹): <math>\nu$ (Mo-Cl) 366(m), 305(m).

2.8. Preparation of $[Mo(di-t-Bu-cat)(NNMePh) \{S(CH_2CH_2S)_2\}]$ (4)

To a suspension of **3c** (0.83 g, 1.9 mmol) in THF (30 ml) was added Na₂(di-t-Bu-cat) [generated in situ from H₂(di-t-Bu-cat) (0.42 g, 1.9 mmol) and NaH (0.1 g, 3.8 mmol) in THF]. After stirring for 24 h the solvent was removed in vacuo to give a dark oil, which was solidified by stirring with n-hexane. The solid was filtered, washed with n-hexane and extracted with CH₂Cl₂ to separate the product from LiCl. The extract was layered with n-hexane and allowed to stand for 2 days at r.t. to afford the green–brown crystalline product. Yield 61%. Elemental analysis: *Anal.* Found: C, 49.2; H, 5.8; N, 4.7. Calc. for C₂₅H₃₆N₂O₂S₃Mo: C; 51.0; H, 6.2; N, 4.8; S, 16.3%.

2.9. Preparation of [Mo(NNMePh)₂{O(CH₂CH₂S)₂}] (5)

To a suspension of **3a** (1.35 g, 3.73 mmol) in MeCN (50 ml) was added NH₂NMe₂ (0.22 g, 3.73 mmol). After stirring for 24 h an orange solid was isolated by filtration, washed with MeCN, Et₂O and dried in vacuo. Yield 78%. Elemental analysis: *Anal.* Found: C, 27.1; H, 5.6; N, 15.8; S, 17.5. Calc. for C₈H₂₀ON₄S₂Mo: C; 27.6; H, 5.8; N, 16.1; S, 18.4%.

2.10. Crystal structure determinations

Crystal data collection and refinement are summarized in Table 1. Preliminary examination and intensitydata collections were carried out on a Kuma KM-4 ĸaxis diffractometer with graphite-monochromated Mo Ka and with scintillation counter or CCD camera. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs [21,22]. The structures were solved by direct methods [23] and refined by the fullmatrix least-squares method on all F^2 data using the SHELXL-97 software [24]. After refinement with isotropic displacement parameters for all atoms, absorption correction based on least-squares fitted against $|F_c|$ – $|F_{\rm o}|$ differences was also applied [25] to the data for structure 2a and 2b. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL-97 default parameters. Other hydrogen atoms were located in a difference map and refined freely. All non-hydrogen atoms were refined with anisotropic displacement parameters.

3. Results and discussion

The molybdenum(VI) complexes MoO_2L , L = thiolates are usually synthesised by either of two possible routes: (1) reaction of $[MoO_2(acac)_2]$ with the appropriate ligand or (2) reaction of $Na_2MoO_4 \cdot 2H_2O$ with a stoichiometric amount of the ligand [26]. In our investigation the route (1) appeared to be the most convenient to reach the research aim summarised in Scheme 1. The reaction of $[MoO_2(acac)_2]$ with an excess of X(CH₂CH₂SH)₂ in MeOH yielded diamagnetic microcrystalline solids of formula $[MoO_2{X(CH_2CH_2S)}]$, which are red-brown for X = O (1a) and burgundy-red for X = S (1b). These complexes are air sensitive as the solid; they are insoluble except sparingly and with fast (few hours) decomposition in dimethyl sulfoxide. Their IR spectra exhibit the characteristic bands at approximately 910 and 950 cm⁻¹ due to the molybdenum-terminal oxygen vibrations v(Mo=O) and agree with those observed for mononuclear $MoO_2(L)$, L =

Table 1 Crystal data and structure refinement for **2a**, **2b** and [NH₂N(CH₂Cl)Me₂]Cl

Compound	2a	2b	[NH2N(CH2Cl)Me2]Cl
Chemical formula	$C_6H_{14}MoN_2O_2S_2$	C ₆ H ₁₄ MoN ₂ OS ₃	$C_3H_{10}Cl_2N_2$
Formula weight	306.25	322.31	145.03
Crystal color; habit	yellow, block	yellow, block	colorless, plate
Crystal size (mm)	$0.5 \times 0.5 \times 0.5$	$0.4 \times 0.4 \times 0.3$	$0.4 \times 0.4 \times 0.2$
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	7.036(3)	13.725(3)	7.052(1)
b (Å)	20.480(4)	7.219(2)	10.527(3)
<i>c</i> (Å)	7.748(3)	11.863(3)	8.792(2)
β (°)	93.80(4)	101.46(8)	90.49(3)
V (Å ³)	1114.0(7)	1152.0(5)	652.7(3)
Ζ	4	4	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.826	1.858	1.476
F(000)	616	648	304:0
$\mu ({\rm mm^{-1}})$	1.525	1.648	0.880
Absorption correction	semi-empirical	semi-empirical	none
Max. and min. transmission	0.982 and 0.791	0.8472 and 0.5151	
Diffractometer	KM-4 four circle κ-geometry	Kuma KM-4 CCD κ-geometry	Kuma KM-4 CCD κ-geometry
Radiation type, λ (Å)	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073
Data collection method	ω – 2 θ	ω	ω
<i>T</i> (K)	100(1)	100(1)	100(1)
θ Range (°)	2.82-25.06	3.50-28.37	3.48-28.40
Number of reflections measured	total: 1931; unique 1858	total: 6993; unique: 2654	total: 4217; unique: 1542
	$R_{\rm int} = 0.0146$	$R_{\rm int} = 0.0539$	$R_{\rm int} = 0.0338$
Number of observed reflections	1784 $[I > 2\sigma(I)]$	2454 $[I > 2\sigma(I)]$	$1322 [I > 2\sigma(I)]$
Final R indices $[F^2 > 4\sigma(F_o^2)]^{a,b}$	$R_1 = 0.0206, wR_2 = 0.0542$	$R_1 = 0.0372, wR_2 = 0.0974$	$R_1 = 0.0335, wR_2 = 0.0623$
R indices (all data) ^{a,b}	$R_1 = 0.0219, wR_2 = 0.0558$	$R_1 = 0.0408, wR_2 = 0.1002$	$R_1 = 0.0468, wR_2 = 0.0658$
Goodness-of-fit (S)	1.195	1.095	1.104
Largest difference peak and hole (e \AA^{-3})	0.534 and -0.556	0.768 and -1.034	0.247 and -0.294

^a
$$R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|.$$

^b $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}.$

(SCH₂CH₂NMe(CH₂)_nNMeCH₂CH₂S)²⁻, n = 2 or 3 [27]. No Mo-O-Mo bridge absorptions at approximately 740 and 440–495 cm⁻¹ were detected for **1a** and **1b**, characteristic for an Mo₂O₃⁴⁺ core in [Mo₂(μ -O)₂(O)₂{X(CH₂CH₂S)₂}] (X = O, S), which was obtained via route (2) by Zubieta et al. [28].

Upon treatment with NH₂NRR' in MeOH or MeCN, THF, complexes 1 give a family of hydrazido(2-) compounds $[MoO(NNRR'){X(CH_2CH_2S)_2}]$ where R = R' = Me, X = O (2a); R = R' = Me, X = S (2b); R = Me, R' = Ph, X = O (2c); R = Me, R' = Ph, X = S(2d) in reasonable yields. Almost quantitative yields of these compounds were obtained via reactions of [MoO(NNRR')(acac)₂] with appropriate thiols (see Scheme 1). Compounds 2a and 2b are mentioned in [14], however, there are no details of their preparation, crystal structures and reactivity. Only the Mo-N, N-N distances of 1.79, 1.29 Å and Mo-N-N angle of 174.3°, for [MoO(NNMe₂){O(CH₂CH₂S)₂] and 1.78, 1.29 Å and 176.2° for [MoO(NNMe₂){S(CH₂CH₂S)₂}], respectively, are presented. Since complexes 2a and 2b gave us X-ray quality crystals, we have determined their structures to allow us to make more detailed comparison with other systems as below. The structures are shown in Figs. 1 and 2; molecular dimensions are in Table 2. Both 2a and 2b have essentially distorted trigonal bipyramidal geometry with the two sulfur-donor ligands and the oxo group in the trigonal plane and the hydrazido(2-) ligand *trans* to the apical ether oxygen (2a) or thioether sulfur (2b) of the thiolate ligands. The short Mo-N and N-N bond distances of 1.79(2) and 1.276(3) Å for 2a and 1.824(3) and 1.271(4) Å for 2b, respectively, together with the Mo-N-N bond angles of 169.7(2) for 2a and 163.2(2) for **2b** are in normal range for five-coordinate hydrazido(2-) complexes of this type e.g., [MoO(N-NMe₂)(SPh)₃]⁺ has Mo-N and N-N distances of 1.806 and 1.30 Å, respectively, and Mo-N-N angle of 176.7° [13] and $[MoCl(NNMe_2)_2(PPh_3)_3]^+$ has Mo-N and N-N distances of 1.761 and 1.25 Å, respectively, and Mo-N-N angle of 173.9° [29]. These data indicate extensive delocalisation through the Mo-N-N unit and are consistent with the description of the hydrazido(2-) ligand acting as the four-electron donor to the Mo atom. The Mo-S thiolate distances 2.358(2), 2.38(1) Å for 2a and 2.383(2), 2.373(1) Å for **2b** are close to the range of Mo-S thiolate distances found in the related trigonal bipyramidal complexes [MoO(N-NHPh {O(CH₂CH₂S)₂} [14], and [Mo(NS₃)(NNR)] R = Me, Ph; NS₃ = $[N(CH_2CH_2S)]^{3-}$ [16].





The ¹H NMR spectra at room temperature consist of one singlet at 3.60 ppm for **2a** and two singlets at 3.73 and 3.70 ppm for **2b** for the methyl groups of the dimethylhydrazido ligand. At 203 K (coalescence point) one singlet at 3.74 ppm due to the NMe₂ group is observed for **2b**. As well as these, three multiplets at 4.63, 3.57, 3.20 ppm for **2a** and 4.05, 3.10, 2.15 ppm for **2b** for the CH₂ groups of the dithiolate ligands are observed.

Attempts to prepare [MoO(NNMe₂){X(CH₂CH₂S)₂}] from [MoO₂{X(CH₂CH₂S)₂}] and NH₂NMe₂ in CH₂Cl₂ led after work-up to a light beige solid. IR data showed a N–H bands at 3258 and 1582 cm⁻¹ while the ¹H NMR spectrum contained three singlet resonances assigned to the CH₃, CH₂ and HO groups at 3.48, 5.54 and 6.54 (broad) ppm, respectively. The X-ray structure analysis showed the solid to be a hydrazinium salt [NH₂N(CH₂Cl)Me₂]Cl consisting of approximately tetrahedral cations $[NH_2N(CH_2Cl)Me_2]^+$, bonded by hydrogen bonds to chloride ions. The central nitrogen in the cation is surrounded by one amino, two methyl and one chloromethane groups (Fig. 3). The average angle between the central nitrogen and the terminal atoms in the cation equals the tetrahedral angle. The N-N distance of 1.460(2) Å is similar to the value of 1.45(3)Å found for 1,1-dimethylhydrazine [30] and is in the range of single bonds [31]. Internuclear distances and angles are listed in Table 3. The distances between the chloride ions and the amino hydrogens 2.42(2) and 2.36(2) Å (Table 4) are shorter than the minimum $H \cdots Cl$ nonbonded distance, indicating that both amino hydrogens form hydrogen bonds to chloride ions. The

Table 2



Fig. 1. The molecular structure of 2a with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.



Fig. 2. The molecular structure of 2b with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

two hydrogen bonds $H(1N)\cdots Cl(2)$ and $Cl(2)^{a}\cdots H(2N)$ link the cations. This results in zigzag chains running parallel to the [010] direction (Fig. 4). Hydrogen bonds have also been reported in the structures of the salts of hydrazinium cations; e.g., $N_2H_6Cl_2$ [32], [CH₃)₃NNH₂]Cl [33].

Further substitution of the oxo ligand in complexes 2a-2d by either dimethyl- and methylphenylhydrazines

Selected bond distances (Å) and angles (°) for (2a) and (2b)			
	2a	2b	
Bond lengths			
Mo-S(1)	2.358(2)	2.383(2)	
Mo-S(2)	2.380(1)	2.373(1)	
Mo-S(3)		2.514(2)	
Mo-O(1)	1.695(2)	1.703(2)	
Mo-O(2)	2.221(2)		
Mo-N(1)	1.790(2)	1.824(3)	
S(1) - C(1)	1.820(3)	1.823(3)	
S(2) - C(4)	1.819(3)	1.824(4)	
S(3) - C(2)		1.808(4)	
S(3) - C(3)		1.819(3)	
N(1) - N(2)	1.276(3)	1.271(4)	

MO-N(1)	1.790(2)	1.824(3)	
S(1)-C(1)	1.820(3)	1.823(3)	
S(2)-C(4)	1.819(3)	1.824(4)	
S(3) - C(2)		1.808(4)	
S(3) - C(3)		1.819(3)	
N(1) - N(2)	1.276(3)	1.271(4)	
N(2)-C(6)	1.453(3)	1.465(4)	
N(2)-C(5)	1.454(4)	1.465(4)	
C(1) - C(2)	1.489(4)	1.511(4)	
C(3)-C(4)	1.498(4)	1.514(4)	
O(2)-C(3)	1.451(3)		
O(2)-C(2)	1.457(3)		
Bond angles			
S(1) - Mo - S(2)	135.49(3)	130.52(4)	
S(1) - Mo - S(3)		82.20(5)	
S(2) - Mo - S(3)		82.34(4)	
O(1)-Mo-N(1)	107.27(11)	106.58(12)	
O(1)-Mo-O(2)	100.03(9)		
O(1)-Mo-S(3)		96.12(9)	
O(1)-Mo-S(1)	108.35(7)	114.83(9)	
O(1)-Mo-S(2)	113.11(8)	113.39(8)	
O(2)-Mo-S(1)	78.88(6)		
O(2)-Mo-S(2)	78.71(6)		
N(1)-Mo-O(2)	152.62(9)		
N(1)-Mo-S(1)	90.41(8)	88.12(9)	
N(1)-Mo-S(2)	92.24(8)	88.58(9)	
N(1)-Mo-S(3)		157.30(10)	
Mo-N(1)-N(2)	169.7(2)	163.2(2)	



Fig. 3. The molecular structure of $[NH_2N(CH_2Cl)Me_2]Cl$ with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

or monosubstituted derivatives such as methyl- and

Table 3 Selected bond distances (Å) and angles (°) for [NH₂N(CH₂Cl)Me₂]Cl

Bond lengths	
Cl(1)-C(1)	1.758(2)
N(1)-N(2)	1.460(2)
N(1)-C(3)	1.494(2)
N(1)-C(2)	1.500(2)
N(1)-C(1)	1.501(2)
Bond angles	
N(2)-N(1)-C(3)	107.60(13)
N(2)-N(1)-C(2)	111.89(13)
C(3)-N(1)-C(2)	110.69(14)
N(2)-N(1)-C(1)	102.56(13)
C(3)-N(1)-C(1)	111.37(13)
C(2)-N(1)-C(1)	112.39(14)
N(1)-C(1)-Cl(1)	111.77(12)

Table 4 Hydrogen bonds for [NH₂N(CH₂Cl)Me₂]Cl] (Å and °)

D-HA	d(D-H)	d(HA)	d(DA)	∠(DHA)
N(2)-H(1N)Cl(2)	0.91(2)	2.36(2)	3.258(2)	168(2)
N(2)-H(2N)Cl(2) ^a	0.81(2)	2.42(2)	3.228(2)	175(2)

^a Symmetry transformations used to generate equivalent atoms: -x+3/2, y+1/2, -z+3/2.



Fig. 4. The crystal packing of $[NH_2N(CH_2CI)Me_2]CI$ viewed down the *a*-axis. Hydrogen bonds are indicated by dashed lines.

phenylhydrazines does not give bis[hydrazido(2-)] complexes even after prolonged refluxing. This indicate that in the case of complexes 2a-2d the basicity of the hydrazine does not play a crucial role in dictating the reaction pathway, in contrast to the system based on $[MoO_2\{(SCH_2CH_2)_2NCH_2CH_2NMe_2\}]$ in which NH_2NMePh replaces only one oxo group but NH_2NHPh forms bis[hydrazido(2-)] complex [15]. We consider that the reactivity of oxo-molybdenum precursors depends on various factors, that include the basicity of hydrazines, the identity of coligands which influence profoundly the geometry of the complexes and the overall electronic effects. Because of this the products of the reactions are not always predictable.

The replacement of the oxo group in 2a-2d by two chlorides occurs in reaction with an excess of Me₃SiCl in methanol to regenerate the six-coordinate compounds $[MoCl_2(NNRR') \{X(CH_2CH_2S)_2\}] R = R' = Me, X = O$ (3a); R = R' = Me, X = S (3b); R = Me, R' = Ph, X = O(3c), R = Me, R' = Ph, X = S (3d), which are insoluble in common organic solvents. The IR bands at approximately 360 and 300 cm⁻¹, attributed to v(Mo-Cl) confirm the presence of Cl ligands in the cis position, while the absence of bands of significant intensity in the $850-1000 \text{ cm}^{-1}$ region is consistent with the absence of the terminal oxo-unit. This means that treatment of the oxo-hydrazido(2-) complexes (3a-3d) with acid does not involve reactions at the hydrazido-nitrogens to give hydrazido(1-) or other protonated nitrogenous products. Similar trend was observed for other oxohydrazido(2-)molybdenum compounds [34].

Both chloride atoms in 3c were successfully substituted by a catecholate ligand in a stoichiometric reaction with $Na_2(di-t-Bu-cat)$ (di-t-Bu-cat = 2,5-di-tert-butylcatecholate) in THF to give brown microcrystals of [Mo(di-t-Bu-cat)(NNMePh){S(CH₂CH₂S)₂}] (4), identified by elemental analysis, IR and ¹H NMR spectroscopy. Compound 4 is stable as the solid in an inert atmosphere; soluble in CH2Cl2, THF, MeCN and insoluble in hydrocarbons. In its ¹H NMR spectrum, complex 4 shows three multiplet resonances for CH₂ groups at δ 3.89, 3.30 and 2.84 ppm and a singlet at δ 3.30 ppm and multiplet at δ 6.89 ppm for the Me and Ph groups of the hydrazido(2-) ligand, respectively, and also the following resonances for the coordinated di*tert*-butylcatecholate: a singlet at δ 1.74 ppm for *tert*butyl and multiplet at δ 7.3 ppm for phenyl group.

The reaction of **3a** with dimethylhydrazine in MeCN gave an orange, insoluble in common organic solvents bis[hydrazido(2-)] compound [Mo(N-NMe₂)₂{O(CH₂CH₂S)₂}] (**5**). Its IR spectrum does not show Mo-Cl frequencies indicating the substitution of chlorides in **3a**. Treatment of **5** with an excess of HCl causes the formation of untractable molybdenum product containing chloride and the liberation of NH₂NMe₂·HCl at 1:1 molar ratio suggesting the protonation of only one hydrazido(2-) ligand.

4. Conclusions

The reaction of the Mo=O unit in complexes 1 with organohydrazines generates hydrazido(2-)-oxo-molybdenum compounds [MoO(NNRR'){ $X(CH_2CH_2S)_2$ }] (2a-2d). The elimination of the oxo group in 2 occurs in the reaction with Me₃SiCl in methanol to form the six-coordinate compounds [MoCl₂(NNRR'){ $X(CH_2CH_2S)_2$ }] (3a-3d). The formation of compounds 3 indicates that acids do not protonate the hydrazido(2-) ligand in 2 but instead attack the molybdenum centre. The chlorides in 3 can be easily substituted by oxygen or nitrogen donor ligands to create the new hydrazido(2-) compounds [Mo(di-tBu-cat)(NNMePh){ $S(CH_2CH_2S)_2$] (4) and [Mo(N-NMe₂)₂{O(CH₂CH₂S)₂}] (5).

5. Supplementary material

Supplementary material is available from the Cambridge Crystallographic Data Centre and comprises experimental data for the X-ray diffraction studies including atom coordinates, thermal parameters and remaining bond lengths and angles for compounds 2a, 2b and [NH₂N(CH₂Cl)Me₂]Cl. Copies of this information may be obtained from The Director, CCDC 188768–188770, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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