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Article

A New Class of Sulfido/Oxo(dithiolene)−Molybdenum(IV) Complexes Derived from Sulfido/Oxo-Bis(tetrasulfido)molybdenum(IV) Anions

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Mono(dithiolene)sulfidomolybdenum(IV) complexes, $[MoS(S_4)(bdt)]^{2-}$ (**2**) and $[MoS(S_4)(bdtCl_2)]^{2-}$ (**3**) (1,2-benzenedithiolate = bdt, 3,6-dichloro-1,2-benzenedithiolate = $bdtCl_2$), were prepared by the substitution reaction of a tetrasulfido ligand in known $[MoS(S_4)_2]^{2-}$ (**1**) with the corresponding dithiol. Complexes **2** and **3** were irreversibly oxidized to give bis(μ-sulfido) dimolybdenum(V) species, $\{[MoS(bdt)]_2(\mu\text{-}S)_2\}^{2-}$ (**4**) and $\{[MoS(bdtCl_2)]_2(\mu\text{-}S)_2\}^{2-}$ (**5**), in aerobic acetonitrile. Mono(dithiolene)oxomolybdenum(IV) complexes, $[MoO(S_4)(bdt)]^{2-}$ (**7**) and $[MoO(S_4)(bdtCl_2)]^{2-}$ (**8**), that are oxo derivatives of **2** and **3** were also synthesized from a known $[MoO(S_4)_2]^{2-}$ (**6**) of an oxo derivative of **1** and the corresponding dithiol. Further, the electrophilic addition of dimethyl acetylenedicarboxylate to **7** gave $[MoO(bdt)(S_2C_2(COOMe)_2)]^{2-}$ (**9**), and ligand substitution of the tetrasulfido group of **7** with bdt and $bdtCl_2$ yielded $[MoO(bdt)_2]^{2-}$ (**10**) and $[MoO(bdt)(bdtCl_2)]^{2-}$ (**11**), respectively. New sulfido/oxo molybdenum complexes were characterized by ^1H NMR, IR, ESI-MS, Raman, and UV−vis spectroscopies; cyclic voltammetry; and elemental analysis, and crystal structures of **2**, **3**, **5**, **7**, and **8** were determined by X-ray analysis.

Introduction

In recent years, much attention has been directed toward the synthesis of metal−dithiolene complexes. This interest is primarily due to their utility in magnetic materials,[1] superconductors,[1] nonlinear optical materials,[1] and luminescent sensors[2] as well as in supramolecular architectures.[3] Molybdenum (Mo)-containing enzymes, except nitrogenase, universally possess pyranopterindithiolene cofactors and are classified into the xanthine oxidase family featured by mono(dithiolene)MoS centers, the sulfite oxidase family characterized by mono(dithiolene)MoO centers, and the DMSO reductase family consisting of bis(dithiolene)Mo centers,[4] and this finding has given new significance to chemistry of dithiolene complexes of Mo.[4] Synthetic analogues of the enzyme reaction centers have been developed for elucidating the structure/reaction relationships.[5−7] Among the synthetic analogues, a limited number of mono(dithiolene)-Mo complexes relating to reaction centers of the xanthine oxidase family and sulfite oxidase family have been reported, whereas many bis(dithiolene) complexes including MoO,[5−8] MoS,[9] and MoSe[10] and des-oxo Mo[5−7,11] functional groups were presented as synthetic analogues of DMSO reductase family reaction centers. In particular, significantly fewer are a type of mono(dithiolene)MoS complex, resulting in only

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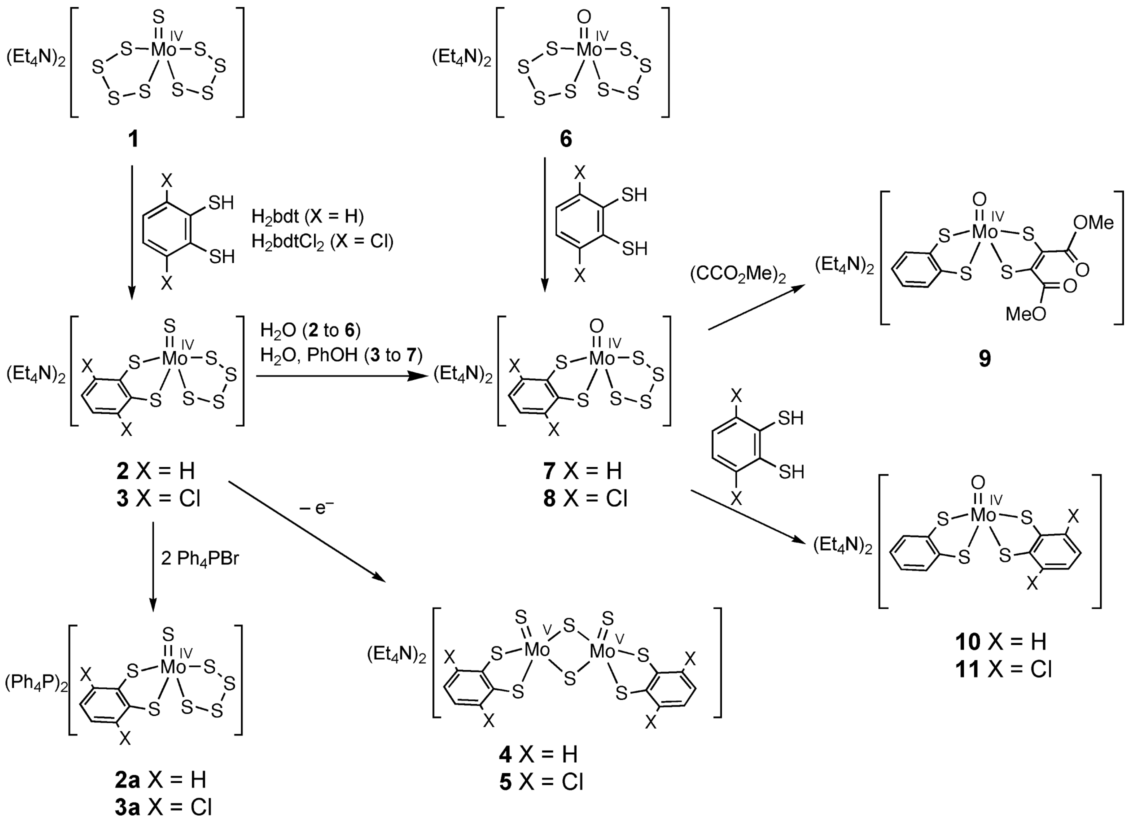
Scheme 1. Preparation Procedures of **2**, **3**, **4**, **5**, **7**, **8**, **9**, **10**, and **11**



one series of [Tp*$Mo^{V/IV}$S(dithiolene)]$^{0/-}$ complexes (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate);[12,13] this indicates that the incorporation of one terminal sulfido group into a mono(dithiolene)Mo center is a still difficult task. With respect to mono(dithiolene)MoO complexes, some types of the species have been synthesized with mono-,[14] di-,[15] or tridentate[16] coligands. Therefore, development of new synthetic procedures for various types of mono(dithiolene)-MoS/O complexes is necessary to expand the fields of bioinorganic chemistry as well as material science.

In this study, we employ the known $(Et_4N)_2[Mo^{IV}S(S_4)_2]$ (**1**) from the literature[17] to prepare novel dithiolene complexes of Mo, because **1** comprises a square pyramidal Mo center with substitutable sulfido and tetrasulfido ligands and can be easily obtained from commercially available reagents of MoS_4^{2-} and elemental sulfur.[17] Here, we describe the synthesis of $(Et_4N)_2[Mo^{IV}S(S_4)(bdt)]$ (**2**, bdt = 1,2-benzenedithiolate) and $(Et_4N)_2[Mo^{IV}S(S_4)(bdtCl_2)]$ (**3**, $bdtCl_2$ = 3,6-dichloro-1,2-benzenedithiolate) from **1** and the corresponding dithiol and characterizations of **2** and **3**. Reaction of the oxo analogue of **1**, $(Et_4N)_2[Mo^{IV}O(S_4)_2]$ (**6**),[18] which is obtained from commercially available reagents $Mo_7O_{24}^{6-}$, S^{2-}, and elemental sulfur, with H_2bdt and H_2bdtCl_2 is also revealed to yield oxo analogues of **2** and **3**, $(Et_4N)_2[Mo^{IV}O(S_4)(bdts)]$ (bdts = bdt (**7**) and $bdtCl_2$ (**8**)). Furthermore, the conversion of **7** to bis(dithiolene)Mo^{IV}O complexes, $(Et_4N)_2$[MoO-(bdt)(dithiolene)] (dithiolene = $S_2C_2(CO_2Me)_2$ (**9**), bdt (**10**), and $bdtCl_2$ (**11**)) is briefly described. The complexes obtained in this study are new members of dithiolene complexes of Mo (Scheme 1).

Experimental Section

General. All reagents and solvents were used as received unless otherwise noted. Acetonitrile was dried over CaH_2 and then P_2O_5 and distilled under dinitrogen prior to use. All reactions were carried out under dinitrogen in a Schlenk tube. $(Et_4N)_2[MoS(S_4)_2]$ (**1**) and $(Et_4N)_2[MoO(S_4)_2]$ (**6**) were prepared by following the literature procedures.[17,18]

Synthesis and Characterization of Complexes. $(Et_4N)_2$[MoS-(S_4)(bdt)] (2). H_2bdt (9.0 μL, 0.078 mmol) was added to **1** (50.0 mg, 0.077 mmol) suspended in acetonitrile (15 mL). Within 30 min of stirring, the suspension changed to a brown solution, which was then concentrated to ca. 3 mL. After removal of the precipitated

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(13) [Tp*$Mo^{V}S(S_2C_2(CO_2Me)_2)$] was obtained as a mixture with the MoO derivative from a reaction of (Et_4N)[Tp*MoS/O(S_4)] and DMAD.[16c]

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elemental sulfur from the solution, an orange microcrystalline powder precipitated from the solution and was collected by filtration. Yield: 30.5 mg (60%). Anal. calcd for $C_{22}H_{44}MoN_2S_7$ (mol wt. 656.96): C, 40.22; H, 6.75; N, 4.26. Found: C, 40.17; H, 6.72; N; 4.24. ^{1}H NMR (CD_3CN, anionic part): δ 6.86 (m, 2H), 7.61 (m, 2H). UV−vis spectrum (CH_3CN): λ_{max} = 336 (ε = 16200), 440 nm (3500 dm^3 mol^{-1} cm^{-1}). ESI-MS (CH_3CN): *m/z* 528 {$[M]^{2-}$ + Et_4N^+}$^-$. CV (CH_3CN): E_{pa}(irrev.) = −0.10 V vs saturated calomel electrode (SCE). IR (KBr): ν 500 (vs), 664 (w), 751 (s), 754 (m), 1002 (s), 1022 (m), 1172 (s), 1239 (m), 1287 (m), 1391 (vs), 1433 (vs), 1457 (vs), 1479 (vs), 1547 cm^{-1} (w).

$(Ph_4P)_2[MoS(S_4)(bdt)]$ (2a). After the addition of Ph_4PBr (64.0 mg, 0.153 mmol) to an acetonitrile solution of **2** (50.0 mg, 0.076 mmol), the resultant brown solution stood for several days to give an orange microcrystalline powder. The powder was collected by filtration and dried *in vacuo*. Yield: 56.0 mg (68%). Anal. calcd for $C_{54}H_{44}MoP_2S_7$ (mol wt. 1075.29): C, 60.32; H, 4.12. Found: C, 60.06; H, 4.09. ESI-MS (CH_3CN): *m/z* 737 {$[M]^{2-}$ + Ph_4P^+}$^-$.

$(Et_4N)_2[MoS(S_4)(bdtCl_2)]$ (3). This complex was prepared as described above for the synthesis of **2** by using H_2bdtCl_2 instead of H_2bdt. Yield: 24.3 mg (43%). Anal. calcd for $C_{22}H_{42}Cl_2MoN_2S_7$ (mol wt. 724.90): C, 36.40; H, 5.83; N, 3.86. Found: C, 36.58; H, 5.68; N; 4.00. ^{1}H NMR (CD_3CN, anionic part): δ 7.01 (s, 2H). UV−vis spectrum (CH_3CN): λ_{max} = 330 (sh), 423 nm (ε = 3700 dm^3 mol^{-1} cm^{-1}). ESI−MS (CH_3CN): *m/z* 596 {$[M]^{2-}$ + Et_4N^+}$^-$. CV (CH_3CN): E_{pa}(irrev.) = +0.04 V vs SCE. IR (KBr): ν 502 (vs), 595 (w), 782 (s), 811 (m), 1000 (s), 1058 (vs), 1155 (s), 1170 (s), 1182 (s), 1270 (s), 1329 (s), 1394 (vs), 1453 (vs), 1477 (vs), 1521 cm^{-1} (w).

$(Ph_4P)_2[MoS(S_4)(bdtCl_2)]$ (3a). This complex was prepared by a similar method as for the preparation of **2a** except that **3** (50.0 mg, 0.069 mmol) was applied instead of **2**. Yield: 56.8 mg (72%). Anal. calcd for $C_{54}H_{42}Cl_2MoP_2S_7$ (mol wt. 1144.18): C, 56.69; H, 3.37. Found: C, 56.85; H, 3.54. ESI-MS (CH_3CN): *m/z* 805 {$[M]^{2-}$ + Ph_4P^+}$^-$.

$(Et_4N)_2[MoS(bdt)]_2(\mu\text{-}S)_2$ (4). An acetonitrile solution (10 mL) containing **2** (24.9 mg, 0.038 mmol) was exposed to the air with stirring for 5 h at 60 °C. After concentration of the obtained brown solution to ca. 3 mL, a brown microcrystalline powder precipitated, which was collected by filtration and dried in the air. Yield: 19.2 mg (57%). The ^{1}H NMR, UV−vis, ESI-MS, and IR spectra were identical to those reported in the literature.[19]

$(Et_4N)_2[MoS(bdtCl_2)]_2(\mu\text{-}S)_2$ (5). This complex was synthesized by a similar method as for the preparation of **4** except that **3** (50.0 mg, 0.069 mmol) was reacted instead of **2**. Yield: 35.0 mg (51%). Anal. calcd for $C_{28}H_{44}Cl_4Mo_2N_2S_8$ (mol wt. 998.89): C, 33.67; H, 4.44; N, 2.80. Found: C, 33.63; H, 4.21; N; 2.89. ^{1}H NMR (CD_3CN, anionic part): δ 7.16 (s, 11H). ESI-MS (CH_3CN): *m/z* 370 {M}$^{2-}$. CV (CH_3CN): $E_{1/2}$ (rev.) = −1.58, E_{pc}(irrev.) = −1.93 V vs SCE. IR (KBr): ν 451 (w), 527 (vs), 600 (w), 792 (w), 819 (m), 998 (w), 1065 (s), 1158 (s), 1267 (s), 1336 (vs), 1397 (vs), 1436 (w), 1455 (w), 1478 (w), 1525 cm^{-1} (w).

$(Et_4N)_2[MoO(S_4)(bdt)]$ (7). Method A. Water (5 mL) was added to an acetonitrile solution (45 mL) of **2** (32.9 mg, 0.050 mmol). The resultant brown solution was stirred for 5 h and concentrated to ca. 2 mL. An orange microcrystalline powder precipitated from the solution, which was collected by filtration. Yield: 21.8 mg (68%). Anal. calcd for $C_{22}H_{44}MoN_2OS_6$ (mol wt. 640.93): C, 41.23; H, 6.92; N, 4.37. Found: C, 41.12; H, 6.86; N; 4.31. ^{1}H NMR (CD_3CN, anionic part): δ 6.79 (m, 2H), 7.50 (m, 2H). UV−vis spectrum (CH_3CN): λ_{max} = 322 (16 000), 422 nm (ε = 3500 dm^3 mol^{-1} cm^{-1}). ESI-MS (CH_3CN): *m/z* 512 {$[M]^{2-}$ + Et_4N^+}$^-$. CV (CH_3CN): E_{pa}(irrev.) = −0.05 V vs SCE. IR (KBr): ν 662 (w), 761 (s), 781 (m), 927 (vs), 1001 (s), 1021 (m), 1091 (w), 1171 (s), 1236 (s), 1391 (vs), 1434 (vs), 1451 (s), 1483 (vs), 1547 cm^{-1} (w).

Method B. To an acetonitrile solution (50 mL) of $(Et_4N)_2[MoO(S_4)_2]$ (100 mg, 0.159 mmol), H_2bdt (18.3 μL, 0.159 mmol) was added. The brown solution was stirred for 3 h at 60 °C and then concentrated to ca. 5 mL. After removal of the precipitated elemental sulfur from the solution by filtration, diethyl ether (20 mL) was then added to the filtrate. A brown microcrystalline powder precipitated and was collected by filtration. Yield: 77.4 mg (76%). The UV−vis and IR spectra were identical with those of **7** prepared by method A.

$(Et_4N)_2[MoO(S_4)(bdtCl_2)]$ (8). As it was difficult to purify this complex by method A for **7** on a synthetic scale, **8** was prepared by method B for **7**, except that H_2bdtCl_2 was used instead of H_2bdt. Yield: 81.2 mg (72%). Anal. calcd for $C_{22}H_{42}Cl_2MoN_2OS_6$ (mol wt. 709.83): C, 37.23; H, 5.96; N, 3.95. Found: C, 37.27; H, 5.94; N; 3.95. ^{1}H NMR (CD_3CN, anionic part): δ 6.95 ppm (s, 2H). UV−vis spectrum (CH_3CN): λ_{max} = 329 (ε = 9200), 429 nm (1400 dm^3 mol^{-1} cm^{-1}). ESI-MS (CH_3CN): *m/z* 580 {$[M]^{2-}$ + Et_4N^+}$^-$. CV (CH_3CN): E_{pa}(irrev.) = +0.05 V vs SCE. IR (KBr): ν 785 (s), 806 (s), 919 (vs), 1001 (s), 1058 (s), 1153 (s), 1171 (s), 1182 (s), 1268 (s), 1330 (s), 1395 (vs), 1457 (vs), 1477 (s), 1527 cm^{-1} (w).

$(Et_4N)_2[MoO(bdt)(S_2C_2(COOMe)_2)]$ (9). To an acetonitrile solution (4 mL) of **7** (100.8 mg, 0.16 mmol), dimethyl acetylenedicarboxylate (28.9 μL, 0.24 mmol) was added. After stirring for 6 h, the resulting solution was concentrated to ca. 1 mL. Elemental sulfur precipitated from the solution and was removed by filtration. An orange powder precipitated from the resultant solution, which was collected by filtration and recrystallized by CH_3CN/diethyl ether. Yield: 62.3 mg (55%). Anal. calcd for $C_{28}H_{50}MoN_2O_5S_4$ (mol wt. 718.92): C, 46.78; H, 7.01; N, 3.90. Found: C, 46.70; H, 6.95; N; 3.87%. ^{1}H NMR (CD_3CN, anionic part): δ 3.69 (s, 6H), 6.73 (m, 2H), 7.49 (m, 2H). ESI-MS (CH_3CN): *m/z* 590 {M + Et_4N}$^-$, 460 {M}$^-$. CV (CH_3CN): $E_{1/2}$(rev.) = −0.24 V vs SCE. IR (KBr): ν 753 (w), 908 (s), 1021 (s), 1234 (vs), 1435 (s), 1481 (w), 1530 (w), 1718 cm^{-1} (vs).

$(Et_4N)_2[MoO(bdt)_2]$ (10). H_2bdt (9.8 μL. 0.085 mmol) was added to an acetonitrile solution (50 mL) of **7** (50.0 mg, 0.08 mmol), and the solution was stirred for 4 h at 40 °C. The resulting green solution was concentrated to ca. 9 mL and then stood for 1 h. After elemental sulfur precipitated and was removed by filtration, a pale microcrystalline powder precipitated from the filtrate, which was collected by filtration and washed with CS_2. Yield: 16.1 mg (32%). The ^{1}H NMR, UV−vis, ESI-MS, and IR spectra were identical with those reported in the literature.[20]

$(Et_4N)_2[MoO(bdt)(bdtCl_2)]$ (11). This complex was prepared as described above for the synthesis of **10** by using H_2bdtCl_2 instead of H_2bdt. Yield: 25.9 mg (46%). Anal. calcd for $C_{28}H_{48}Cl_2MoN_2O_2S_4$ (mol wt. 721.80): C, 46.59; H, 6.62; N, 3.88. Found: C, 46.68; H, 6.24; N, 3.78. ^{1}H NMR ($(CD_3)_2SO$, anionic part): δ 6.66 (m, 2H), 6.84 (s, 2H), 7.43 (m, 2H). UV−vis spectrum (CH_3CN): λ_{max} = 330 (sh), 423 nm (ε = 3700 dm^3 mol^{-1} cm^{-1}). ESI-MS (CH_3CN): *m/z* = 592 {$[M]^{2-}$ + Et_4N^+}$^-$, 462 {$[M]^{2-}$ − e^-}$^-$. CV (CH_3CN): $E_{1/2}$(rev.) = −0.24 V vs SCE. IR (KBr): ν

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Table 1. Crystallographic Data for **1**−**8a**

	2	**2a·DMF**	**3a·DMF**	**5**	**7**	**8a**
formula	$C_{22}H_{44}MoN_2S_7$	$C_{57}H_{51}MoNOP_2S_7$	$C_{57}H_{49}Cl_2MoNOP_2S_7$	$C_{28}H_{44}Cl_4\ Mo_2N_2S_8$	$C_{22}H_{44}MoN_2OS_6$	$C_{38}H_{42}Cl_2MoNOPS_6$
fw	656.96	1148.34	1217.23	998.84	640.89	918.94
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/a$	*Pbcn*	$P2_1/c$
a, Å	9.229(2)	11.1008(2)	10.421(1)	17.118(3)	30.103(2)	16.427(2)
b, Å	30.116(6)	22.032(3)	13.519(2)	13.014(3)	14.4075(7)	14.070(2)
c, Å	10.893(2)	21.427(4)	20.424(3)	18.085(4)	13.6530(7)	17.529(2)
α, deg	90	90	80.555(7)	90	90	90
β, deg	100.803(2)	91.921(3)	88.458(7)	92.013(4)	90	95.436(3)
γ, deg	90	90	75.768(6)	90	90	90
V, Å^3	2974(1)	5238(2)	2750.9(6)	4027(1)	5921.4(5)	4033.3(9)
Z	4	4	2	4	8	4
ρ, g cm^{-3}	1.467	1.456	1.469	1.648	1.438	1.513
μ, mm^{-1}	0.947	0.632	0.700	1.325	0.884	0.839
data	26598	52277	29465	37589	40479	41869
unique data	7021	11962	12400	9212	6413	9207
R1^a	0.0446	0.0743	0.0723	0.0790	0.0627	0.0708
wR2 (F^2)^b	0.1026	0.1503	0.1729	0.1511	0.1103	0.1939
GOF	1.085	0.992	0.992	1.140	1.319	1.004

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = \{\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2\}^{1/2}$.

755 (m), 784 (w), 805 (m), 907 (s), 998 (s), 1055 (s), 1151 (s), 1172 (s), 1267 (m), 1324 (m), 1392 (s), 1433 (w), 1482 (vs), 1524 (w) cm^{-1}.

Physical Measurements. FT-IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer. Resonance Raman (rR) scattering was excited at 488 nm with an Ar$^+$ ion laser (Spectra Physics, 2017) and detected with a triple polychromator (Jasco, NRS-1800) equipped with a CCD detector (Princeton Instruments). rR spectra were measured at ambient temperature in a spinning cell (3000 rpm). Raman shifts were calibrated with inden. Solid FT Raman (FTR) spectra were measured with a Perkin-Elmer Spectrum GX-Raman spectrometer. ^{1}H NMR spectra were recorded with a JEOL Lambda 300, and the TMS signal was adjusted to 0 ppm. ESI-MS spectra were measured with a JEOL JMS-700S. UV−vis spectra were recorded on a HP-8453 spectrometer.

Electrochemistry. Cyclic voltammetric measurements were performed under dinitrogen with a Hokuto Denko HZ-3000 potentiostat. A set of a glassy-carbon working electrodes with a circle 3 mm in diameter, a SCE reference electrode, and a platinum counter electrode were used.

X-ray Crystallography. Single crystals of $(Ph_4P)_2[MoS(S_4)(bdt)]\cdot DMF$ (**2a·DMF**) and $(Ph_4P)_2[MoS(S_4)(bdtCl_2)]\cdot DMF$ (**3a·DMF**) were obtained by the diffusion of diethyl ether into DMF solutions of **2** and **3** in the presence of Ph_4PBr. Single crystals of **2**, **5**, and **7** were obtained by recrystallization from acetonitrile/diethyl ether. A single crystal of $(Et_4N)(Ph_4P)[MoO(S_4)(bdtCl_2)]$ (**8a**) was obtained by the diffusion of diethyl ether into an acetonitrile−H_2O solution containing **3** and Ph_4PBr. Each single crystal obtained was mounted on top of glass fibers. All X-ray data were collected by Rigaku CCD diffractometer with monochromated Mo Kα (graphite for **2a·DMF**, **3a·DMF**, **7**, and **8a** and multilayer mirror for **2** and **5**) at −160 °C. The structures were solved by a direct method (SIR-92)[21] and expanded using DIRDIF 99.[22] The non-hydrogen atoms, except two methyl carbon atoms of the DMF molecule in **3a·DMF**, were refined anisotropically by full-matrix least squares on F^2. The hydrogen atoms, except the formamide group of **2a·DMF** and **3a·DMF**, in all structures were attached at idealized positions on carbon atoms and were not refined. All structures converted in the final stages of refinement showed no movement in the atom positions. Calculations for **2**, **2a·DMF**, **3a·DMF**, **5**, **7**, and **8a** were performed using the Single-Crystal Structure Analysis Software, version 3.8.[23] The crystallographic parameters are summarized in Table 1.

Results and Discussion

Preparation and Crystal Structural Characterization of Dithiolene Complexes of $Mo^{IV}S(S_4)$. $(Et_4N)_2[Mo^{IV}S(S_4)(bdt)]$ (**2**; bdt = 1,2-benzenedithiolate) and its chlorine-substituted analogue $(Et_4N)_2[Mo^{IV}S(S_4)(bdtCl_2)]$ (**3**; 3,6-dichloro-1,2-benzenedithiolate) were obtained in good yields (60 and 43%) when 1 equiv of the corresponding dithiol was added dropwise slowly to an acetonitrile solution of $(Et_4N)_2[Mo^{IV}S(S_4)_2]$ (**1**). The yields became lower (<50% and <35%) when the dithiols were added rapidly. Methathesis of **2** and **3** with 2 equiv of Ph_4PBr gave the corresponding Ph_4P^+ salts, **2a** and **3a**.

The crystal structures of the anionic complexes of **2**, **2a·DMF**, and **3a·DMF** are shown in Figure 1, and the selected bond distances and angles are listed in Table 2. The Mo1 atom of **2** is coordinated by a terminal sulfido S1, two sulfur atoms S2 and S5 of a tetrasulfido group, and two sulfur atoms S6 and S7 of bdt. The S2, S5, S7, and S6 atoms are almost on the same plane, and four bond angles of S1−Mo1−S2 (108.74(3)°), −S5 (108.55(3)°), −S6 (108.18(4)°), and −S7 (108.12(3)°) are very close to each other. The bond angle of S2−Mo1−S7 (142.51(3)°) is also very close to S5−Mo1−S6 bond angles (143.14(3)°). These observations indicate that the Mo1 center adopts a slightly distorted square pyramidal geometry, where the Mo1 atom is raised above the plane toward the S1 atom by 0.75 Å. For the tetrasulfido group, the S2, S3, S4, and S5 atoms form a zigzag structure in which the torsion angle defined by S2−S3−S4−S5 is 47°. The coordination environment of the Mo1 center of **2a** is similar to that of **2**, and the four sulfur atoms S2, S3, S4,

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(21) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(22) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.

(23) *Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC: The Woodlands, TX, 2000−2006.

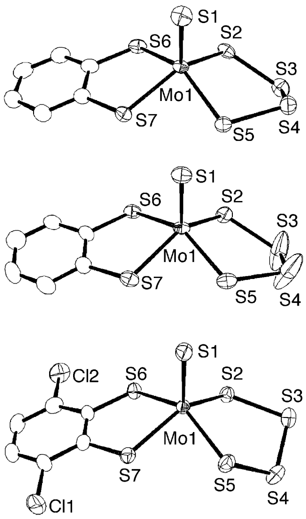

Figure 1. Crystal structures of the anionic complexes of (Et$_4$N)$_2$[MoS(S$_4$)(bdt)] (**2**, above), (Ph$_4$P)$_2$[MoS(S$_4$)(bdt)]·DMF (**2a·DMF**, middle), and (Ph$_4$P)$_2$[MoS(S$_4$)(bdtCl$_2$)]·DMF (**3a·DMF**, below) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of **2**, **2a·DMF**, and **3a·DMF**

	2	**2a·DMF**	**3a·DMF**
Mo1−S1	2.138(1)	2.126(2)	2.146(2)
Mo1−S2	2.3087(8)	2.307(2)	2.314(2)
Mo1−S5	2.3518(9)	2.341(2)	2.323(2)
Mo1−S6	2.3917(8)	2.402(2)	2.377(1)
Mo1−S7	2.3945(8)	2.391(2)	2.392(1)
S1−Mo1−S2	108.74(3)	109.40(8)	110.05(5)
S1−Mo1−S5	108.55(3)	107.71(7)	110.29(6)
S1−Mo1−S6	108.18(4)	104.61(7)	106.24(5)
S1−Mo1−S7	108.12(3)	110.08(7)	106.69(6)
S2−Mo1−S5	91.37(3)	92.00(7)	91.57(5)
S2−Mo1−S6	79.84(3)	83.2(1)	82.54(4)
S2−Mo1−S7	142.51(3)	140.19(7)	142.88(6)
S5−Mo1−S6	143.14(3)	147.03(6)	142.76(6)
S5−Mo1−S7	83.35(3)	80.87(7)	80.53(5)
S6−Mo1−S7	82.48(3)	82.16(6)	82.39(4)

and S5 adopt a zigzag form having a torsion angle of 46°. In **2a**, however, somewhat larger bond angles of S1−Mo1−S2 and −S7 (mean 110°) and S5−Mo1−S6 (147.03(6)°) than those of S1−Mo1−S5 and −S6 (mean 106°) and S2−Mo1−S7 (140.19(7)°), respectively, suggest that a small amount of a trigonal bipyramidal geometry having the S5−Mo1−S6 bond as the axis is involved in the stereochemistry of the Mo1 center, reflecting a ca. 10 times larger τ value of **2a** (0.1117) compared with **2** ($\tau = 0.0105$), in which τ describes a parameter used to measure the distortion of geometries between square pyramid and trigonal bipyramid.[24] Packing forces are considered to be responsible for these minor differences between **2** and **2a**.

The coordination environment of the Mo1 center of **3a** with a τ value of 0.00183 is similar to that of **2** rather than **2a** and is described as a square pyramid with the Mo center displaced 0.75 Å from the 4S equatorial plane. A torsion angle of 46° comprising four sulfur atoms of the tetrasulfido group is almost the same as those values for **2** and **2a**. The bond angles of S1−Mo1−S2 and −S5 (110.05(5) and 110.29(6)°) are larger than those of S1−Mo1−S6 and −S7 (106.24(5) and 106.69(6)°), reflecting a lean of the Mo−S1 axis to the bdtCl$_2$ side. A mononuclear five-coordinate MoS structure is rare and is found in only **1**,[17] bis(dithiolene)-Mo^{IV}S complexes including cyclohexene-1,2-dithiolate[9a] and 1,2-dimethyl-1,2-ethylenedithiolate,[9b] and (Et$_4$N)$_2$[MoS(CS$_4$)$_2$][25] in the literatures.

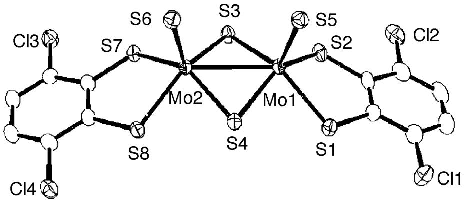

Figure 2. Crystal structure of the anionic complex of (Et$_4$N)$_2$[MoS(bdtCl$_2$)](μ-S)$_2$ (**5**) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of **5**

	5		
Mo1−S1	2.397(2)	Mo2−S7	2.402(2)
Mo1−S2	2.403(2)	Mo2−S8	2.400(2)
Mo1−S3	2.336(2)	Mo2−S4	2.318(2)
Mo1−S4	2.321(2)	Mo2−S3	2.329(2)
Mo1−S5	2.108(2)	Mo2−S6	2.119(2)
Mo1−Mo2	2.8551(9)		
S1−Mo1−S3	145.20(7)	S7−Mo2−S4	142.15(6)
S2−Mo1−S4	142.20(6)	S8−Mo2−S3	144.10(7)
S5−Mo1−S1	104.16(7)	S6−Mo2−S7	107.00(7)
S5−Mo1−S2	106.94(7)	S6−Mo2−S8	105.55(7)
S5−Mo1−S3	109.26(7)	S6−Mo2−S4	108.83(7)
S5−Mo1−S4	108.98(7)	S6−Mo2−S3	109.17(7)
Mo1−S3−Mo2	75.48(5)	Mo1−S4−Mo2	75.97(6)

Electrochemical Property of 2 and 3: Structural Change from the [Mo^{IV}S(S$_4$)] Unit to the [Mo^{V}S]$_2$(μ-S)$_2$ Unit. Complexes **2** and **3** exhibited an irreversible oxidation wave at −0.10 V and + 0.04 V versus SCE in acetonitrile, respectively. The potential difference is an indication of the stronger bdt → Mo^{IV} donation compared with the bdtCl$_2$ → Mo^{IV} donation. Upon oxidizing **2** and **3** by air in acetonitrile, black-brown microcrystalline powders were obtained. IR, UV−vis, and ESI-MS spectra of the black-brown species derived from **2** were identical with those of known (Et$_4$N)$_2$[Mo^{V}S(bdt)]$_2$(μ-S)$_2$ (**4**) prepared from (NH$_4$)$_2$[Mo^{V}S(S$_2$)$_2$]$_2$(μ-S)$_2$ and 2 equiv of H$_2$bdt.[19] The powder derived from **3** was characterized as (Et$_4$N)$_2$[Mo^{V}S(bdtCl$_2$)]$_2$(μ-S)$_2$ (**5**) by ^{1}H NMR, IR, and ESI-MS spectra and elemental analysis. Although a crystal structure of the dinuclear complex **4** of bdt has not been determined yet, that of bdtCl$_2$ complex **5** was determined in this study. Table 3 lists the selected bond distances and angles. As indicated in Figure 2, the anion consists of two [MoS(bdtCl$_2$)]$^+$ units bridged by two sulfido groups. The two terminal sulfido groups are located in syn configuration. The bond angle of S1−Mo1−S3 (145.20(7)°) is close to that of S2−Mo1−S4 (142.20(6)°), indicating that the Mo1 atom possesses a square-pyramidal geometry. The bond angles of S1−Mo1−S5 and S2−Mo1−S5 (mean 106°) are smaller than those of S3−Mo1−S5 and S4−Mo1−S5 (mean 109°) due to electronic repulsions between two terminal sulfido groups, S5 and S6. The stereochemistry of

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(24) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(25) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.

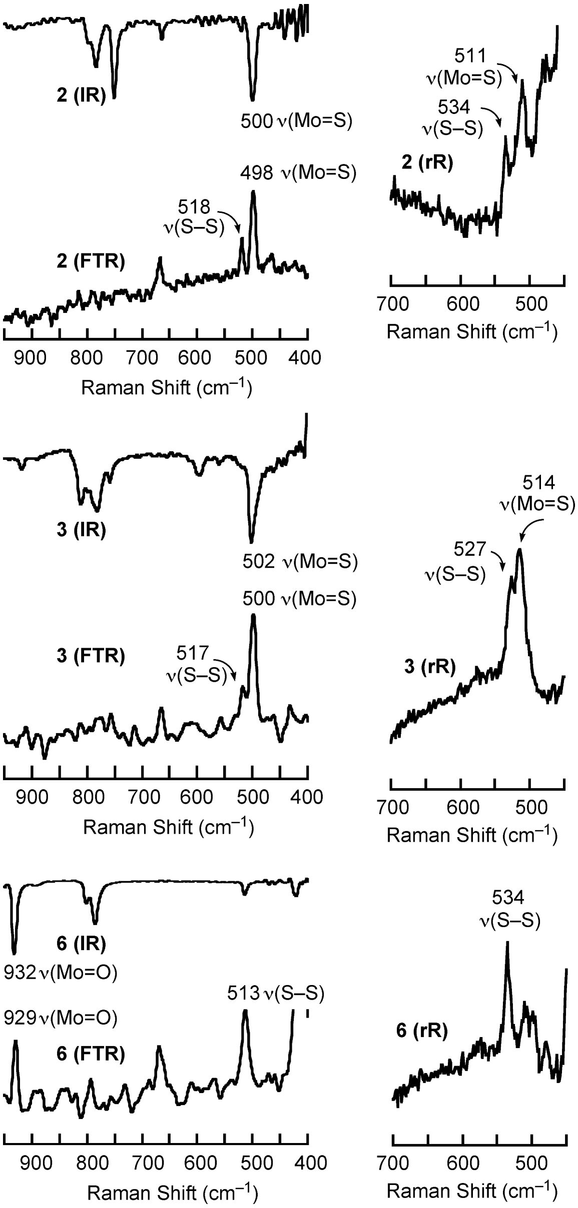

Figure 3. IR spectra (left above) and FT Raman (FTR) spectra (left, below) of $(Et_4N)_2[MoS(S_4)(bdt)]$ (**2**), $(Et_4N)_2[MoS(S_4)(bdtCl_2)]$ (**3**), and $(Et_4N)_2[MoO(S_4)_2]$ (**6**) and rR spectra (right) of acetonitrile solutions of **2** (5.1×10^{-4} M), **3** (6.4×10^{-4} M), and **6** (1.7×10^{-3} M) using an Ar^+ ion laser with excitation at 488 nm.

Mo2 is almost the same as that of Mo1. The *syn*-$[Mo^{V}S](\mu\text{-}S)_2$ core structure is precedented in thiomolybdate systems.[17,25]

FT- and Resonance-Raman Spectroscopic Characterization of 2 and 3. IR and FTR spectra of solid samples of **2** and **3** in a region from 400 to 950 cm^{-1} are presented in Figure 3 together with that of a known complex of $(Et_4N)_2[MoO(S_4)_2]$ (**6**).[18,26] The FTR spectra in a region from 300 to 2000 cm^{-1} are indicated in Figure S1 (Supporting Information). It is well-known that stretchings of M=S and S−S bonds in coordination compounds appear in a region from 450 to 550 cm^{-1}.[27] In that region, **2** showed one IR peak at 500 cm^{-1} and two FTR peaks at 498 and 518 cm^{-1}. Among these, the peaks at 500 (IR) and 498 (FTR) cm^{-1} are tentatively assigned to the ν(Mo=S) stretching band because **6** with no Mo=S bond did not exhibit such a strong IR peak near 500 cm^{-1} and ν(Mo=S) stretching bands are IR- and Raman-active.[27] The remaining peak at 518 cm^{-1} (FTR) of **2** is assignable to the ν(S−S) stretching band, as **6** with a S_4^{2-} group has a peak at 513 cm^{-1}. This tentative assignment is further supported by the IR and FTR spectra of **7**, which is a simple oxo derivative of **2** (**2** (bdt)MoS(S_4) vs **7** (bdt)MoO(S_4)), where no strong peak appeared near 500 cm^{-1}, but a weak peak was observed at 509 cm^{-1} instead (see below). Similarly, for **3**, the peaks observed at 502 (IR) and 500 (FTR) cm^{-1} and the FTR peak appearing at 517 cm^{-1} are tentatively assigned to the ν(Mo=S) and the ν(S−S) stretching bands, respectively, on the basis of a comparison with IR and FTR spectra of **6** with no Mo=S bond and **8** being a simple oxo derivative of **3**. In the rR spectrum of an acetonitrile solution of **2**,[28,29] bands at 534 and 511 cm^{-1} are assignable to the ν(S−S) and ν(Mo=S) stretchings, respectively, referring to the rR spectrum of **6** in acetonitrile (Figure 3). This tentative assignment can be also explained by comparing the rR spectrum of **2** with that of **7**, being an oxo derivative of **2** (vide infra). Similarly, bands at 527 and 514 cm^{-1} in the rR spectrum of **3** in acetonitrile are tentatively assigned to the ν(S−S) and ν(Mo=S) stretchings, respectively.

Preparation and Characterization of Dithiolene Complexes of $Mo^{IV}O(S_4)$. Because **1** was revealed to be a good precursor for mono(dithiolene)MoS complexes, its oxo derivative, $(Et_4N)_2[MoO(S_4)_2]$ (**6**), was treated with H_2bdt and H_2bdtCl_2, and $(Et_4N)_2[Mo^{IV}O(S_4)(bdt)]$ (**7**) and $(Et_4N)_2[MoO(S_4)(bdtCl_2)]$ (**8**) were isolated in 76 and 72%, respectively. Complexes **7** and **8** were also derived from **2** and **3** in H_2O−CH_3CN or excess phenol containing H_2O−CH_3CN. The crystal structure of **7** is shown in Figure 4, and the selected bond distances and angles are listed in Table 4. The Mo1 atom is coordinated by a terminal oxo group O1, two sulfur atoms S3 and S6 of the tetrasulfido group, and two sulfur atoms S1 and S2 of bdt. The bond angle of S1−Mo1−S3 (143.54(4)°) is close to that of S2−Mo1−S6 (145.15(3)°), and four bond angles of O1−Mo1−S (1, 2, 3, and 6) are almost same, indicating that the Mo1 center adopts a square pyramidal stereochemistry with a τ value of 0.0265. The crystal structure of $(Et_4N)(Ph_4P)[MoO(S_4)(bdtCl_2)]$ (**8a**) was determined. As shown in Figure 4, the Mo1 atom possesses a square-pyramidal stereochemistry with a τ value of 0.0535, and bond distances and angles around the Mo1 are also close to those of **7** (Table 4). Whereas the Mo1=O1 distance at 1.730(4) Å of **7** is somewhat longer than those of $(Et_4N)_2[Mo^{IV}O(S_4)_2]$ (1.685(7) Å)[17] and $(Et_4N)_2[Mo^{IV}O(bdt)_2]$ (1.699(6) Å),[20] the ν(Mo=O)

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(26) In spite of our great efforts, measurements of resonance Raman spectra of solid samples of **2** and **3** were unsuccessful because of decomposition of the compounds by photo-irradiation.

(27) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; John Wiley & Sons: New York, 1997.

(28) The solubility of **2**, **3**, and **6** into acetonitrile was not sufficient enough to measure their FT Raman spectra of the solutions.

(29) The complexes exhibit a shoulder peak at 488 nm with ε values larger than 800 M^{-1} cm^{-1}.

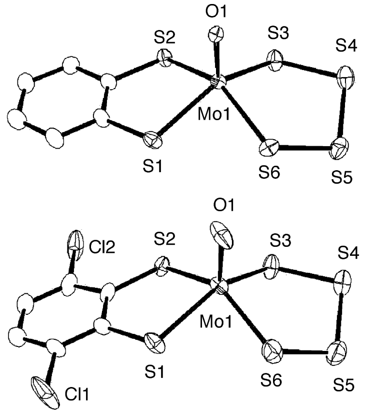

Figure 4. Crystal structures of the anionic complexes of (Et$_4$N)$_2$-[MoO(S$_4$)(bdt)] (**7**, above) and (Et$_4$N)(Ph$_4$P)[MoO(S$_4$)(bdtCl$_2$)] (**8a**, below) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) of **7** and **8a**

	7	8a
Mo1−O1	1.730(4)	1.732(4)
Mo1−S1	2.406(1)	2.405(2)
Mo1−S2	2.397(1)	2.388(3)
Mo1−S3	2.361(1)	2.363(2)
Mo1−S6	2.337(1)	2.335(2)
S1−Mo1−S3	143.54(4)	145.08(6)
S2−Mo1−S6	145.15(3)	141.87(6)
O1−Mo1−S1	106.73(9)	107.6(2)
O1−Mo1−S2	106.25(9)	107.3(2)
O1−Mo1−S3	109.34(9)	106.9(2)
O1−Mo1−S6	107.96(9)	110.6(2)

stretching value of **7** (IR: 927 cm^{-1}) is close to that of the former (932 cm^{-1})[17] and significantly larger than that of (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O(bdt)$_2$] (IR: 905 cm^{-1}).[20] In contrast, the ν(Mo=O) stretching value of **8** (IR: 919 cm^{-1}) is almost equal to an average value (921 cm^{-1}) of those of (Et$_4$N)$_2$[MoO(S$_4$)$_2$] (IR: 932 cm^{-1})[17] and (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O-(bdtCl$_2$)$_2$] (IR: 910 cm^{-1}).[30,31] Complexes **7** and **8** exhibited an irreversible oxidation wave at −0.05 and +0.05 V versus SCE, respectively, in acetonitrile. As in the case of their sulfido derivatives **2** and **3**, the irreversible oxidation process may be ascribed to dimerization of the (Et$_4$N)[Mo$^{\mathrm{V}}$O(bdts)] species, giving the (Et$_4$N)$_2$[Mo$^{\mathrm{V}}$O(bdts)]$_2$(μ-S)$_2$ species. A comparison of the ν(Mo=O) stretching values of **7**; **8**; and the Mo$^{\mathrm{IV}}$O complexes of bis(S$_4$), bis(bdt), and bis(bdtCl$_2$) suggests that bdt presents an electronic effect similar to that of the tetrasulfido ligand, but bdtCl$_2$ provides a different electronic effect from it. IR and FTR spectra of solid **7** and **8** and rR spectra of acetonitrile solutions of **7** and **8** are shown in Figure 5. The FTR spectra in a region from 300 to 2000 cm^{-1} are indicated in Figure S2 (Supporting Information). When the spectra of **7** and **8** are compared with those of **2**, **3**, and **6**, the peaks observed at 509 (FTR) and 536 cm^{-1} (rR) for **7** and the peaks appearing at 516 (FTR) and 536 cm^{-1} (rR) for **8** are tentatively assigned to the ν(S−S) stretching band. In the FTR spectra, several peaks appearing in the lower-energy region can be attributable to the ν(Mo−S) stretching, referring to the assignment of Raman spectra of dithiolene complexes of Mo.[33]

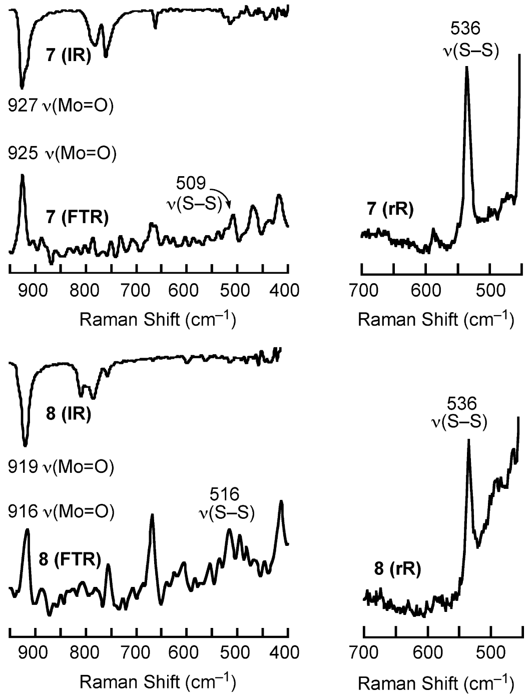

Figure 5. IR spectra (left above) and FT Raman (FTR) spectra (left, below) of (Et$_4$N)$_2$[MoO(S$_4$)(bdt)] (**7**) and (Et$_4$N)$_2$[MoO(S$_4$)(bdtCl$_2$)] (**8**) and rR spectra (right) of acetonitrile solutions of **7** (4.2 × 10^{-3} M) and **8** (4.4 × 10^{-3} M) using an Ar^{+} ion laser with an excitation at 488 nm.

Formation of Bis(dithiolene) Mo$^{\mathrm{IV}}$O Complex from 7. Referring to the established methods of preparing various (dithiolene)Mo complexes from (polysulfido)Mo complexes and activated alkynes,[12b,16c,18,34] new [Mo(S/O)(S$_4$)(bdt)]$^{2-}$ complexes were treated with dimethyl acetylenedicarboxylate (DMAD). In the case of **2**, the treatment with DMAD did not give [Mo$^{\mathrm{IV}}$S(bdt)(S$_2$C$_2$(COOMe)$_2$)]$^{2-}$ but rather a mixture comprising (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$(bdt)(S$_2$C$_2$(COOMe)$_2$)$_2$] and unreacted **2** in a 1:1 ratio. The reaction of **7** with DMAD gave a pale brown solid in 55% yield, which was identified as (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O(bdt)(S$_2$C$_2$(COOMe)$_2$)] (**9**). Attempts to synthesize (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$S(bdts)$_2$] complexes by the reaction of **2** or **3** with an equal amount of H$_2$bdt or H$_2$bdtCl$_2$ were unsuccessful, yielding a 1:1 mixture of (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$(1,2-benzenedithiolates)$_3$][35,36] and the unreacted precursor. However, the reactions of **7** with H$_2$bdt and H$_2$bdtCl$_2$ were found to give the known (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O(bdt)$_2$] (**10**)[8] and the new (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O(bdt)(bdtCl$_2$)] (**11**) in 32 and 46% yields, respectively. New complexes **9** and **11** were characterized by ^{1}H NMR, UV−vis, and ESI-MS spectra; CV; and elemental analysis (see the Experimental Section). Because

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(30) Sugimoto, H.; Tarumizu, M.; Miyake, H.; Tsukube, H. *Dalton Trans.* **2005**, 3558.

(31) The crystal structure of (Et$_4$N)$_2$[Mo$^{\mathrm{IV}}$O(bdtCl$_2$)$_2$] has not been determined.[30,32]

(32) Sugimoto, H.; Tarumizu, M.; Miyake, H.; Tsukube, H. *Eur. J. Inorg. Chem.* **2006**, 4494.

(33) Johnson, M. L. *Prog. Inorg. Chem.* **2004**, *52*, 213, and references therein.

(34) (a) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476. (b) Soricelli, C. L.; Szalai, V. A.; Burgmayer, S. J. N. *J. Am. Chem. Soc.* **1991**, *113*, 9877. (c) Rauchfuss, T. B. *Prog. Inorg. Chem.* **2004**, *52*, 1, and references therein.

(35) Isfort, C.; Pape, T.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2005**, 2607.

(36) Sugimoto, H.; Furukawa, Y.; Tarumizu, M.; Miyake, H.; Tanaka, K.; Tsukube, H. *Eur. J. Inorg. Chem.* **2005**, 3088.

only two examples of $(Et_4N)_2[MoO(mnt)(S_2C_2H_2)]$[37] and $(Et_4N)_2[MoO(bdt)(S_2C_2(CF_3)_2)]$[38] include two different dithiolene ligands in bis(dithiolene)MoO complexes in the literature, **7** was also revealed to be a precursor opening an alternative route to MoO complexes including two different dithiolenes.

Conclusions

The present study provided a synthetic method starting from the bis(tetrasulfido)$Mo^{IV}S$ complex, **1**. Mono(dithiolene)-$Mo^{IV}S$ complexes, **2** and **3**, were synthesized from precursor **1** and 1,2-benzenedithiols. One-electron oxidation of the obtained complexes gave dinuclear $Mo^{V}S$ complexes, **4** and **5**, bridged by two sulfido groups. The $Mo^{IV}O$ species were also prepared by the substitution of one tetrasulfide group of the bis(tetrasulfido)$Mo^{IV}O$ complex, **6**, with 1,2-benzenedithiols. The reactions of DMAD and H_2bdtCl_2 with the derived $Mo^{IV}O$ species, **7**, gave $Mo^{IV}O$ complexes, **9** and **11**, including two different dithiolenes. New complexes prepared, excluding the bis(dithiolene)$Mo^{IV}O$ species, were crystallographically characterized. The new and convenient methods in this report will allow for an introduction to other, more biologically relevant ligands to further expand model complexes.

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Supporting Information Available: The FT Raman spectra in a region from 300 to 2000 cm^{-1} of solid **2**, **3**, **6**, **7**, and **8** (Figures S1 and S2). CIF files of **2**, **3**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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