Synthesis and characterization of the monomeric molybdenum trithiolate $Mo(\eta^7\text{-dmpt})(\eta^1\text{-dmpt})_2$ (dmpt = 2,6-dimesitylphenylthiolate)

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Treatment of $MoCl_3(THF)_3$ with 3 equiv. of $LiSC_6H_3Mes_2$-2,6 (Mes = $C_6H_2Me_3$-2,4,6) (Lidmpt) affords the monomeric molybdenum trithiolate $Mo(\eta^7\text{-dmpt})(\eta^1\text{-dmpt})_2$, 1, which is spectroscopically and structurally characterized; the MoS_3 array has distorted trigonal pyramidal geometry which is caused by strong π-interactions between molybdenum and an *ortho*-mesityl group from one of the thiolate substituents.

Stable, well characterized examples of monomeric, three-coordinate Mo^{III} complexes are rare. In general, such compounds are dimerized to form triply bonded species of formula $L_3Mo{\equiv}MoL_3$ (L = uninegative ligand) which have been extensively studied.[1] Although it is probable that the incompletely characterized, sterically encumbered derivatives $Mo\{N(Pr^i)_2\}_3$ and $Mo\{N(SiMe_3)_2\}_3$ are monomers,[2] the first well established three-coordinate Mo^{III} compound was $Mo[N\{C(CD_3)_2CH_3\}C_6H_3Me_2\text{-}3,5]_3$[3] which, like the related molybdenum triamidoamine derivative $[Mo(OTf)(\{C_6F_5N(CH_2)_2\}_3N)]$,[4] activates dinitrogen at room temperature to form a variety of complexes, including imines and nitrides. The stabilization of these unusual and interesting complexes by bulky aryl amido substituents suggested that it should be possible to isolate further examples of monomeric, low coordinate trivalent complexes with other ligands. Here it is shown that the use of the thiolate ligand $SC_6H_3Mes_2$-2,6 (dmpt)[5] enables the isolation of the first monomeric homoleptic molybdenum trithiolate complex $Mo(\eta^7\text{-dmpt})(\eta^1\text{-dmpt})_2$, **1**.

Complex **1** was synthesized in moderate yield‡ by the reaction of 3 equiv. of $LiSC_6H_3Mes_2$-2,6 with $MoCl_3(THF)_3$.[6] The dark red, almost black, crystalline product, **1**, has good solubility in hydrocarbon solvents. The electronic absorption spectrum is almost featureless with a rapid rise in absorption at <400 nm and a very weak shoulder at 490 nm (ε = 4600) is apparent. Magnetic studies confirm the paramagnetic character with $\mu_B = 3.6$ (T = 293 K). The monomeric structure of **1** was established by a single crystal X-ray crystal study of its pentane solvate, **1**·0.25pentane.§ The Mo atom is bound to three thiolate sulfurs and two of the Mo–S distances have almost equal values of 2.393(2) and 2.394(2) Å, whereas the other is slightly shortened to 2.314(2) Å. The MoS_3 array is grossly distorted from planarity as indicated in the three S–Mo–S angles, which have the values 88.68(6), 105.59(7), and 91.67(7)°. The Mo–S–C angles also are different with an angle of 102.3(2)° being observed at S(1) (which bears the mesityl ring that interacts with Mo, *vide infra*) which is 14–16° narrower than the corresponding angles at S(2) and S(3). The coordination sphere of Mo is completed by a strong interaction with the C(11) *ortho*-mesityl ring. This ring is bent along the C(7)···C(10) axis (fold angle = 159.4°) such that these two atoms are closest to Mo [Mo–C distances = 2.220(6) and 2.248(7) Å] while the Mo–C distances to the remaining ring carbons are in the range 2.295(6)–2.502(6) Å.

Previous examples of related Mo^{III} thiolates [*e.g.* $Mo_2(SMes)_6$[7] or the heteroleptic species $Mo_2\{S(Bu^t)\}_2(NMe_2)_4$[8]] have been shown to be dimeric with Mo–Mo triple bonds. The monomeric structure observed for **1** (Fig. 1) is a consequence of the large size of the $SC_6H_3Mes_2$-2,6 ligand and the π-interaction between one of the mesityl groups on the ligand and the metal. The metal–ligand π-interaction may arise in part from the unique reactivity of the trigonal Mo^{III} fragment[4] which in the case of the $Mo[N\{C(CD_3)_2CH_3\}C_6H_3Me_2\text{-}3,5]_3$ complex is capable of activating N_2[3b,9] to afford, *inter alia*, the nitride $N{\equiv}Mo[N\{C(CD_3)_2CH_3\}C_6H_3Me_2\text{-}3,5]_3$. In the case of **1**, the strong interaction between the metal and a π-ring system apparently prevents the dinitrogen activation observed for the amide complexes. Note that the synthesis and manipulation of **1** were conducted under an N_2 atmosphere. Furthermore, hexane solutions of purified **1** show no sign of reaction with N_2 upon standing for 3 days at room temperature. Although the structure of **1** is unique it may be compared to that described for the Mo^{II} species $[Mo(\eta^7\text{-dpt})(\eta^1\text{-dpt})(CO)]$, **2** (dpt = $SC_6H_3Ph_2$-2,6)[10a] which also possesses a Mo–η^6-Ph ring interaction involving a thiolate ligand.[10b] However, the η^6-coordination of the *ortho*-phenyl ring may be displaced by the addition of CO or bidentate neutral ligands such as 2,2′-bipyridyl. The Mo–S distances in **2** [2.239(4) and 2.358(3) Å] are quite similar to those in **1**. However, the distortions in the geometry of the η^6-interacting Mes ring in **1** are not observed in the η^6-Ph ring of **2** although in the latter the *ipso*-carbon is displaced slightly (by *ca.* 0.14 Å) from the averaged plane of the other five ring carbon atoms.

The structural distortion observed in the mesityl ring which interacts with Mo has similarities to those observed in a variety of transition metal complexes.[11] In many instances this results in a 1,4-diene type of localization of multiple bond character within the aromatic ring. In **1**, however, the localization does not show a regular pattern. Thus, although the C(8)–C(9) distance, 1.360(9) Å, is short, the C(11)–C(12) distance, 1.420(10) Å, is

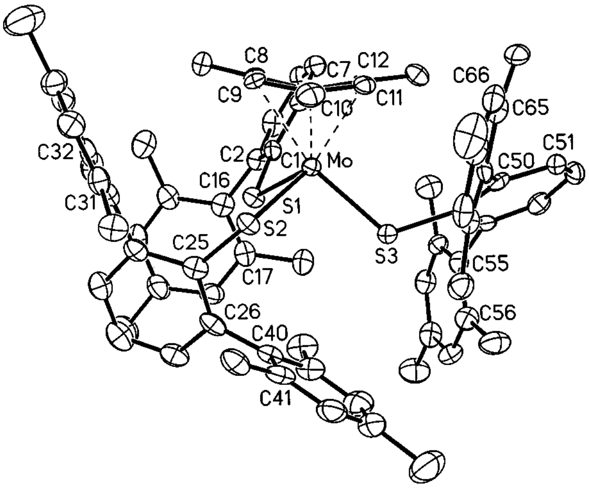

Fig. 1 Thermal ellipsoid plot of **1**. Important bond distances (Å) and angles (°) are as follows: Mo–S(1) 2.393(2), Mo–S(2) 2.394(2), Mo–S(3) 2.314(2), Mo–C(7) 2.220(6), Mo–C(8) 2.502(6), Mo–C(9) 2.433(6), Mo–C(10) 2.248(7), Mo–C(11) 2.295(6), Mo–C(12) 2.389(8), S(1)–Mo–S(2) 88.68(6), S(1)–Mo–S(3) 105.59(7), S(2)–Mo–S(3) 91.67(7), Mo–S(1)–C(1) 102.3(2), Mo–S(2)–C(25) 116.1(2), Mo–S(3)–C(49) 118.6(2)°.

near normal for an aromatic ring, whereas the C(7)–C(8) bond is lengthened to 1.494(9) Å. Perhaps the most structurally related Mo environment to that seen in **1** is in $[\{(\eta^6\text{-PhMe})\text{Mo}(\mu\text{-SMe})_2\}_2][\text{PF}_6]_2$.[12] In this case, the oxidation state of Mo is also 3+; however, the Mo–S distances [2.451(1)–2.462(1) Å] are, of course, considerably longer owing to their bridging nature. Nonetheless, the range of Mo–C distances [2.287(3)–2.416(3) Å] is similar to the 2.220(6)–2.502(6) Å range observed in **1**. In essence, the Mo–ring π-interaction in **1** is as strong as that seen for other Mo species with neutral 6π-electron ring donors. Furthermore, the Mo–S distances are similar to those observed in $\text{Mo}_2(\text{SMes})_6$[7] but longer than the 2.262(1) Å in the Mo^{4+} species $\text{Mo}(\text{SC}_6\text{H}_2\text{-Pr}^i_3\text{-2,4,6})_4$.[13]

In summary, the $\text{SC}_6\text{H}_3\text{Mes}_2$-2,6 ligand permits the isolation of the first monomeric complex of formula Mo(SR)_3 (R = alkyl or aryl group). However, intramolecular interactions between the Mo atom and a ligand Mes ring prevent the molecule from displaying significant reactivity toward N_2 under ambient conditions.

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Notes and References

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‡ All manipulations were carried out under anaerobic and anhydrous conditions. The thiol $\text{HSC}_6\text{H}_3\text{Mes}_2$-2,6 was synthesized as described in the literature.[5] **1**·0.25pentane: $\text{HSC}_6\text{H}_3\text{Mes}_2$-2,6[5] (1.91 g, 5.5 mmol) was dissolved in diethyl ether (25 ml) and treated slowly with Bu^nLi (3.6 ml of a 1.6 M solution in hexane; 5.5 mmol) with cooling in an ice bath. The mixture was stirred for 30 min at 0 °C and allowed to warm to room temperature with continuous stirring for a further 1 h. The solution was then added slowly to a suspension of $\text{MoCl}_3(\text{THF})_3$[6] (0.767 g, 1.83 mmol) in diethyl ether (25 ml) at *ca*. 0 °C. The mixture became deep red and stirring was continued for 18 h at room temperature. The precipitate was allowed to settle and the supernatant, deep red solution was decanted to another Schlenk tube *via* a cannula. The ether was evaporated under reduced pressure and hexane (40 ml) was added to the dark red residue. Filtration through Celite gave a clear, dark red solution. Reduction of the volume under reduced pressure to *ca*. 15 ml and storage of the solution in a −20 °C freezer gave black crystals of **1**·0.25pentane, which were suitable for X-ray structure determination. Total yield: 1.08 g, 51%, mp 112–115 °C. Anal. Calc. for **1**, $\text{C}_{72}\text{H}_{75}\text{S}_3\text{Mo}$: C, 76.36; H, 6.68. Found C, 75.94; H, 6.81%. UV–VIS (λ_{max}, ε): 490 nm (sh), 4600 dm^3 mol^{-1} cm^{-1}. IR (Nujol, ν/cm^{-1}): 3040sh, 2950s, 2920s, 2850s, 2720w, 1720w, 1610m, 1560w, 1460s, 1450s, 1370s, 1255m, 1090w, 1020w, 845, 800m, 740w, 730w, 710w. Magnetic moment μ_B = 3.6 (T = 293 K).

§ *Crystal data* for **1** at T = 130 K with Mo-Kα (λ = 0.71073 Å) radiation: M = 1150.48, a = 27.927(6), b = 19.974(4), c = 23.346(5) Å, β = 103.82(3)°, V = 12646(4) Å^3, μ = 0.347 mm^{-1}, monoclinic, space group $C2/c$, Z = 8, R_1 = 0.062 for 6177 [$I > 2\sigma(I)$] data. CCDC 182/922.

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