Synthesis and characterization of the first doubly-bridging pyridine-2-thionate (pys) molybdenum complex: crystal structure of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]_2(\eta^1:\eta^2:\mu\text{-pyS})_2$

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Abstract

The doubly-bridging pyridine-2-thionate (pyS) molybdenum complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{CO})_2]_2(\eta^1:\eta^2:\mu\text{-pyS})_2$ ($\text{R} = \text{H}$, **1a**; CH_3 , **1b**) are accessible by the reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}]$ with pySK in CH_2Cl_2 at room temperature. Complexes **1a** and **1b** are dimers with each pyS unit chelating through sulfur and nitrogen to one metal center and bridging both metals through sulfur. Treatment of **1a** with piperidine affords complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-pyS})(\text{C}_5\text{H}_{10}\text{NH})(\text{CO})_2]$ (**2**). Complex **1a** is characterized by X-ray diffraction analysis.

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Molybdenum complexes containing Mo–S and Mo–N bonds are of special interest because of their relevance to a variety of molybdenum-containing enzymes [1] and hydrosulfurization catalysts [2]. To date, a variety of allyl complexes of molybdenum(II) containing bidentate anionic sulfur donor ligands such as dithiocarbamates have been described [3a]. Notably, the 16-electron allyl dithio complexes such as $[\text{Mo}(\eta^3\text{-allyl})(\eta^2\text{-S}_2\text{CNR})(\text{CO})_2]$ ($\text{R} = \text{Et}$, C_4H_8) [3b] and $[\text{Mo}(\eta^3\text{-allyl})(\eta^2\text{-Pz}_2^*\text{BR}_2)(\text{CO})_2]$ ($\text{R} = \text{H}$, Et , Ph) [4] and the 18-electron allyl dithio complexes $[\text{Mo}(\eta^3\text{-allyl})\{\eta^3\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{CH}_3\text{CN})(\text{CO})_2]$ [5] and $[\text{Mo}(\eta^3\text{-allyl})(\eta^2\text{-S}_2\text{COEt})(\text{CH}_3\text{CN})(\text{CO})_2]$ [6] containing the sulfur or nitrogen bidentate ligands have been studied clearly. However, no detailed information has been presented on a mixed bidentate (N, S) ligand such as pySH. In this paper, we describe the preparation and characterization of the first doubly-bridging pyS allyl molybdenum(II) complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{CO})_2]_2(\eta^1:\eta^2:\mu\text{-pyS})_2$.

A number of 16 electron allyl complexes of the type $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-S}_2\text{CNR}_2)(\text{CO})_2]$ ($\text{R}_2 = \text{Me}$, Et , C_4H_8 , C_5H_{10}) have been prepared from the reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{AN})_2(\text{Br})]$ and NaS_2CNR ligand [3b]. We expected the reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{AN})_2(\text{Br})]$ with pyridine-2-thionate would produce a 16 electron pyridine-2-thionate complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-pyS})(\text{CO})_2]$ or an 18 electron acetonitrile solvate complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-pyS})(\text{CH}_3\text{CN})(\text{CO})_2]$. Instead, the product of this reaction was found to be a dimer, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]_2(\eta^1:\eta^2:\mu\text{-pyS})_2$. Equimolar quantities of complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{AN})_2(\text{CO})_2\text{Br}]$ and pySK react in CH_2Cl_2 at room temperature to give the novel doubly-bridging pyS complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{CO})_2]_2(\eta^1:\eta^2:\mu\text{-pyS})_2$ ($\text{R} = \text{H}$, **1a**; CH_3 , **1b**) with a good yield (Scheme 2). The yellow complexes **1a** and **1b** are soluble in DMSO and slightly soluble in CH_2Cl_2 , CH_3CN and THF. The IR spectra of **1a** and **1b** [7] show four terminal carbonyl stretching bands and this phenomenon is similar to other 16-electron complexes $[\text{Mo}(\eta^3\text{-allyl})(\eta^2\text{-L})(\text{CO})_2]$ ($\text{L} = \text{Et}_2\text{NCS}_2$, $\text{C}_4\text{H}_8\text{NCS}_2$, $\text{C}_5\text{H}_{10}\text{NCS}_2$, Et_2BPz_2 , Ph_2BPz_2), which was crystallographically

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Scheme 1.

characterized in the case of $L = Et_2BPz_2$ [4]. However, we cannot obtain the parent peak $[M]^+$ molecular mass with the typical Mo isotope distribution of **1a** from the FAB mass spectrum. The room-temperature 1H NMR spectrum shows five allyl proton resonances at δ 1.00, 1.33, 3.06, 3.43 and 3.83, and the $^{13}C\{^1H\}$ NMR spectrum of **1a** reveals two singlets at lowest field, which are assigned to the carbon atoms of the two terminal carbonyl groups. The 1H and $^{13}C\{^1H\}$ NMR spectra assignment of **1a** are determined by $^1H - ^1H$ COSY and $^1H - ^{13}C$ HMQC experiments. Thus it is clear that the allyl and the two carbonyl groups of **1a** show a chemical nonequivalent environment. Because only one methyl and H_{syn} resonance of **1b** were detected in 1H NMR spectrum, complex **1b** is not a mixture of diastereomers and the two methyl groups are in the syn position respect to the H_{center} of the allyl ligand of **1b**.

To demonstrate the structure of the first allyl pyridine-2-thionate VIB group compound, complex **1a** was confirmed by single-crystal X-ray diffraction study [8]. The ORTEP diagram with atom labels is shown in Fig. 1. Complex **1a** is a dimer with each pyS unit chelating through sulfur and nitrogen to one metal center and bridging both metals through sulfur. The Mo–S distances are not equal and the Mo_2S_2 ring is non-planar with a dihedral angle of $31.15(4)^\circ$ between the $Mo(1)S(1)Mo(1A)$ and $Mo(1)S(1A)Mo(1A)$ planes. What distortions there are from octahedral geometry appear to be associated with the small interligand angle $64.43(12)^\circ$ (SMoN angles in chelate rings) and $95.70(5)^\circ$ (SMoS angles). The structure confirms unequivalent allyl groups. The sulfur atom of the pyS ligand is *trans* to the allyl: $S(1)-Mo(1)-C(4)$, $152.60(18)^\circ$, whereas the nitrogen atom of pyS ligand is *trans* to one carbonyl: $N(1)-Mo(1)-C(1)$, $166.5(2)^\circ$. The remaining carbonyl is *trans* to the sulfur atom of another pyS ligand: $S(1A)-Mo(1)-C(2)$, $159.95(18)^\circ$. The molybdenum–sulfur bond $2.5669(14)$ Å (*trans* to allyl) is significantly shorter than the molybdenum–sulfur bond $2.6184(14)$ Å (*trans* to

Fig. 1. ORTEP plot of the molecular structure with atom numbering scheme of complex $[Mo(\eta^3-C_3H_5)(CO)_2]_2(\eta^1:\eta^2:\mu-pyS)_2$ (**1a**). Selected bond distances (Å) and angles ($^\circ$) are as follows: $Mo(1)-C(1)$, 1.970(7); $Mo(1)-C(2)$, 1.948(7); $Mo(1)-C(3)$, 2.349(6); $Mo(1)-C(4)$, 2.209(6); $Mo(1)-C(5)$, 2.305(6); $Mo(1)-N(1)$, 2.253(5); $Mo(1)-S(1)$, 2.5669(14); $Mo(1)-S(1A)$, 2.6184(14); $N(1)-Mo(1)-S(1)$, $64.43(12)$; $C(4)-Mo(1)-S(1)$, $152.60(18)$; $N(1)-Mo(1)-C(1)$, $166.5(2)$; $S(1A)-Mo(1)-C(2)$, $159.95(18)$; $S(1A)-Mo(1)-N(1)$, $86.74(11)$; $C(1)-Mo(1)-C(2)$, $77.9(2)$; $C(1)-Mo(1)-S(1)$, $102.09(18)$; $C(3)-C(4)-C(5)$, $116.1(7)$.

carbonyl) because of the greater *trans* effect induced by the CO group than the allyl group. The $S(1)-Mo(1)-N(1)$ angle of $64.43(12)^\circ$ in **1a** is similar to $63.6(1)^\circ$ in $Mo_2(CO)_9(C_5H_4NS)$ [9] within the range of experimental error. The Mo–C(3), C(4) and C(5) bond distances are 2.349(6), 2.209(17) and 2.253(5) Å, respectively. The bond distances and intercarbon angle of allyl group in **1a** (1.393(8), 1.394(7) Å and $116.1(7)^\circ$) is insignificantly different and in the region of related Mo^{II} -allylic compounds (1.31–1.42 Å, 115 – 125°) [10]. The Mo–Mo distance is 3.8446(9) Å, indicating no significant metal–metal interaction. To our knowledge, a Group VIB complex containing M–S and M–N bonds involving a pyridine-2-thionate (pyS) moiety as

Scheme 2.

a doubly-bridging bidentate ligand has not been reported in the literature, although Group VB [11], Group VIIB [12] and Group VIIIB [13] metal complexes with pyS ligands are known.

Although the dinuclear compound **1a** is apparently strongly held by sulfur bridges and is thermally stable, these bridges are easily cleaved by addition of σ donor ligands. Thus treatment of **1a** with $\text{C}_5\text{H}_{10}\text{NH}$ at ambient temperature yields a mononuclear complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-pyS})(\text{C}_5\text{H}_{10}\text{NH})(\text{CO})_2]$ (**2**) in good yield (Scheme 1) in which the pyS ligand acts as a chelating three-electron (counted as a radical) ligand. The yellow compound **2** is slightly air-sensitive, soluble in polar solvent, and slightly soluble in *n*-hexane. The FAB mass spectrum of **2** shows a parent peak corresponding to the $[\text{M}^+]$ molecular mass. Similar spectroscopic phenomena of the carbonyl group and allyl moiety in IR, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra [7] lead us to believe that complex **2** contains the similar intramolecular trigonal twist rotational behavior as those of the 18 electron dithiophosphate complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^3\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{CH}_3\text{CN})(\text{CO})_2]$ [5], $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^3\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{C}_5\text{H}_{10}\text{NH})(\text{CO})_2]$ [5] and the dithiocarbonate complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-S}_2\text{COEt}_2)(\text{CH}_3\text{CN})(\text{CO})_2]$ [6]. Treatment of **2** with CS_2 no 16 electron dithiocarbamate complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-S}_2\text{CNC}_5\text{H}_{10})(\text{CO})_2]$ can be obtained. Complexes **1** and **2** can be prepared by the reactions of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^3\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{CH}_3\text{CN})(\text{CO})_2]$, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^3\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{C}_5\text{H}_{10}\text{NH})(\text{CO})_2]$ and pySH with releasing of the $(\text{EtO})_2\text{P}(\text{S})\text{SH}$ ligand, respectively (Scheme 2). Attempt to synthesis a bisalkyne product as that of complex $[\text{Mo}(\text{PhC}\equiv\text{CPh})_2\{\eta^2\text{-S}_2\text{P}(\text{OEt}_2)\}_2]$ [14] from the reaction of **1a** with diphenylacetylene, no reaction occurred even in refluxing acetonitrile for 1 h. From the mention of above, one can conclude that the pySH ligand is a stronger π -acceptor ligand than the $(\text{EtO})_2\text{P}(\text{S})\text{SH}$ ligand. Currently, the reactions of **1a** with nitrogen, sulfur and phosphorus ligands are under investigation.

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- [7] Spectroscopy for **1a**: IR (KBr, cm^{-1}) $\nu(\text{CO})$ 1937(vs), 1922(vs), 1875(vs), 1858(vs). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 298 K): δ 1.00, 1.33 (d, $J_{\text{H-H}} = 9.6$ Hz, 2H, Hanti of allyl), 3.06, 3.43 (br, 2H, Hsyn of allyl), 3.83 (m, 1H, CH of allyl), 6.77 (d, $J_{\text{H-H}} = 8.1$ Hz, 1H, SCCH), 6.83 (t, $J_{\text{H-H}} = 6.3$ Hz, 1H, NCHCH), 7.39 (t, $J_{\text{H-H}} = 7.7$ Hz, 1H, SCCHCH), 7.88 (d, $J_{\text{H-H}} = 4.6$ Hz, 1H, NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{DMSO}-d_6$, 298 K): δ 51.9, 62.9 (s, $\text{C}=\text{CH}_2$), 74.6 (s, $\text{C}=\text{CH}_2$), 117.3 (s, 5-C of pyS), 126.2 (s, 3-C of pyS), 136.9 (s, 4-C of pyS), 146.2 (s, 6-C of pyS), 176.7 (s, 2-C of pyS), 228.9, 231.2 (s, CO). mp 195 °C dec. Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2\text{Mo}_2$: C, 39.61; H, 2.99; N, 4.62%. Found: C, 39.80; H, 2.60; N, 4.50. Spectroscopy for **1b**: IR (KBr, cm^{-1}) $\nu(\text{CO})$ 1933(vs), 1915(vs), 1870(vs), 1849(vs). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 298 K): δ 1.53 (d, $J_{\text{H-H}} = 6.4$ Hz, 2H, Hanti of allyl), 2.49 (br, 2H, Hanti of allyl), 3.45 (br, 2H, Hsyn of allyl), 3.92 (s, 6H, CH_3 syn of allyl), 4.34 (s, 2H, Hc of allyl), 7.40 (d, $J_{\text{H-H}} = 8.0$ Hz, 2H, SCCH), 7.46 (t, $J_{\text{H-H}} = 6.2$ Hz, 2H, NCHCH), 8.00 (br, 2H, SCCHCH), 8.56 (br, 2H, NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ 18.2 (s, CH_3), 45.8, 62.9 (s, $\text{C}=\text{CH}_2$), 78.5 (s, $\text{C}=\text{CH}_2$), 120.7 (s, 5-C of pyS), 129.1 (s, 3-C of pyS), 134.8 (s, 4-C of pyS), 148.3 (s, 6-C of pyS), 178.7 (s, 2-C of pyS), 225.9, 230.2 (s, CO). mp 205 °C dec. Anal. Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2\text{Mo}_2$: C, 41.65; H, 3.50; N, 4.42%. Found: C, 41.82; H, 3.46; N, 4.31. Spectroscopy for **2**: IR (KBr, cm^{-1}) $\nu(\text{CO})$ 1924(vs), 1838(vs). ^1H

- NMR (500 MHz, DMSO- d_6 , 298 K): δ 1.16, 1.26 (d, $J_{\text{H-H}} = 8.9$ Hz, 2H, Hanti of allyl), 1.64 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.88 (m, 4H, NCH_2), 3.20, 3.51 (br, 2H, Hsyn of allyl), 3.60 (m, 1H, CH of allyl), 3.89 (br, 1H, NH), 6.71 (t, $J_{\text{H-H}} = 6.1$ Hz, 1H, NCHCH), 6.87 (d, $J_{\text{H-H}} = 8.2$ Hz, 1H, SCCH), 7.25 (t, $J_{\text{H-H}} = 7.1$ Hz, 1H, SCCHCH), 7.67 (br, 1H, NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6 , 298 K): δ 23.8 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 25.1 (s, NCH_2CH_2), 46.1 (s, NCH_2), 54.2, 62.6 (s, $\text{C}=\text{CH}_2$), 70.7 (s, $\text{C}=\text{CH}_2$), 117.3 (s, 5-C of pyS), 125.0 (s, 3-C of pyS), 136.0 (s, 4-C of pyS), 147.0 (s, 6-C of pyS), 170.3 (s, 2-C of pyS), 226.6 (s, CO). MS (FAB, NBA, m/z): 389 [M^+], 321 [$\text{M}^+ - \text{CO}$], 293 [$\text{M}^+ - 2\text{CO}$]. mp 187°C dec. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2\text{SMo}$: C, 46.51; H, 4.95; N, 7.23%. Found: C, 46.85; H, 5.01; N, 7.12.
- [8] Crystal data for **1a**: $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2\text{Mo}_2$ ($M_r = 606.36$); triclinic; space group Pbcn, $a = 8.3128(1)$ Å, $b = 16.1704(2)$ Å, $c = 16.6140(2)$ Å, $V = 2233.28(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.803$ gcm⁻³, $\mu = 1.339$ mm⁻¹, observed reflections 14552, $\theta_{\text{range}} = 2.45\text{--}27.50^\circ$. Data were collected with MoK α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer at 295(2) K. Total number of parameters: 137. $R_1 = 0.0510$, $wR_2 = 0.1063$; $\text{GOF} = 1.159$; $\Delta F = 1.670, -1.980$ e Å⁻³.
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