Inorganica Chimica Acta, 53 (1981) L51–L52
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Synthesis and Properties of Dioxobis(ferrocenedithiocarboxylato)molybdenum(VI) and μ-Oxo-bis[oxobis(ferrocenedithiocarboxylato)molybdenum(V)]

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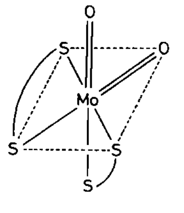
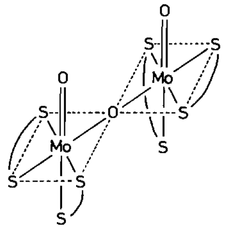
Received September 2, 1980

Much attention has been paid to molybdenum complexes containing iron and sulfur atoms as model compounds for nitrogenase and xanthine oxidase [1, 2]. Recently, we have undertaken the synthesis of oxomolybdenum complexes with ferrocenedithiocarboxylate as a dithio-chelate. This letter reports the preparation of dioxobis(ferrocenedithiocarboxylato)-molybdenum(VI), $Mo^{VI}O_2(S_2CFc)_2$ (1) (Fc = $C_5H_4FeC_5H_5$), and μ-oxo-bis[oxobis(ferrocenedithiocarboxylato)molybdenum(V)], $Mo_2^{V}O_3(S_2CFc)_4$ (2), and a disproportionation reaction of 2 in dibromomethane, giving 1 and $Mo^{IV}O(S_2CFc)_2$ (3).



1: $\widehat{S\,S} = S_2CFc$



2: $\widehat{S\,S} = S_2CFc$

A methanol solution of diethylammonium ferrocenedithiocarboxylate, $[Et_2NH_2][S_2CFc]$ (3.4 g, 10 mmol) prepared by the literature method [3] was added to a stirred methanol solution of MoO_2Cl_2 [4] (1.0 g, 5.0 mmol) in an acetone-dry ice bath. A greenish blue precipitate formed immediately which was collected by filtration, washed with methanol and dried *in vacuo* to give 1 in a 42% yield, Mp > 120 °C (dec.). *Anal.* Found: C, 40.80; H, 2.99%. Calcd. for $C_{22}H_{18}Fe_2MoO_2S_4$: C, 40.63; H, 2.79%. MW in benzene 628 (calcd. 650). The infrared spectrum of 1 in Nujol mull exhibits two strong $\nu(Mo = O)$ bands at 922 and 889 cm^{-1} (Fig. 1a), which are compared with those of the corresponding dithiocarbamates, $Mo^{VI}O_2(S_2CNR_2)_2$ (R = Me, Et, n-Pr, n-Bu), with *cis*-dioxo configuration (912–905 cm^{-1} and 877–875 cm^{-1}) [5]. Complex 1 is therefore formulated as *cis*-$Mo^{VI}O_2(S_2CFc)_2$. Complex 2 was prepared as follows: to a stirred aqueous solution containing $Na_2MoO_4 2H_2O$ (1.2 g, 5.0 mmol) and $[Et_2NH_2]$-$[S_2CFc]$ (3.4 g, 10 mmol) was added dropwise a 2*N* HCl solution to adjust the pH 5.5. The resulting dark blue precipitate was collected by filtration, washed with water and then diethyl ether, and dried *in vacuo*, 20% yield, Mp > 115 °C (dec.). *Anal.* Found: C, 41.49; H, 2.92%. Calcd. for $C_{44}H_{36}Fe_4Mo_2O_3S_8$: C, 41.14, H, 2.82%. MW 1296 in benzene (calcd. 1284). Complex 2 in Nujol mull exhibits only one $\nu(Mo = O)$ band at 940 cm^{-1} (Fig. 1b), which is compared with that of the dithiocarbamate analogs, $Mo_2^{V}O_3(S_2CNR_2)_4$ (R = Me, Et, i-Pr, *etc.)* (943–938 cm^{-1}) [6].

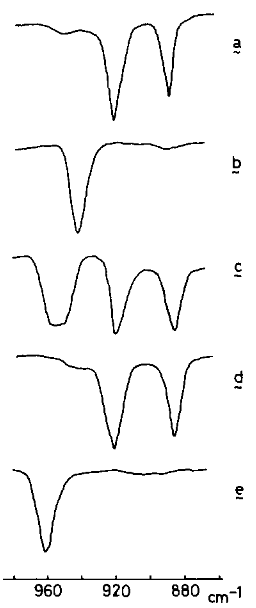


Fig. 1. Infrared spectra of (a) $Mo^{VI}O_2(S_2CFc)_2$ in Nujol mull, (b) $Mo_2^{V}O_3(S_2(CFc)_4$ in Nujol mull, (c) $Mo_2^{V}O_3$-$(S_2CFc)_4$ in dibromomethane, (d) $Mo^{VI}O_2(S_2CFc)_2$ in dibromomethane, and (e) the equimolar mixture of $Mo^{VI}O_2$-$(S_2CFc)_2$ and Ph_3P in dibromomethane after refluxing for 30 min.

A dibromomethane solution of 2 displays three infrared bands at 955, 920, and 885 cm^{-1} in the $\nu(Mo = O)$ region (Fig. 1c), of which the two lowest frequency bands are consistent in positions with $\nu(Mo = O)$ bands of 1 in dibromomethane (Fig. 1d), respectively. This is suggestive of the occurrence of the disproportionation reaction of 2 to generate 1 in dibromomethane, then 3 should be produced as a counter species, according to Eqn. 1.

$$Mo_2^{V}O_3(S_2CFc)_4 \rightarrow Mo^{VI}O_2(S_2CFc)_2 + Mo^{IV}O(S_2CFc)_2 \qquad (1)$$

Several attempts to isolate 3 have unfortunately been unsuccessful. A dibromomethane solution containing equimolar amounts of 1 and Ph_3P, however, after refluxing for 30 min, exhibits a $\nu(Mo = O)$ band at 962 cm^{-1} (Fig. 1e), which is compared with that of $Mo^{IV}O(S_2CNEt_2)_2$ (966 cm^{-1}) [7]. This is suggestive of the occurrence of oxo-abstraction reaction from 1, giving 3. A reaction of this type is well known between dioxomolybdenum(VI) complexes and Ph_3P [8]. Thus, the broad band centered at 955 cm^{-1} ranging from 970 to 940 cm^{-1} in the spectrum of 2 in dibromomethane may be contributed from the $\nu(Mo = O)$ vibration of 3 as the counter species formed in the disproportionation reaction. Moreover, the addition of an equimolar amount of 1 to the resultant solution of 1 with Ph_3P displayed the infrared spectrum quite similar to that of 2 in dibromomethane, confirming that Eqn. 1 is an equilibrium reaction. Similar disproportionation equilibria have been reported to exist in complexes of the $Mo_2^VO_3L_4$ type, where L = S_2CNEt_2 [6, 7, 9], S_2PPh_2 [9], S_2CS-i-Pr [10], *etc.*

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