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Preliminary communication

SYNTHESIS AND STRUCTURE OF THE *S*-METHYLSULFENATO BRIDGED CATION $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Mo}(\mu\text{-S(O)Me})(\mu\text{-SMe})_3\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)]^{2+}$

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Summary

The novel *S*-methylsulfenato bridged cation $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Mo}(\mu\text{-S(O)Me})(\mu\text{-SMe})_3\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)]^{2+}$ has been synthesized by $KMnO_4$ oxidation of the cation $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)]^{2+}$ and characterized by IR, and ^{1}H NMR spectroscopy.

In the course of investigating the chemistry of the cation $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)]^{2+}$ (I) [1] we have found that the reaction of its bisulfate salt in 2 *M* HCl with an excess of $KMnO_4$ at −10°C yields a new, diamagnetic cation of stoichiometry: $[\text{Mo}_2(\text{MeC}_6\text{H}_5)_2(\text{SMe})_4(\text{O})]^{2+}$ (II). The cation was isolated as the hexafluorophosphate salt in ca. 50% yield by addition of an excess of NH_4PF_6 to the reaction mixture. The complex was recrystallized from acetone/ethanol. Analysis: Found: C, 24.9; H, 3.3; S, 15.0; P, 7.1; F, 25.2; Mo, 22.1. $C_{18}H_{28}OS_4P_2F_{12}Mo$ calcd.: C, 24.8; H, 3.2; S, 14.7; P, 7.1; F, 26.2; Mo, 22.0%.

Addition of H_2SO_4 to an acetone solution of II yielded a crystalline, water soluble bisulfate salt from which the tetraphenylborate salt was obtained by metathesis in aqueous solution. The analytical and spectral data obtained for compound II strongly support a structure containing a bridging *S*-methyl sulfenato ligand (Fig. 1) derived from compound I by oxidation of one of the four bridging methyl mercaptide ligands. Large dark red crystals of compound II thought to be suitable for X-ray investigation were grown by slow evaporation of an acetonitrile solution of the tetraphenylborate salt. Unfortunately, because of disorder present in the region of the bridging groups in the cation, the X-ray structural analysis is not unambiguous but the most sensible crystallographic model seems to confirm the deductions from the spectral data [2].

A medium strong band at 1075 cm^{-1} (KBr) in the IR spectrum of compound II not present in that of compound I is assigned as the S=O stretch arising from an *S*-bonded methylsulfenato ligand. This assignment is supported by previous investigations on the non-bridging *S*-methylsulfenato complexes, $IrCl_2(MeSO)(CO)L_2$ (L = PPh_3 or PPh_2Me), where the S=O stretch was observed near 1000 cm^{-1} (KBr) [3].

The solution ^1H NMR spectrum of compound II (PF_6 salt) supports the structure shown in Fig. 1. A series of overlapping resonances attributable to the bridging SMe ligands are observed centered at δ 2.1 (DMSO-d_6, TMS as internal standard). The complexity of the spectrum in this region is consistent with the structural inequivalence of the SMe ligands shown in Fig. 1. A singlet resonance at δ 3.5 ppm integrating to 3 protons is assignable to the methyl group of the bridging sulfenato ligand. Resonances assignable to the η^6-toluene ligand are observed at δ 2.24 ppm (singlet, MeC_6) and δ 6.7 ppm (complex, C_6H_5).

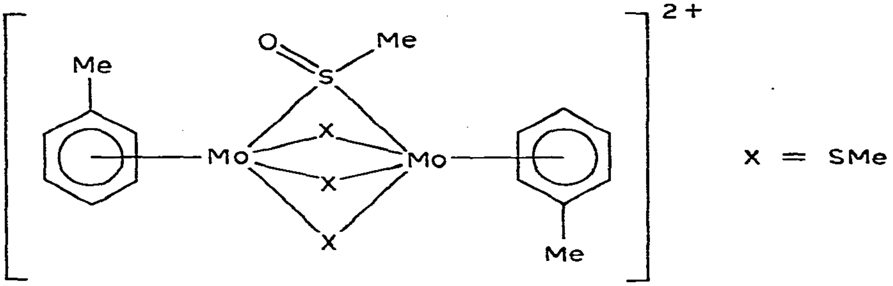

Fig. 1.

Previous investigations have shown that the square planar iridium(I) complexes, $IrCl(CO)L_2$ (L = PPh_3 or PPh_2Me), oxidatively add MeS(O)Cl to give the octahedral *S*-methylsulfenato iridium(III) complexes, $IrCl_2(S(O)Me)(CO)L_2$ [3], while hydrogen peroxide oxidation of the cobalt(III) cation $[Co(en)_2\{NH_2CH(COO)CH_2S\}]^+$ (en = ethylenediamine) has been shown to lead to the cysteinesulfenato cation $[Co(en)_2\{NH_2CH(COO)CH_2SO\}]^+$ [4]. The cation $[Co(en)_2\{(R)\text{-}NH_2CH(COOH)CH_2SO\}]^{2+}$ also has been synthesized and its structure determined by X-ray crystallography [5]. The cobalt(III) complexes readily underwent further oxidation to the crysteinesulfinato cations $[Co(en)_2\{NH_2CH(COO)CH_2SO_2\}]^+$ [4] and $[Co(en)_2\{NH_2CH(COOH)CH_2SO_2\}]^{2+}$ [5]. The isolation of stable sulfenato- and sulfinato-cobalt(III) complexes was attributed to the non-labile nature of cobalt(III) complexes which would maximize the chance that the sulfur ligand would remain coordinated during and after the oxidation reaction [4]. We have previously shown that compound I is non-labile in strong acids [1]. In contrast to what was seen with the cobalt(III) complexes, we do not observe further reaction of compound II to a sulfinato complex. This is presumably due to the fact that in the bridging system the lone pair of electrons belonging to the S atom is strongly bonded to an Mo atom and is therefore not available for further reaction. Compound II appears to be the first example of a complex containing a bridging sulfenato ligand.

Acknowledgments

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