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LETTER

Dimolybdenum(II) and Dirhenium(II) Complexes of 2-Mercaptoquinoline

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Dimolybdenum complexes that contain monoanionic ligands based upon the bridging $N-C-O^-$ and $N-C-N^-$ units are well known [1] but there are very few examples of complexes in which the bridging ligands contain the corresponding $N-C-S^-$ unit [2, 3]. These are the complex $Mo_2(dmmp)_4$ (dmmp is the anion of 4,6-dimethyl-2-mercaptopyrimidine) [2] and some interesting isomeric dimolybdenum(II) complexes that contain ambidentate ligands of the type $[R_2PC(S)NR']^-$ [3]. We now report a new example of this type, namely the dimolybdenum complex $Mo_2(2\text{-mq})_4$ (2-mq is the monoanion of 2-mercaptoquinoline).

In studies of the reactions between $Mo_2(O_2CR)_4$ (R = Me or Ph) and different stoichiometric quantities of 2-mercaptoquinoline (2-mqH) in methanol, in which we attempted to prepare the series of intermediate mixed carboxylate–mercaptoquinoline complexes $Mo_2(O_2CR)_{4-x}(2\text{-mq})_x$, we found that the tetrakis(2-mercaptoquinoline) complex $Mo_2(2\text{-mq})_4$ was the predominant product. Indeed, we have no evidence (from IR and electronic absorption spectroscopy and cyclic voltammetric measurements) that such 'intermediates' are formed in any significant quantities. The yield of $Mo_2(2\text{-mq})_4$ was optimized by use of the following procedure. A mixture of $Mo_2(O_2CCH_3)_4$ (0.114 g, 0.265 mmol), and four equivalents of 2-mqH (0.171 g, 1.061 mmol) was stirred for 30 min in 10 ml of methanol (or n-butanol) and then refluxed for 6 h. The deep red reaction mixture was cooled to room temperature and filtered. The insoluble product was washed with methanol and then dried in vacuum; yield 0.19 g (85%). *Anal.* Calc. for $C_{36}H_{24}Mo_2N_4S_4$: C, 51.92; H, 2.91; N, 6.73. Found: C, 52.39; H, 2.88; N, 6.55%. Crystals suitable for an X-ray structure determination were grown by the slow diffusion of hexane vapor into a dichloromethane solution of this complex.

To fully characterize this product we carried out a single-crystal X-ray structure analysis [4, 5] (for scattering factors used in the structure solution, see ref. 5b). The structure of $Mo_2(2\text{-mq})_4$ is shown in Fig. 1; the pertinent structural parameters are listed in the captions to the Figure. A dark red rhomboidal crystal of approximate dimensions 0.28 × 0.14 × 0.13 mm was used. It was monoclinic, space group $P2_1$(No. 4) with $a = 9.127(1)$, $b = 9.076(1)$, $c = 19.967(3)$ Å; $\beta = 94.66(1)°$, $V = 1648.5(6)$ Å^3, $Z = 2$, and $D_{calc} = 1.678$ g/cm^3. X-ray diffraction data were collected at 20 °C for 2494 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD-4 diffractometer using graphite crystal monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection and reduction methods were by standard procedures. An empirical absorption correction was applied [4]; the linear absorption coefficient μ was 10.19 cm^{-1}. The Mo, S, N and C atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms [5]. Hydrogen atoms were located and added to the structure factor calculations but

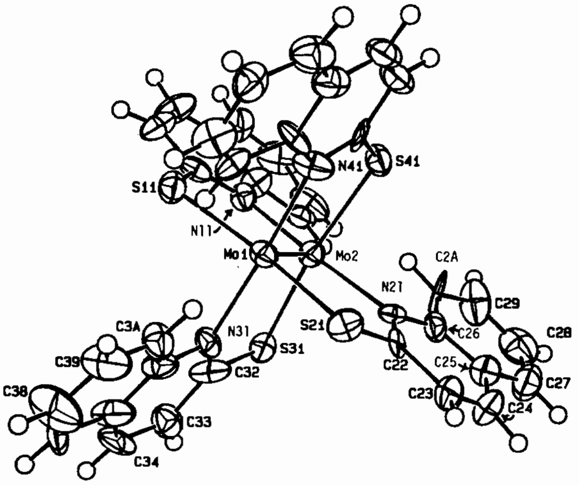

Fig. 1. ORTEP representation of the structure of $Mo_2(2\text{-mq})_4$. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) and angles (°) are as follows: Mo(1)–Mo(2), 2.089(1); Mo(1)–S(11), 2.447(4); Mo(1)–S(21), 2.460(4); Mo(2)–S(31), 2.465(4); Mo(2)–S(41), 2.446(4); Mo(1)–N(31), 2.19(1); Mo(1)–N(41), 2.20(1); Mo(2)–N(11), 2.20(1); Mo(2)–N(21), 2.19(1); Mo(2)–Mo(1)–S(11), 97.5(1); Mo(2)–Mo(1)–S(21), 96.6(1); Mo(2)–Mo(1)–N(31), 96.8(3); Mo(2)–Mo(1)–N(41), 96.6(3).

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their positions were not refined. The final residuals were $R = 0.046$ and $R_w = 0.068$ for 2233 data with $I > 3\sigma(I)$. The highest peak in the final difference Fourier map had a height of 0.99 e/Å^3.

The structure of $Mo_2(2\text{-mq})_4$ bears a close resemblance to the structures reported for $Mo_2(dmmp)_4$ [2] and $Mo_2[Ph_2PC(S)NMe]_4$ [3]. These two complexes have identical Mo–Mo bond lengths (2.083(2) and 2.083(1) Å, respectively), which are in turn very similar to that found for $Mo_2(2\text{-mq})_4$ (2.089(1) Å). The same type of *trans*-MoN_2S_2 geometry is observed in all three cases, and the Mo–S and Mo–N average distances are also very similar between the three structures.

The electronic absorption spectrum of this complex in CH_2Cl_2 shows absorption maxima at 494, 346 and 258 nm, while its IR spectrum (Nujol mull) exhibits the following bands between 2700 and 600 cm^{-1}: 1610sh, 1598s, 1544m–s, 1498w, 1418m, 1380s, 1345sh, 1318m, 1280m–s, 1258m–w, 1158s, 1145sh, 1110vs, 956w, 866m–w, 858m–w, 812s, 775s, 734s, 655w and 622m–w. Cyclic voltammetric measurements on solutions of this complex in 0.1 M $n\text{-Bu}_4NPF_6/CH_2Cl_2$ show a reversible oxidation at $E_{1/2} = +0.52$ V and an irreversible process at $E_{p,a} = +1.32$ V (all potentials versus Ag/AgCl)†. The reversible process at $E_{1/2} = +0.52$ V can be compared with an $E_{1/2}$ value of +0.64 V associated with the reversible one-electron oxidation of the isomeric form of $Mo_2[Ph_2PC(S)NMe]_4$ that contains four bridging ligands with $N–C–S^-$ units [3].

The ability of 2-mercaptoquinoline to complex the dirhenium(II) core has been demonstrated by the reaction of 2-mqH with $Re_2Cl_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) [6] to produce $Re_2Cl_4(dppm)_2(2\text{-mqH})$. A mixture of $Re_2Cl_4(dppm)_2$ (0.22 g, 0.17 mmol) and 2-mqH (0.028 g, 0.17 mmol) in 10 ml of acetone was stirred at room temperature for 24 h. The dark blue precipitate was filtered off, washed with 10 ml of acetone and dried in a vacuum; yield 0.25 g (95%). *Anal.* Calc. for $C_{62}H_{57}Cl_4NOP_4Re_2S$ (i.e. $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$): C, 49.57; H, 3.82; Cl, 9.44. Found: C, 50.04; H, 4.37; Cl, 9.35%. Its IR spectrum (Nujol mull) showed a ν(CO) mode for lattice acetone at 1710 cm^{-1}.

One of the most interesting characteristics of this complex is its electrochemical properties as measured by the cyclic voltammetry technique. Solutions of this complex in 0.1 M $n\text{-Bu}_4NPF_6/CH_2Cl_2$ show reversible looking one-electron oxidations at $E_{1/2} = +0.08$ V and $E_{1/2} = +0.83$ V versus Ag/AgCl. The accessibility of the first process was demonstrated by the oxidation of this complex with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. A quantity of $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$ (0.074 g, 0.049 mmol) was reacted with a slight excess of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.018 g, 0.054 mmol) in 10 ml of acetone for 48 h. The red solution was evaporated to dryness and the residue washed with 15 ml of diethyl ether; yield 0.056 g (73%). *Anal.* Calc. for $C_{59}H_{50}Cl_3F_6NP_5Re_2S$ (i.e. $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$: C, 45.64; H, 3.25. Found: C, 44.68; H, 3.40%. The resulting product dissolved in acetone to give solutions with conductivities typical of a 1:1 electrolyte (Λ_m = 107 ohm^{-1} cm^2 mol^{-1} for $c_m \simeq 1.0 \times 10^{-3}$ M). Its electrochemical properties (recorded on solutions in 0.1 M $n\text{-Bu}_4NPF_6/CH_2Cl_2$) showed conclusively that this oxidation was accompanied by a structural rearrangement since the potentials for $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ were different from those of the precursor 1:1 adduct, viz., $E_{1/2} = -0.24$ V and $E_{1/2} = +0.79$ V versus Ag/AgCl. The first process corresponds to a one-electron reduction; the second to a one-electron oxidation. Further studies of the one-electron oxidation of $Re_2Cl_4(dppm)_2(2\text{-mqH})$ and the accompanying structural rearrangement are underway**, together with investigations of the related bromide complex.

Supplementary Material

Further details concerning the structure solution of $Mo_2(2\text{-mq})_4$, including tables of crystallographic data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, and bond distances and bond angles are available from R.A.W.

Acknowledgement

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† In all CV measurements described in this report the potentials are quoted relative to the ferrocenium/ferrocene couple having $E_{1/2} = +0.47$ V versus Ag/AgCl. Measurements were conducted with the use of a Pt-bead electrode at a scan rate of 200 mV s^{-1}.

** The structural identity $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ has now been confirmed by a single crystal X-ray structure analysis (P. E. Fanwick, unpublished results). Full details will be made available in due course.

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