The rotational spectrum of a weakly bound dimer formed between dimethyl ether and OCS has been observed by Fourier-transform microwave spectroscopy. The rotational constants of the normal isotopic species are found to be $A = 4069.4106(23)$ MHz, $B = 1431.7413(7)$ MHz and $C = 1074.2925(5)$ MHz and the dipole moment components are $\mu_a = 1.3046(25)$ D and $\mu_b = 0.8159(35)$ D. The rotational constants and dipole moment components are consistent with a heavy atom planar structure in which the OCS lies across the $C_2$ axis of the dimethyl ether (the O=C...O angle is estimated to be about $83^\circ$ by ab initio calculation); the oxygen atom of OCS appears to interact with one of the methyl group hydrogen atoms. Isotopic shifts in the spectra of the DME-O$^{18}$CS and DME-O$^{34}$S isotopomers have been found to be consistent with this structure. Ab initio optimizations at the MP2/6-311++G(2d,2p) level will be presented and shown to give very good agreement with the rotational constants obtained from experiment.