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Photochemistry of Molybdenum. Preparation, Characterization, and X-ray Crystal Structure of Photosensitive Isothiocyanato Molybdenum(VI) Complex with Dimethylsulfoxide as Ligand, $[\{Mo(O)_2(NCS)(dmso)_2\}_2O]$

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Much attention has been paid to clarifying the role of molybdenum in the enzymatic redox reaction [1]. On the photochemical redox behaviors of molybdenum complexes, few reports, however, have appeared for those with [2] and without porphyrins [3] as ligand. We describe here the preparation of μ-oxo-bis[isothiocyanato-bis(dimethylsulfoxide)dioxomolybdenum(VI)] and its reversible intramolecular redox reaction when exposed to sunlight, and furthermore the X-ray crystal structure of the compound.

The complex was prepared by the following procedure: a mixture of $(pyH)_4[Mo_2O_4(NCS)_6]\cdot H_2O$ [4] (5 g) and dimethylsulfoxide (20 ml) in methanol (50 ml) was refluxed for a couple of hours. Filtration followed by the addition of diethylether (40 ml) gave pale yellow crystals after standing for a week in a refrigerator. Yield 1.8 g.

The compound crystallizes in the monoclinic system, space group $P2_1/n$ with cell dimensions $a = 7.995(3)$, $b = 21.688(7)$, $c = 7.916(?)$ Å, $\beta = 107.20(3)°$, $V = 1311.2$ Å^3, $Z = 2$, $D_m = 1.76$, $D_c = 1.774$ g cm^{-3}, μ(Mo Kα) = 14.4 cm^{-1}. Intensity data were collected on a Phillips PW 1100 four-circle diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) with ω-scan technique. The structure was solved by Patterson and Fourier procedures and refined by block-diagonal least squares method to an R value of 0.037 for 1772 ($F_0{}^2 > 3\sigma(F_0{}^2)$) reflections collected in the $2\theta \leqq 50°$ range. All but hydrogen atoms were refined anisotropically.

Perspective views of the molecule together with pertinent molecular parameters are presented in Fig. 1. The bridging oxygen atom resides on a crystallographic inversion center and the Mo–O–Mo′ sequence is required to be linear. The result of the X-ray analysis confirmed the coordination of dmso through oxygen and thiocyanate ion through nitrogen, in agreement with the data from the infrared spectroscopy ($\nu_{SO} = 1000$ and $\nu_{CN} = 2065$ cm^{-1}) [5].

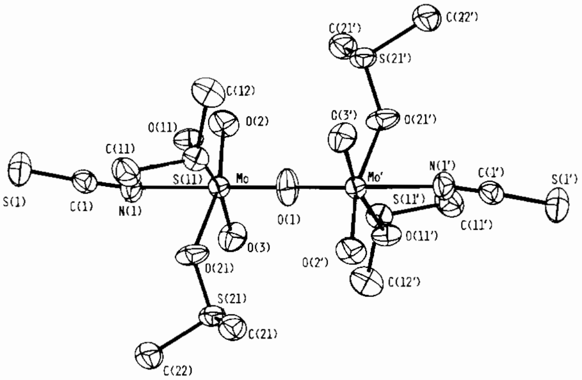

Fig. 1. Molecular structure of $[\{Mo(O)_2(NCS)(dmso)_2\}_2O]$ showing atom labelling scheme. (The primed atoms are centrosymmetric of the unprimed ones.) Relevant bond lengths (l/Å) and angles (ϕ/°) are: Mo–O(1), 1.864(1); Mo–O(2), 1.691(5); Mo–O(3), 1.686(5); Mo–O(11), 2.214(4); Mo–O(21), 2.213(5); Mo–N(1), 2.094(5); O(1)–Mo–O(2), 101.0(2); O(1)–Mo–O(3), 100.4(2); O(1)–Mo–O(11), 83.3(1); O(1)–Mo–O(21), 85.7(1); O(2)–Mo–O(3), 104.6(2); O(2)–Mo–O(11), 88.6(2); O(2)–Mo–N(1), 90.5(2); O(3)–Mo–O(21), 90.2(2); O(3)–Mo–N(1), 94.3(2); O(11)–Mo–O(21), 75.7(2); O(11)–Mo–N(1), 78.6(2): O(21)–Mo–N(1), 78.4(2).

The very pale yellow color of the methanol solution of the complex under N_2 atomosphere turns orange ($\lambda_{max} = 465$ nm) within ten second of exposure to sunlight (Fig. 2(A)). The resultant orange solution shows a clear ESR signal ($g = 1.940$, $a^{Mo} = 47.0$ G) indicating that a reduction of Mo(VI) to Mo(V) takes place (Fig. 2(B))*. This orange còlor fades away with $t_{1/2} \approx 10$ days at room temperature when the solution is kept in the dark; such a change of color can be repeated reversibly. The effectiveness of UV-light in coloration was examined by using a monochromatic light source.

The NCS radical could not be detected by ESR measurement; a dichloromethane solution of the complex containing excess PBN, #however, showed a ESR signal of PBN spin adduct ($g = 2.007$, $a^N = 13.5$ G, $a^H = 2.2$ G) after sunlight irradiation (Fig. 3).

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*Similar phenomena can also be observed when dichloromethane is used as a solvent.

#Abbreviations: PBN, phenyl-N-tert-butylnitrone; phen, 1,10-phenanthroline; bpy, 2,2′-bipyridine; tppo, triphenylphosphineoxide.

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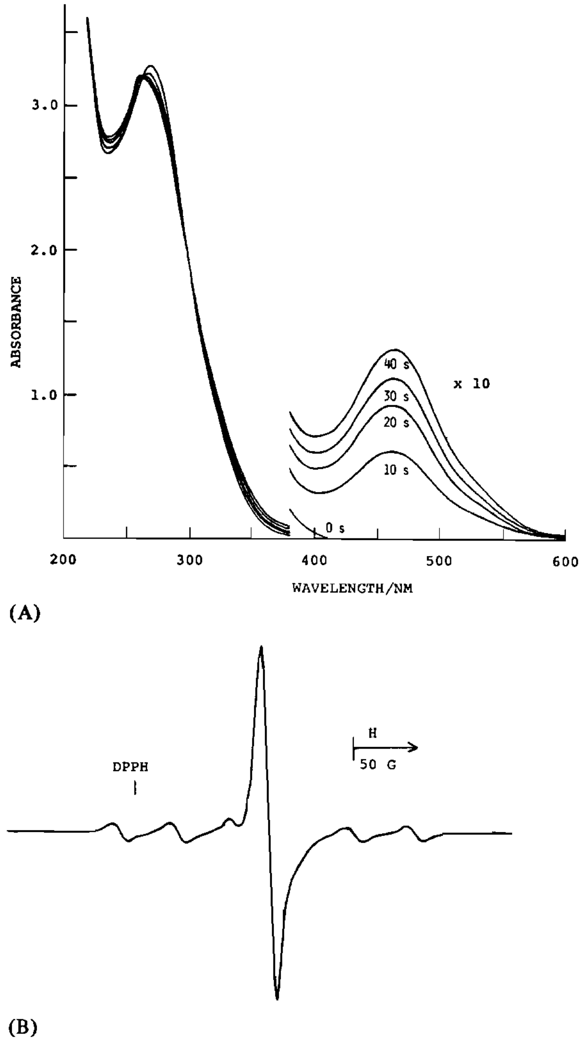

Fig. 2. UV-VIS (A) and ESR (B) spectra of [{$Mo(O)_2(NCS)(dmso)_2$}$_2O$] in methanol (2.09×10^{-3} *M*) before and after sunlight exposure. (A) After t second exposure to sunlight in a 0.1 cm quartz cell. (B) After sunlight exposure.

The mechanism of the coloration and appearance of the ESR signals can be explained by an intramolecular electron transfer from the thiocyanato ligand to a molybdenum(VI) metal center, although the fate of the NCS radical has not yet been determined. The laser Raman spectrum of the methanol solution of the complex did not show any peak assignable to the S–S bond of thiocyanogen which could have arisen from thiocyanate radical.

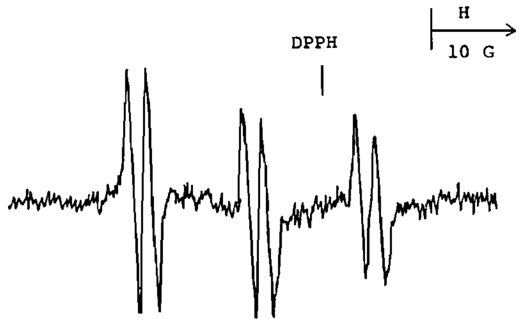

Fig. 3. ESR spectrum of PBN spin adduct formed upon sunlight exposure of [{$Mo(O)_2(NCS)(dmso)_2$}$_2O$] in CH_2Cl_2.

Although reports have been made on the preparation [6] and X-ray crystal structures [7] of several molybdenum(VI) complexes with NCS^- ligand, no detailed reference to photochemistry has been made in them. Therefore the photochemical investigation of a series of analogous Mo(VI) complexes## containing one or more NCS^- ligands were carried out: {$(CH_3)_4N$}$_2$[$Mo(O)_2(NCS)_4$] [6] (pale yellow to orange in methanol), [{$Mo(O)_2(NCS)(phen)$}$_2O$] [7-b)] (pale yellow to purple in CH_2Cl_2), [{$Mo(O)_2(NCS)(bpy)$}$_2O$] (pale yellow to purple in CH_2Cl_2), [$Mo(O)_2(NCS)(OCH_3)(phen)$] (pale yellow to purple in CH_2Cl_2), and [$Mo(O)_2(NCS)_2(tppo)_2$] (pale yellow to orange in dioxane); in all colorations and appearance of ESR signals were seen after sunlight exposure.

The color of [$Mo(O)_2Cl_2(phen)$] in methanol eventually turns purple from colorless, and this can also be explained by intramolecular electron transfer (*vide supra*). The lower sensitivity of this complex, as compared to that of NCS-coordinated complexes, could be ascribable to the higher redox potential of Cl_2 than that of $(NCS)_2$ [8]. Details of the photochemistry of these halogeno and above-mentioned thiocyanato complexes of Mo(VI) will be reported elsewhere.

Acknowledgements

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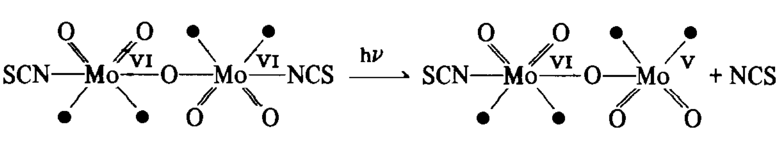

•, dmso

##Satisfactory elemental analytical data were obtained for all compounds.

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