blies containing **2a** can be regenerated by gentle heating under vacuum.

When glass slides containing monolayer assemblies of **2a** or **2b** are immersed in water and irradiated through Pyrex with a 100-W medium-pressure mercury lamp, a steady production of gas is observed. In a typical experiment irradiation of a set of ten slides containing a single outer monolayer of **2a** led to the production of 0.5 cm^3 of gas (~1 atm of pressure) during a 24-h period. (The average absorption per slide in the visible-near uv region was 0.1-1%). The **2a** used in the gas generation is evidently almost completely recyclable since an estimated turnover of more than 10^3 molecules of gas/molecule of **2a** has been observed in a system now in its second week of operation. Analysis of the gas in a mass spectrometer indicated that it contained molecular hydrogen and oxygen;[14] this was confirmed by an experiment in which the collected gas was found to undergo explosive combustion upon ignition.

The reasonable conclusion from the above results is that the net reaction observed is given by eq 1-2.[14]

$$2a \xrightarrow{h\nu} 2a^* \tag{1}$$

$$2(2a^*) + H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 + 2(2a) \tag{2}$$

The reaction is reasonable on energetic grounds since the 45-40 kcal/mol excited state of **2a** has more than enough energy to promote the separation of water (28 kcal/mol of electrons). The ruthenium(III) complex produced by oxidation of **2a*** should be able to oxidize OH^-; in fact, it has recently been shown[15] that oxidized **1** reacts with OH^- to generate O_2. The fact that similar ruthenium(II) complexes are reactive in monolayer assemblies but not in solution is evidently due to a lowering of the barrier to the electron transfer process in the assembly or to provision in the assembly of a barrier to the geminate recombination with the ruthenium site since the lifetime of the excited state of the complex in the dry assembly and in solution are not very different. It seems likely that the hydrophobic environment provided by the assemblies assists in establishing these barrier conditions although a detailed mechanism cannot yet be established.

The results presented here represent a novel method for preparation of hydrogen and oxygen that appears extremely promising as a means of solar energy conversion. Experiments are currently in progress to determine the scope, efficiency, and mechanism of this process.[16]

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References and Notes

(1) Photochemical Reactions in Organized Monolayer Assemblies III; paper II: F. H. Quina, D. Möbius, F. A. Carroll, F. R. Hopf, and D. G. Whitten, *Z. Phys. Chem.* (*Frankfurt am Main*), in press.

(2) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).

(3) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).

(4) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).

(5) G. S. Lawrence and V. Balzani, *Inorg. Chem.*, **13**, 2976 (1974).

(6) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).

(7) A. Fujishima and K. Honda, *Bull. Chem. Soc. Jpn.*, **44**, 304 (1971).

(8) A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972).

(9) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, *Proc. Nat. Acad. Sci. U.S.A.*, **72**, 1518 (1975).

(10) Synthetic details will be reported in the full paper.

(11) We thank Dr. D. Möbius at the Max Planck Institute in Göttingen, Germany for making these measurements.

(12) H. Kuhn, D. Möbius, and H. Bücher, "Physical Methods of Chemistry", Vol. I, Part 3B, A. Weissburger and B. Rossiter, Ed., Wiley, New York, N.Y., 1972, p. 588.

(13) F. E. Lytle and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 253 (1969).

(14) Although both mass spectral analysis and combustion clearly establish the production of hydrogen, the determination of oxygen as the major oxidative product is less certain since a background from oxygen in the air was unavoidably present. However, this point is not critical since it has been shown that ruthenium(III) complexes liberate O_2 from OH^-.[15] Note Added in Proof. Recent experiments have established that oxygen is the major oxidative product of water in these reactions; in some cases the hydrogen/oxygen ratio appears to be lower than that predicted by eq 2. This may be due to trapping of the hydrogen precursor by unsaturated groups in the monolayer.

(15) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).

(16) The quantum yield can be very approximately estimated to be ca. 0.1 when pure water is used as the substrate. The reaction appears to be somewhat pH dependent with a slight retardation at high pH.

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Binuclear Nature of the Aquomolybdenum(IV) Ion in Solution

Sir:

In a recent communication[1] Sykes and co-workers rejected the binuclear structure $Mo_2O_2^{4+}$ assigned to the molybdenum(IV) aquo ion by Ardon and Pernick,[2] and support the mononuclear structure[3] MoO^{2+} (or $Mo(OH)_2^{2+}$). The purpose of the present communication is to show why a mononuclear structure of Mo(IV) is unacceptable and to report new data that confirm the binuclear structure of this ion.

In 1966, Souchay[3] and co-workers discovered the existence of Mo(IV) as a stable species in aqueous solution. Unfortunately, this important discovery was totally overlooked by the numerous reviews and textbooks dealing with molybdenum chemistry that were published in the U.S.A. and U.K. between 1966 and 1973, all of which upheld the wrong notion that Mo(IV) could *not* exist as a stable species because of a supposed disproportionation reaction. These unusual circumstances explain, though by no means justify, Ardon and Pernick's unawareness of Souchay's work when they reported their own findings.[2]

The charge of a metal ion cannot usually be determined solely by its ion-exchange elution behavior, but a definite distinction may be made between a 2+ and 4+ charge of a transition metal ion by comparing its elution behavior with that of related ions of known charges.[4] The binuclear structure $Mo_2O_2^{4+}$ was assigned to the Mo(IV) aquo ion[2] on the basis of a charge per atom determination (2.0 ± 0.1) and the elution behavior which corresponded to that of other tetrapositive ions, but was in marked contrast to the elution behavior of dipositive transition metal aquo ions (including dipositive oxo ions). Further evidence of the binuclear structure is now presented.

The degree of polymerization of transition metal ions and other species which are stable only in acidic solutions may be determined directly by *acid cryoscopy*.[5]

Eutectic aqueous perchloric acid was the first solvent to be employed successfully for this purpose[6] and enabled the confirmation of the binuclear structure of the chromic dimer[6a] and of the Mo(V) aquo ion.[7] This solvent, however, could not be employed for the determination of the degree of polymerization of Mo(IV) since it is reduced by it to Cl^-. A second solvent, eutectic aqueous trifluoroacetic acid, was found to be suitable for cryoscopic work[8] and is not reduced by Mo(IV) or any other transition metal ion. At the concentration of 5.1 M this solvent has a eutectic freezing point of −22.465 ± 0.005 °C. The cryoscopic constant derived from freezing point depression by nine different solutes (at the concentration range of 0.02–0.05 *m*) yielded an average of $K_f = 6.53$. Values for all solutes, some as different from each other as Th^{4+}, Mg^{2+}, and ClO_4^- fell within the range of 6.4–6.7. Three solutions of Mo(IV) in this solvent were prepared by absorption of Mo(IV) on a Dowex 50 X2 cation-exchange column followed by elution with eutectic acid and dilution to the desired concentration. The freezing point of each solution was measured four times by the procedure described in ref 8. The cryoscopic constants calculated from these measurements were 3.4 ± 0.1, 3.4 ± 0.2, and 3.2 ± 0.2 for solutions which were 0.10, 0.06, and 0.04 *m* in Mo(IV), respectively (gram-atoms of molybdenum per kilogram of solvent). The average value $K_f = 3.37 \pm 0.08$ derived from these data is 0.52 ± 0.01, or very nearly one-half of the average molal freezing-point depression of a mononuclear ion.

Sykes and co-workers[1] deduce from results of a kinetic study of the equilibrium reaction between Mo(IV) and NCS^- that this system should be presented by the equation

$$\text{Mo(IV) monomer} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\text{Mo}^{\text{IV}})\text{NCS}$$

They support this assumption by an ion exchange separation and analysis of the reaction product which revealed Mo:NCS ratios of 1:0.95. Ion exchange separation and analysis experiments carried out in this laboratory established that the reactants Mo(IV) and NCS^- (in 1 M acid) were in equilibrium with *two* complexes, rather than one, in the range of concentrations employed by Sykes et al.[1] in their kinetic studies. When an excess of Mo(IV) was employed the main product was "complex I" with a Mo:NCS ratio of 2:1. With NCS^- in excess, the main product was "complex II" with a Mo:NCS ratio of 1:1. With both reactants in approximately equal concentrations both complexes could be isolated in good yields along with some unreacted Mo(IV) aquo ion, as in the following experiment.

A solution containing $(NCS^-) = 5 \times 10^{-3}$ M, Mo(IV) = 4×10^{-3} M, and $(H^+) = 0.3$ M was equilibrated for 30 min at 25 °C before absorption on an ice-cooled cation exchange column (Dowex 50 X2; 100–200 mesh). Elution with 0.5 M acid revealed three distinct bands: a diffuse brown band which was eluted by this acid (complex II), a sharp brown band which was eluted with 1 M acid (complex I), and a sharp red band of the free aquo ion[2] which was eluted with 3 M acid.

Complex I conforms to a composition $(MoO)_{2n}(NCS)_n{}^{3n+}$. This composition is incompatible with a mononuclear structure. The only reasonable choice of *n* is $n = 1$, i.e., $(MoO)_2NCS^{3+}$ (or $Mo_2O_2NCS^{3+}$). The charge 3+ of this ion accounts well for its slow elution by 1 M acid. Complex II conforms to a composition of $(MoO)_m(NCS)_m{}^{m+}$. One could hardly justify the choice $m = 1$ since the corresponding monopositive ion $MoONCS^+$ would not be absorbed as a distinct band on an ion exchange column from a strongly acidic solution which contains a 100-fold excess of (H^+). A binuclear structure ($m = 2$), i.e., $Mo_2O_2(NCS)_2{}^{2+}$, conforms to the observed interaction with the ion-exchange resin as well as to the structure of complex I. We conclude that the system Mo(IV) + NCS^- under the conditions of the kinetic study[1] involves the following stepwise equilibria:

$$Mo_2O_2{}^{4+} + NCS^- \rightleftarrows Mo_2O_2NCS^{3+}$$

$$Mo_2O_2NCS^{3+} + NCS^- \rightleftarrows Mo_2O_2(NCS)_2{}^{2+}$$

This scheme does not conform to the kinetic results of Sykes et al.[1] which were obtained by employing the solutions of the reagents in perchloric acid.

Previous work in this laboratory was restricted to solutions of Mo(IV) in p-toluenesulfonic acid (HPTS),[2] except for one determination (of the oxidation state) which was conducted at 0 °C in perchloric acid. The use of $HClO_4$ was discontinued after preliminary tests demonstrated that Mo(IV) is oxidized by it to an appreciable extent at ambient temperatures (even in acid concentrations as low as 0.3 M). The lack of relevant experimental details in the paper by Sykes and co-workers[1] (such as the method of preparation and duration of storage of Mo(IV) solutions) makes it difficult to estimate the effect of $HClO_4$ on the kinetic results and the charge per molybdenum ion determination. However, their detailed account of the determination of the charge per Mo atom enables us to offer an explanation for the discrepancy between their reported experimental result, +2.20 per atom, and the expected value, +2.00. In the original determination of the charge per Mo(IV) atom by an ion-exchange saturation procedure, Ardon and Pernick[2] reported a charge per atom of 2.0 ± 0.1. Sykes and co-workers[1] repeated this procedure with $HClO_4$ and obtained a value of 2.20 which they regarded as an upper limit to the true value (2.00). A partial oxidation of Mo(IV) by $HClO_4$ in this experiment would decrease its concentration and consequently increase the apparent oxidation number.

References and Notes

(1) T. Ramasami, R. S. Taylor, and A. G. Sykes, *J. Am. Chem. Soc.*, **97**, 5918 (1975).

(2) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973); **96**, 1643 (1974).

(3) (a) P. Souchay, M. Cadiot, and M. Duhameaux, *C. R. Acad. Sci.*, **262**, 1524 (1966); (b) P. Souchay, M. Cadiot, and B. Viossat, *Bull. Soc. Chim. Fr.*, **3**, 892 (1970).

(4) For a striking example illustrating the reliability of this method cf. (a) W. P. Griffith, W. P. Lewis, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958); (b) M. Ardon, *Bull. Res. Counc. Isr., Sect. A*, **11**, 183 (1962); *Isr. J. Chem.*, **2**, 181 (1964); (c) R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964); (d) B. F. Hoskins, F. B. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Commun.*, 69 (1969).

(5) Ordinary cryoscopy (in water) as well as cryoscopy in a saturated solution of Na_2SO_4 (salzkryoskopie) are not suitable for this purpose (cf. ref 8).

(6) (a) M. Ardon and A. Linenberg, *J. Phys. Chem.*, **65**, 1443 (1961); **76**, 4040 (1972); (b) M. Ardon and L. Halicz, *Inorg. Chem.*, **12**, 1903 (1973).

(7) M. Ardon and A. Pernick, *Inorg. Chem.*, **12**, 2484 (1973).

(8) M. Ardon and G. Yahav, *Inorg. Chem.*, **15**, 12 (1976).

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Selenium Protection against Mercury Toxicity. Binding of Methylmercury by the Selenohydryl-Containing Ligand

Sir:

Since the hitherto unknown Minamata disease was identified as methylmercury intoxication from contaminated fish, mercury compounds, in particular methylmercury, have drawn considerable attention in scientific circles. In detoxification of heavy metals such as cadmium and mercury, the role of metallothionein, a sulfhydryl-rich protein, has been frequently implied.[1] Recent NMR investigations indicate that of the potential binding sites in cysteine, penicillamine, and glutathione, the sulfhydryl group binds methylmercury most strongly.[2] Ganther et al.[3] reported that selenium and mercury tend to accumulate together in tuna, and adequate protection against mercury toxicity has been avidly researched. At present, some of the most promising protective agents against acute mercury toxicity are the seleni-