

ference between the two extremes being a factor of only 2. In the present study the difference between the extremes of concentration used varied from 4 to 16.

The range of concentration of manganese used by Brisbin and Balahura was a magnitude of 4 less than that used in the present study. The deviations from first-order kinetics in manganese were so small that over the range of concentration used they would probably not have been obvious for protoporphyrin dimethyl ester. While the reactions with $\alpha, \beta, \gamma, \delta$ -tetra(4-pyridyl)porphine and hematoporphyrin have been shown to be first order with respect to metal, it seems quite likely that if the kinetics were investigated over a larger range of concentration, the simple rate laws would be found not to hold. In fact, Kingham and Brisbin's own published graphs for Fe^4 bear out the conclusions of the present paper: they give values for k_1 of 1.03, 1.04, and $1.25 \text{ M}^{-1} \text{ sec}^{-1}$ at 45° for $[\text{Fe}] = 7.5 \times 10^{-3}$, 5.0×10^{-3} , and $2.5 \times 10^{-3} \text{ M}$, respectively, showing the same trend found in the present study.

One could postulate more than one reason for the failure of these reactions to follow simple order kinetics.

It was noted that the half-order dependence on nickel ion concentration in glacial acetic acid with hematoporphyrin² could be the result of ion pairing, since ion pairing is not uncommon in this solvent. The rate of the reaction would be proportional to the square root of nickel acetate added, if $\text{Ni}(\text{OAc})_2$ were the predominant species and NiOAc^+ the species that interacts with porphyrin, so that $[\text{NiOAc}^+] = K^{1/2} [\text{Ni}(\text{OAc})_2]^{1/2}$ where K is the dissociation constant for the reaction $\text{Ni}(\text{OAc})_2 \rightleftharpoons \text{NiOAc}^+ + \text{OAc}^-$. $[\text{NiOAc}^+] \simeq [\text{OAc}^-]$ since the contribution of OAc^- from the self-ionization of glacial acetic acid which is very small would be negligible.

The possibility of several species being present in solution cannot be overlooked. Cobalt acetate, for example, is known to exist in acetic acid partly as CoOAc^+ , $\text{Co}(\text{OAc})_3^-$, and $\text{Co}(\text{OAc})_4^{2-}$, but mainly as $\text{Co}(\text{OAc})_2$ and to some extent the dimer^{5,6} $\text{Co}_2(\text{OAc})_4$. These various species may be expected to react with porphyrin at different rates—some perhaps not at all—and the proportion of cobalt in these different forms would vary with concentration.

Probably, however, the most important consideration in the kinetics is the presence of the dimer species. The dimer species is known to exist for cobalt, nickel, and copper,⁵⁻⁹ although the only metal for which quantitative data appear to be available is copper.⁷⁻⁹ Using the dissociation constants for the copper acetate dimer of Kochi and Subramanian⁷ for the temperature range of 41 – 82° and drawing a graph of $\log K$ vs. T , one can estimate the dissociation constant at 17° to be 5.8×10^{-5} . The proportion of copper existing as a dimer would vary from 51% at the lowest concentration used in this study ($5.75 \times 10^{-5} \text{ M}$) to 77% at the highest concentration ($3.96 \times 10^{-4} \text{ M}$). If, however, the dissociation constant is actually considerably

smaller ($\approx 10^{-8}$) as subsequent data have shown,⁸ then the amount of copper present as the dimer would be exceedingly large. According to Sawada, *et al.*,⁹ copper(II) acetate in dry acetic acid appears essentially as the dimer between 5×10^{-4} and $2 \times 10^{-2} \text{ M}$. If we then consider that an equilibrium exists between the dimers and monomers in solution, $\text{M}_2(\text{OAc})_4 \rightleftharpoons 2\text{M}(\text{OAc})_2$, and that it is the monomeric species which reacts with porphyrin in a rate-determining step, a half-order dependence on the metal can be explained. In the case of cobalt, nickel, and copper in the concentration ranges used the dimer must be considered to be predominant. The rate of the reaction is then proportional to $[\text{M}(\text{OAc})_2][\text{P}]$ where $[\text{M}(\text{OAc})_2] = K_{\text{eq}}^{1/2} [\text{M}_2(\text{OAc})_4]^{1/2}$.

Manganese in the concentration range used may exist to a greater extent as the monomer and hence the rate of the reaction is closer to first order with respect to the metal. The K_{eq} constant would be expected to be several orders of magnitude greater than that for copper acetate and a value in excess of the metal ion concentration used.

Zinc possibly exists as a mixture of both the monomer and dimer. If data could be collected over a larger concentration range in spite of the low solubility of its acetate in acetic acid, an equilibrium constant could probably be calculated.

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Studies on the Aquomolybdenum(III) Ion

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Bowen and Taube¹ have recently reported the preparation of the hexaaquamolybdenum(III) ion, $\text{Mo}(\text{H}_2\text{O})_6^{3+}$. As these authors have indicated, this congener of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ shows great promise as an electron-transfer agent. Kinetic studies of redox reactions employing $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ cannot be adequately interpreted, however, without some knowledge of the rate constants for substitution of ligands into the primary coordination sphere of the metal ion. Furthermore, information regarding the lability of the trivalent cations of the second and third transition series is relatively scant. We wish to report further characterization of the $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ ion and preliminary results of studies of the kinetics of formation of the monothiocyanatomolybdenum(III) complex ion.

$\text{Mo}(\text{H}_2\text{O})_6^{3+}$ was prepared by the method of Bowen and Taube,¹ with the following two precautions. (1) Preparations of solutions of the ion (by aqation of MoCl_6^{3-} in 2.0 M *p*-toluenesulfonic acid (HPTS) for >36 hr), as well as subsequent manipulations, were conducted under argon. (2) Cation-exchange separations were carried out on a column (Dowex 50W-X2) which had been pretreated by exposure to 0.1 M $\text{Cr}(\text{II})$ for *ca.* 100 hr. The number of reducing equivalents

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per mole of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ for the reaction $\text{Mo}(\text{III}) \rightarrow \text{Mo}(\text{VI})$ was determined by addition of aliquots of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ to excess deaerated $\text{Ce}(\text{IV})$ followed by back-titration of residual $\text{Ce}(\text{IV})$ by $\text{Fe}(\text{II})$. Total molybdenum was determined by either atomic absorption or volumetric analysis using a Jones reductor;² 3.05 ± 0.06 equiv/mol was found (six determinations on two separate preparations).

The uv-vis spectrum of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$, consisting of bands at 293 ($\epsilon 6.0 \times 10^2 M^{-1} \text{cm}^{-1}$) and 253 nm ($\epsilon 7.2 \times 10^2 M^{-1} \text{cm}^{-1}$), was reported in the earlier work. In contrast to these results, the spectrum of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ in 2.0 M HPTS, prepared by the method outlined above, shows no absorption maxima at these wavelengths ($\epsilon_{293} 3.7 \times 10^2 M^{-1} \text{cm}^{-1}$). Exposure to air, however, results in a significant increase in absorbance at 293 nm.

The molar susceptibility of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ in 2.0 M HPTS was determined by the nuclear magnetic resonance technique of Evans.³ The molar susceptibility, χ_m , obtained from the shift of the methyl protons of HPTS in the $\text{Mo}(\text{III})$ environment, was found to have the value $(5.66 \pm 0.05) \times 10^{-3}$ at 25°. The effective magnetic moment, μ_{eff} , of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ is then calculated to be 3.69 BM, in excellent agreement with the moments of about 3.7–3.85 BM for other $\text{Mo}(\text{III})$ complexes^{4,5} and with μ_s , the theoretical spin-only moment of 3.87 BM. This result, taken with the ion-exchange characteristics reported by Bowen and Taube and confirmed in this study, provides excellent evidence that the $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ ion is monomeric in solution.

Addition of aliquots of a solution of KNCS to $2.4 \times 10^{-3} M$ $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ in 1.0 M HPTS results in an immediate and significant increase in excess absorbance at 320 nm. A plot of absorbance vs. $[\text{NCS}^-]_{\text{added}}$ is linear over the region of $[\text{NCS}^-]$ from 1.7×10^{-4} to $1.5 \times 10^{-3} M$. From the slope of the plot, corrected for absorption due to excess $\text{Mo}(\text{H}_2\text{O})_6^{3+}$, we obtain the value of $3.9 \times 10^2 M^{-1} \text{cm}^{-1}$ for the extinction coefficient of the $\text{Mo}(\text{III})$ - NCS^- complex, presumably $\text{Mo}(\text{H}_2\text{O})_5\text{NCS}^{2+}$. The increasing slope of the plot above $1.5 \times 10^{-3} M$ NCS^- suggests the possibility of formation of further complexes. From a consideration of the extinction coefficients of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ and of the complex ion we calculate a lower limit for K_1 , the equilibrium constant for first complex formation, of $10^4 M^{-1}$. (An attempt to determine the value of K_1 by the spectrophotometric method of Furman and Garner⁶ proved futile, since, under all conditions employed, the concentration of complex was in great excess

over the concentration of free ligand.) The possibility that the observed absorbance changes are due to oxidation or reduction of the thiocyanato ligand can be dismissed for the following reasons. If powerful reductants, such as $\text{Cr}(\text{II})$ and Zn amalgam are incapable of the reduction of $\text{Mo}(\text{III})$,^{1,2} it is unlikely that oxidation of NCS^- by $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ will occur. The oxidation of $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ by NCS^- , in acidic media, would generate reduction products such as HCN and H_2S ; these were not detected. We conclude that a $\text{Mo}(\text{H}_2\text{O})_5\text{NCS}^{2+}$ complex has been formed, which appears to be considerably more stable than the analogous $\text{Cr}(\text{H}_2\text{O})_5\text{NCS}^{2+}$ ion,⁷ for which the value of K_1 is $74 M^{-1}$ (ionic strength 1.0 M).

The rates of interaction between $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ and NCS^- in 1.0 M HPTS were studied in the stopped-flow spectrophotometer (320 nm). We find that, over long periods of time, solutions of KNCS in HPTS undergo color changes, becoming faintly pink. Recrystallization of HPTS did not eliminate this effect. Solutions of KNCS in H_2O , mixed with HPTS in the stopped-flow device, showed no significant absorbance changes at 320 nm in the time period of these studies, however. All solutions were used immediately after preparation. Under pseudo-first-order conditions ($2.70 \times 10^{-4} M$ NCS^- , $(2.77\text{--}5.54) \times 10^{-3} M$ $\text{Mo}(\text{H}_2\text{O})_6^{3+}$) the bimolecular rate constant for complex ion formation was observed to be $10 \pm 2 M^{-1} \text{sec}^{-1}$. This result is surprising, in light of both the lethargic loss of chloro ligands from MoCl_6^{3-} in HPTS and the corresponding rate constant for NCS^- substitution on $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ($1.92 \times 10^{-6} M^{-1} \text{sec}^{-1}$, in HClO_4 at 55°).⁸ The rapid rate of NCS^- substitution on $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ can possibly be rationalized by invoking an $\text{S}_\text{N}2$ type mechanism, wherein bond formation with the entering NCS^- ligand plays a significant role in formation of the activated complex. The high stability of the thiocyanato complex, in contrast to the relatively unstable chloro complex, tends to support this hypothesis. In the absence of further studies, however, the possibility that the observed interaction between $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ and NCS^- may involve processes other than substitution cannot be excluded. For example, the effect of trace amounts of higher oxidation states of molybdenum present in these solutions on the rate of substitution is unknown.

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