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Preparation and the Acid Hydrolysis of *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetate Complex of Di-*μ*-oxo-bis(oxomolybdenum(V))

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Synopsis. A hedta (H_3hedta=*N*-(2-hydroxyethyl)-ethylenediamine-*N*,*N'*,*N'*-triacetic acid) complex of molybdenum(V), $Mo_2O_4(hedta)(H_2O)^-$, has been prepared and characterized. The rate of acid hydrolysis of this complex in an aqueous perchloric acid solution ($[H^+]=0.5$—2.0 mol dm^{-3}; $I=2.0$) is of similar magnitude to that of $Mo_2O_4(edta)^{2-}$ (H_4edta=ethylenediaminetetraacetic acid), increasing with increase in $[H^+]$.

A dimeric unit, $Mo_2O_4^{2+}$, di-*μ*-oxo-bis(oxomolybdenum(V)) is common in molybdenum(V) chemistry in aqueous media. The ligand substitution reactions on the $Mo_2O_4^{2+}$ center have been studied with various ligands such as $edta^{4-}$,[1] ida^{2-} (H_2ida=iminodiacetic acid),[2] $C_2O_4^{2-}$,[2] and NCS^-.[3] The results show that the rate of substitution reactions on the $Mo_2O_4^{2+}$ center varies remarkably with ligand, spanning six orders of magnitude. The number of ligating atoms of a ligand, and/or the location on the oxo metal moiety at which substitution occurs (*cis* or *trans* to oxo ligand) would be important factors controlling the substitution rate. In order to obtain further information on the substitution reactions on the $Mo_2O_4^{2+}$ center, we used $hedta^{3-}$ as a ligand, the structure of which is similar to that of $edta^{4-}$.

Experimental

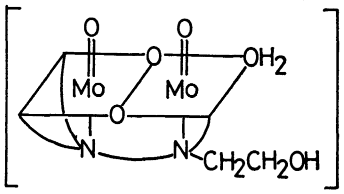
Material. *Sodium Salt of Aqua*[N-*(2-hydroxyethyl)ethylenediamine*-N, N', N'-*triacetato*]-*di-μ-oxo-bis(oxomolybdate(V)) Complex*, *$Na[Mo_2O_4(hedta)(H_2O)]\cdot 2H_2O$*: Nine grams of dipyridinium pentachlorooxomolybdate(V), $(pyH)_2[MoOCl_5]$,[4] and 2.8 g of H_3hedta were dissolved in 100 cm^3 of water. The solution was warmed at 90 °C for about 3 h with constant stirring, and then cooled to room temperature. To this solution were added 5 g of $NaClO_4$ and then 100 cm^3 of ethanol, and the solution was kept in a refrigerator for a day. Orange crystals were filtered off, washed with ethanol, and dried in air. They were recrystallized from water. Found: C, 19.53; H, 3.62; N, 4.74; Mo, 31.15%. Calcd for $C_{10}H_{21}N_2O_{11}NaMo_2$: C, 19.75; H, 3.48; N, 4.61; Mo, 31.55%.

Measurements. Ultraviolet and visible absorption spectra were recorded with a Hitachi 323 spectrophotometer. For kinetic studies, a Hitachi 124 spectrophotometer with a Hitachi recorder QPD-34 was used. The acid dissociation constant of the complex was determined by pH titration with a pH-meter E300B of Metrohm Herisau. The meter was standardized against perchloric acid solutions in 2 M $LiClO_4$ (M=mol dm^{-3}) so that H^+ concentration rather than activity was measured. Thermal decomposition curves of the complexes were obtained with a Shinku Riko TGD-3000 differential thermal microbalance with a heating rate of 10 K/min.

Kinetic Runs. All the solutions used for kinetic runs were prethermostatted at a given temperature for at least 20 min. A solution of the complex was mixed with a perchloric acid solution for starting the kinetic run. The solutions contained appropriate amounts of lithium perchlorate to adjust ionic strength. The change of absorbance was followed at a fixed wavelength (mostly at 295 nm). Rate constants were evaluated from the first-order plots of absorbance changes. Since the aqua ion of molybdenum(V), $Mo_2O_4(aq)^{2+}$,[5] undergoes slow oxidation by oxygen,[1] some runs were carried out under a nitrogen atmosphere.

Results and Discussion

It was suggested that the two peaks at *ca.* 300 nm (ε=3000—10000 l mol^{-1} cm^{-1} per dimer) and at *ca.* 390 nm (100—400) are characteristic of complexes containing the dimeric unit, $Mo_2O_4^{2+}$.[2,6] The present complex has two peaks in these two regions, indicating the presence of $Mo_2O_4^{2+}$ group. The complex liberates two water molecules at 20—90 °C and one at 100—140 °C. We assigned the former to the water of crystallization and the latter to the coordinated water. This was supported by the patterns of thermal decomposition of other molybdenum(V) complexes, $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (liberate three water molecules at 20—100 °C and two at 140—180 °C)[7] and $Na[Mo_2O_4(edta)]$ (no weight loss up to 370 °C). On the basis of these findings, the structure of the present complex is considered as follows.



The pH of an aqueous solution of the hedta complex (*ca.* 5×10^{-3} mol dm^{-3}) is *ca.* 2. The solution was titrate with 0.1 M sodium hydroxide. There was one sharp break for one equivalent sodium hydroxide to the complex, no further inflection being observed up to pH=11. The sharp break would be associated with the deprotonation of the coordinated water as follows.

$$\underset{\text{(aqua form)}}{Mo_2O_4(hedta)(H_2O)^-} \overset{K_a}{\rightleftharpoons} \underset{\text{(hydroxo form)}}{Mo_2O_4(hedta)(OH)^{2-}} + H^+ \qquad (1)$$

The pK_a value for this process was estimated from the pH titration curve; 3.02±0.03 at 25 °C and I=2.0 M. The absorption spectrum of the aqua complex was measured in 0.1 M perchloric acid in the presence of the ligand added in order to avoid dissociation of the ligand from the complex. The spectrum of the hydroxo complex was measured in an acetate buffer at pH 5. Peak positions (and intensities) are 383 nm (ε=300) and 295 nm (9200) for the aqua complex, and 393 nm (300) and 305 nm (9500) for the hydroxo complex.

In acidic aqueous solution, the complex decomposed to give $Mo_2O_4(aq)^{2+}$ and the protonated forms of the free ligand.

$$Mo_2O_4(hedta)(H_2O)^- + nH^+ \xrightarrow{k_f} Mo_2O_4(aq)^{2+} + H_n hedta^{(3-n)-} \qquad (2)$$

The rate of this reaction was measured at $[H^+]=0.5$—2.0 M, $I=2.0$ M and at 20—35 °C. (The k_f was not obtained accurately at $[H^+]<0.5$ M since reaction (2) did not proceed completely.) The observed first-order rate constant (k_f) was of similar magnitude to that of the acid hydrolysis of $Mo_2O_4(edta)^{2-}$,[1] and much smaller than that of other complexes of $Mo_2O_4^{2+}$.[2,3] The dependence of k_f on $[H^+]$ is not simple (Fig. 1).

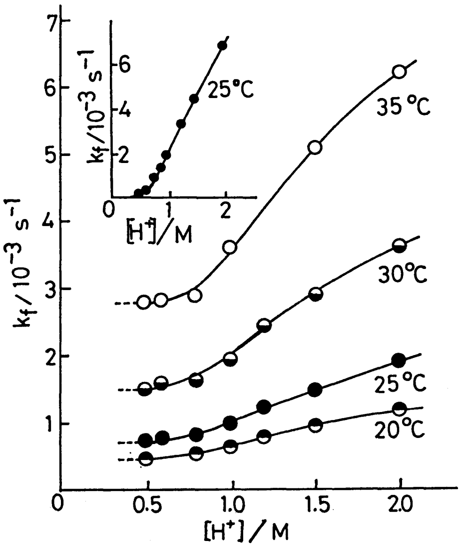


Fig. 1. $[H^+]$-Dependence of k_f for the acid hydrolysis of $Mo_2O_4(hedta)(H_2O)^-$ in aqueous perchloric acid solutions. Each point represents the average of at least 3 runs. The inset is a similar plot for $Mo_2O_4(edta)^{2-}$.[2]

As in the case of the edta complex, k_f increases when $[H^+]$ exceeds 1.0 M. There is a slight tendency for the k_f value to saturate when $[H^+]$ increases. For the edta complex, it was suggested from the analysis of $[H^+]$ dependence that the cleavage of the last acetate group, *viz.* the dissociation of H_3edta^- (uni- or bidentate), is rate-determining, its rate being of similar magnitude to that of the overall rate.[1] A similar rate-determining process would be possible for the hedta complex at least in a higher $[H^+]$ region. It should be noted that the multi-step preequilibria would not be necessarily responsible for the slow rate of acid hydrolysis of these complexes.

In a lower $[H^+]$ region ($[H^+]<1.0$ M), unlike the edta complex, k_f does not approach zero. The difference can be explained by considering equilibrium (1) of the hedta complex. If both aqua and hydroxo forms of the complex contribute to the dissociation reaction (rate constants are expressed as k_{H_2O} and k_{OH}, respectively), k_f is written as follows under the conditions $K_a \ll [H^+]$.

$$k_f = K_a k_{OH}[H^+]^{-1} + k_{H_2O} \qquad (3)$$

Here both k_{H_2O} and k_{OH} may change with $[H^+]$. No path corresponding to k_{OH} is expected for the edta complex in which no coordinated water exists. No discussion will be given on the mechanism as for the edta complex,[1] since we cannot estimate each term of (3) accurately.

The sequence of the apparent rate of acid hydrolysis of various ligands from the $Mo_2O_4^{2+}$ center is given in the following, with order of rate (s^{-1}) at 25 °C and at $[H^+]=1.0$ M in parentheses.[1-3]

$$\begin{array}{ccccccccc} edta^{4-} & \approx & hedta^{3-} & < & ida^{2-} & < & C_2O_4^{2-} & < & NCS^- \\ (10^{-3}) & & (10^{-3}) & & (10^{-2}\ \text{at}\ 0^\circ C) & & (10^0) & & (10^2) \end{array}$$

The rate decreases remarkably as the dentate number of the ligand increases.

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References

1) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1974**, 1468.

2) Y. Sasaki and A. G. Sykes, *J. Less-common Metals*, **36**, 125 (1974); unpublished data.

3) Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1975**, 396.

4) H. Sabat, M. F. Rudolf, and B. Jezowska-Trzebiatowska *Inorg. Chim. Acta*, **7**, 365 (1973).

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

6) D. T. Brown, P. G. Perkins, and J. T. Stewart, *J. Chem. Soc., Dalton Trans.*, **1972**, 1105.

7) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **26**, 1967 (1964).