To be sure, conclusive evidence for mechanism C would be provided by the direct detection of the postulated intermediates $CrXI.^+$ Various attempts were made to detect $CrClI^+$ in the flow apparatus. By using 2.0 M chloride ion concentration we hoped to build up the steady-state concentration of $CrClI^+$ to the point where it could be observed spectrophotometrically. However, all that could be seen in the 700–230-mμ region was the disappearance of CrI^{2+}, and we must conclude that, if mechanism C obtains, the steady-state concentration of $CrICl^+$ is too small and/or its spectral properties are too similar to those of CrI^{2+} and $CrCl^{2+}$.

Some indirect evidence in favor of mechanism C comes from studies[45] of the effect of added chloride ion on the well-known $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction.[35] In the presence of 0.50 M chloride ion, the reaction products consist of 97% $CrCl^{2+}$ and 3% $CrCl_2^+$. This result demonstrates that even for a reaction as rapid as the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction ($k \approx 10^6 \, M^{-1} \, sec^{-1}$)[46] the addition of chloride ion leads to its incorporation into the coordination sphere of the chromium(III) product. Additional examples of incorporation of an anion from the solution into the coordination sphere of the chromium(III) product formed by an inner-sphere reaction are: $Co(NH_3)_5Cl^{2+} + P_2O_7^{4-}$ [35] and $Co(NH_3)_5$-$OCOCHCHCOOH^{2+} + Cl^-$.[42] In all of these cases, the most plausible formulation of the transition state is $[(NH_3)_5CoLCrL'^{n+}]$, where L is the bridging ligand (chloride, fumarate) and L' the nonbridging ligand (chloride, pyrophosphate). This transition state is entirely analogous to the one postulated in eq 9 of mechanism C.

(45) D. E. Pennington and A. Haim, to be published.

It is interesting to note that the order of efficiency of the halide ions in promoting electron transfer ($F^- \gg Cl^- > Br^-$) is remarkably similar for all of the reactions of Table VII, in spite of the fact that both outer-sphere and inner-sphere (with variable bridging ligands) mechanisms are featured in these reactions. Possibly, there is some relation between the stability of the product formed ($F^- \gg Cl^- > Br^-$) and the catalytic efficiency of the halide ion.

Finally, it is useful to point out why the halide ion effects are readily observed in the CrI^{2+}–Cr^{2+} reaction at low halide ion concentrations, whereas very high concentrations are necessary to bring out the halide ion dependent path in the case of the inner-sphere reactions of Table VII. Taking as an example the $Co(NH_3)_5Cl^{2+}$–Cr^{2+}–Cl^- system, it is clear that the halide ion effect will be observed only if reaction 17 is competitive with reaction 18. As indicated above, the

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} + Cl^- \longrightarrow Co^{2+} + CrCl_2^+ \quad (17)$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrCl^{2+} \quad (18)$$
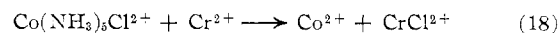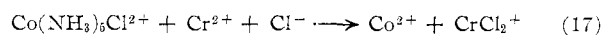
halide ion nonbridging ligand effects are quite modest, and high concentrations of chloride ion are necessary to observe reaction 17. For the CrI^{2+}–Cr^{2+}–Cl^- system, the reactions to be compared are (2) and (14). Reaction 14 does not lead to any chemical change and can only be detected by using radioactive chromium, whereas reaction 2 produces a net chemical change and can, therefore, be readily observed at low chloride ion concentrations, *e.g.*, under conditions where reaction 2 is not competitive with reaction 14.

(46) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

Proton Nuclear Magnetic Resonance Studies of Several Molybdenum(V) Chelates

By LOUIS V. HAYNES and DONALD T. SAWYER

Proton nmr measurements have been employed to study the formation, stability, and dynamics of the ethylenediaminetetraacetate (EDTA), *dl*-1,2-propylenediaminetetraacetate (PDTA), *trans*-(1,2-cyclohexylenedinitrilo)tetraacetate (CyDTA), N-methyliminodiacetate (MIDA), and nitrilotriacetate (NTA) complexes of molybdenum(V). The EDTA, PDTA, and NTA chelates have been synthesized, isolated, and analyzed for the elements. Nmr spectral evidence indicates the formation of a Mo(V)–MIDA complex in solution; no evidence has been observed for the formation of the CyDTA complex. The nmr spectra establish that these chelates are diamagnetic which implies the existence of dimeric molybdenum units in the chelate structures. Structures have been proposed on the basis of the nmr spectra for the EDTA and PDTA complexes.

Molybdenum(V) (d[1] electronic configuration) forms a variety of complexes, many of which contain bridging oxygen atoms (bonded to two molybdenum atoms) and terminal oxygen atoms (multibonded to one molybdenum atom).[1,2] Magnetic moment measure-

(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 776–800.

ments indicate some of these complexes are diamagnetic while others are paramagnetic.[3,4] The paramagnetic

(2) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 2, Oxford University Press, London, 1950, pp 1032–1053.
(3) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).
(4) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 444.

complexes generally are considered to contain either monomeric molybdenum or linear-bridged binuclear molybdenum (Mo–O–Mo) where the dihedral angle is about 45° (the most favorable angle for the triplet state).[3,5,6] The diamagnetic complexes are considered to contain either linear-bridged binuclear molybdenum where the dihedral angle approaches zero (the most favorable angle for the singlet state)[5] or dioxo-bridged binuclear molybdenum.[3,6] In the dioxo-bridged binuclear complexes spin pairing is believed to occur through the oxo bridges or by direct formation of a metal–metal bond.[3,5,7]

The infrared spectra, electronic spectra, and magnetic properties of many of the molybdenum(V) complexes have been summarized by Mitchell.[3] Although proton nmr studies have not been reported for diamagnetic complexes derived from organic ligands, such studies should prove useful in the elucidation of the stabilities, structures, and dynamics of these chelates in solution.

Complexes of molybdenum(V) have been reported for 2,2'-bipyridyl,[7,8] oxalate,[9–11] acetylacetone,[12] ethylenediaminetetraacetic acid,[13,14] 8-hydroxyquinoline,[3,15,16] alkyl dithiocarbamates and alkyl xanthates,[17] and dialkyl dithiophosphates.[18]

In the present study the ethylenediaminetetraacetic acid (EDTA), 1,2-propylenediaminetetraacetic acid (PDTA), *trans*-(1,2-cyclohexylenedinitrilo)tetraacetic acid (CyDTA), methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA) complexes of molybdenum(V) have been investigated. In particular, the proton nmr spectra of these chelates have been recorded as a function of pH. Conclusions regarding the labilities of the chelate–metal bonds as well as possible structures of the complexes have been made.

Experimental Section

Proton nmr spectra were recorded using either a Varian A-60 high-resolution spectrometer equipped with a Varian variable-temperature controller or a Varian HA/HR-100 high-resolution spectrometer operating at 35°. Varian precision-bore nmr tubes were used for all measurements. Chemical shift values were calculated relative to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TMS*) used as an internal standard. Deuterium oxide was used as the solvent for all of the nmr studies.

A Leeds and Northrup line-operated pH meter (No. 7401) equipped with a Leeds and Northrup miniature pH electrode assembly (No. 134138) was employed for pH measurements. The meter was standardized with Leeds and Northrup reference buffer solutions, and measurements were made at 25°.

Ethylenediaminetetraacetic acid (assay 100%) was obtained from J. T. Baker Co., methyliminodiacetic acid from Aldrich

Chemical Co., nitrilotriacetic acid from Matheson Coleman and Bell Co., and *trans*-(1,2-cyclohexylenedinitrilo)tetraacetic acid from Geigy Industrial Chemicals. These chelating agents were used without further purification. *dl*-1,2-propylenediaminetetraacetic acid was prepared by the method of Dwyer and Garvan.[19] The nmr spectrum of the product dissolved in D_2O was identical with the published spectrum of PDTA.[20] Molybdenum in the form of molybdic acid anhydride was obtained from Baker and Adamson, and molybdenum pentachloride was from Alfa Inorganics, Inc. Deuterium oxide (assay 99.86%) was supplied by International Chemical and Nuclear Corp., and 3(trimethylsilyl)-1-propanesulfonic acid sodium salt (TMS*), by Eastman Organic Chemical Co. All other chemicals used were reagent grade quality.

The potassium salt of molybdenum(V) EDTA was prepared by combining 400 ml of 0.5 F Mo(V) solution (prepared by reduction of a molybdenum(VI) solution with mercury in the presence of 3 F hydrochloric acid)[21] and 29 g of EDTA (H_4Y) in a 1-l. beaker.[13] The beaker was placed in an ice bath above a magnetic stirrer, and potassium hydroxide pellets were added slowly (vigorous stirring) to adjust the pH to approximately 5. The mixture, containing a small amount of light brown precipitate, was filtered to give a clear, dark, red-brown solution. This solution was concentrated to 200 ml on a steam bath, and then ethanol was added until a turbidity persisted. The hot solution was quickly filtered and allowed to stand 24 hr at room temperature. The red-orange crystals were removed by filtration and repeatedly recrystallized from water and ethanol until a negative chloride ion test resulted (silver nitrate test). The crystals were finally dried at 110° (yield 16 g).

The resulting crystals were analyzed for carbon and hydrogen by Elek Microanalytical Laboratories, Los Angeles, Calif. Molybdenum was determined by sample combustion at 700° to MoO_3 and KOH, followed by reduction to Mo(V) with a silver reductor column and titration with a standard cerium(IV) solution.[22] Potassium was determined by weight difference of the combusted samples. The results indicate a molecular formula $K_2Mo_2O_{13}H_{14}C_{10}N_2$. *Anal.* Calcd for $K_2Mo_2O_{13}H_{14}C_{10}N_2$: C, 18.75; H, 2.20; Mo, 29.97; K, 12.22. Found: C, 18.78; H, 2.38; Mo, 29.89; K, 12.01.

The potassium salt of molybdenum(V) PDTA was prepared and recrystallized in the same way as the EDTA complex. The final product consisted of needlelike, red-orange crystals (yield 13 g). The elemental analysis indicates a molecular formula $K_2Mo_2O_{13}H_{16}C_{11}N_2$. *Anal.* Calcd for $K_2Mo_2O_{13}H_{16}$-$C_{11}N_2$: C, 20.20; H, 2.47; Mo, 29.35; K, 11.90. Found: C, 20.95; H, 2.73; Mo, 29.33; K, 11.95.

The potassium salt of the Mo(V)–NTA chelate was prepared by addition of 38.2 g of NTA to 400 ml of 0.5 F Mo(V) solution, adjustment of the solution pH to approximately 5 with KOH pellets, filtration, concentration of the resulting dark red-orange solution, and crystallization of the chelate by addition of ethanol. The product, a red-orange crystalline powder, was recrystallized repeatedly until a negative chloride ion test was obtained. The nmr spectrum of the product indicated a contamination of approximately 10% free NTA. Further recrystallization did not remove the excess acid. Other attempts to prepare the chelate produced the same results.

All attempts to prepare the MIDA and CyDTA chelates of molybdenum(V) in a crystalline form failed. The nmr spectrum of the Mo(V)–CyDTA solution gave no evidence of chelate formation from pH 0 to 12. The nmr spectrum of the Mo(V)–MIDA solution indicated the formation of a chelate between pH 3 and 9. Although partial precipitation of the molybdenum occurs in this pH range, a 1:1 metal-to-ligand ratio was established for the chelate by considering the nmr spectrum and the molybdenum titration of the filtered solution.

(5) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).
(6) L. Sacconi and R. Cini, *ibid.*, **76**, 4239 (1954).
(7) P. C. H. Michell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1963).
(8) D. A. Edwards, *ibid.*, **27**, 303 (1965).
(9) R. J. James and W. Wardlaw, *J. Chem. Soc.*, 2145 (1927).
(10) R. J. James and W. Wardlaw, *ibid.*, 1748 (1931).
(11) R. J. James and W. Wardlaw, *ibid.*, 2742 (1928).
(12) G. T. Morgan and R. A. S. Castell, *ibid.*, 3252 (1928).
(13) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5496 (1956).
(14) D. T. Sawyer and J. M. McKinnie, *ibid.*, **82**, 4191 (1960).
(15) A. I. Busev and C. Fan, *Talanta*, **9**, 107 (1962).
(16) J. T. Spence and E. R. Perlen, *Inorg. Chem.*, **1**, 277 (1962).
(17) L. Malatesta, *Gazz. Chim. Ital.*, **69**, 408 (1939).
(18) G. Spengler and A. Weber, *Chem. Ber.*, **92**, 2163 (1959).

(19) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).
(20) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).
(21) D. E. Carrit, Ph.D. Thesis, Harvard University, 1947.
(22) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1953, p 114.

Solutions of the chelates were prepared for nmr studies by either dissolving the solid chelate in D_2O or by weighing out the appropriate amounts of solid ligand and molybdenum pentachloride and carefully adding D_2O. pH adjustments were made with D_2O solutions of KOH and HCl.

Results and Conclusions

Ethylenediaminetetraacetate Complex of Molybdenum(V).

—The proton nmr spectrum of the Mo(V)–EDTA system exhibits an AB quartet of intensity 8 and a singlet of intensity 4 from pH 0 to 9.5 (Figure 1). The AB quartet is assigned to the eight acetate protons and the singlet to the four ethylenic protons of the EDTA ligand on the basis for the spectrum integral and previous studies of EDTA complexes. In 2 F HCl the major peaks of the nmr spectrum are assigned to free ligand; however, the quartet and singlet of the chelate are still observed. Above pH 9.5 precipitation occurs. The chemical shift and coupling constant for the quartet are 3.42 ppm and 17.2 cps, respectively; the chemical shift for the singlet is 2.64 ppm. These values are constant over the stability range of the chelate.

Preliminary X-ray analysis[23] of the solid chelate indicates the EDTA ligand is wrapped around a dioxo-bridged binuclear molybdenum unit with one terminal oxygen ligand bonded to each molybdenum atom (Figure 1). The terminal oxygen ligands are *cis* with respect to each other. A molecular model of the chelate shows two forms are possible, a *dl* pair, which are interchangeable by a slight twisting of the molecule. On the basis of the model a complex nmr spectrum, consisting of two AB quartets and an A_2B_2 pattern, is expected if the chelate is in a rigid configuration in solution. However, a rapid interconversion between the two isomeric forms would average the chemical environments of the four ethylenic protons, giving a singlet instead of an A_2B_2 pattern, and would average the expected two AB patterns for the acetate protons into a single AB pattern. The nmr spectrum supports a rapid interconversion between the two isomeric forms of the chelate in solution.

A low-temperature nmr study has been made in an effort to elucidate the dynamics of the chelate. At 0° the AB quartet collapses to a broad single line and the ethylenic singlet also becomes very broad. These results are compatible with a slowing down of the interconversion between two species; a broadening of the simple time-averaged spectrum followed by the formation of a more complex spectrum is expected for this case as the temperature is lowered.[24] On the other hand, if the chelate were in a rigid form at 38°, little change in the spectrum would be expected as the temperature is lowered. Significant changes in the nmr spectrum are not observed from 38 to 90°.

dl-Propylenediaminetetraacetate Complex of Molybdenum(V).

—The Mo(V)–PDTA complex can be pictured in terms of the Mo(V)–EDTA complex (Fig-

(23) R. M. Wing, K. P. Callahan, L. V. Haynes, and D. T. Sawyer, unpublished results.
(24) J. A. Pople, W. C. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.
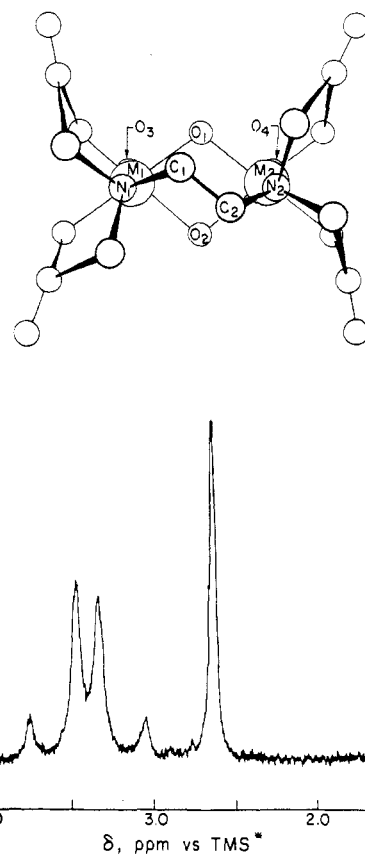

Figure 1.—Proton nmr spectrum (60 Mc) and molecular structure of Mo(V)–EDTA. The chemical shift, coupling constant, and chemical shift difference for the AB quartet are 3.42 ppm, 17.2 cps, and 0.306 ppm, respectively. The chemical shift for the ethylenic peak is 2.64 ppm. In the molecular structure diagram M_1 and M_2 designate the molybdenum atoms, N_1 and N_2 the nitrogen atoms, C_1 and C_2 the ethylenic carbon atoms, O_1 and O_2 the bridging oxygen atoms, and O_3 and O_4 the terminal oxygen atoms. The remaining unlabeled atoms correspond to the four acetate groups.

ure 1) where a methyl group is substituted for one of the protons on the ethylenic fragment. The addition of the methyl group removes the symmetry of the complex and a complicated nmr spectrum results (Figure 2). The complex portion of the spectrum consists of four AB patterns corresponding to the four nonequivalent acetate groups and a spectral pattern for the methine and methylenic hydrogens of the propylene fragment which is immediately upfield, overlapping to some extent the four AB quartets. Tentative line assignments of the four AB patterns are shown in Figure 2; assignment to specific acetate groups is not attempted. The remaining lines of this part of the spectrum are assigned to the propylene fragment. The high-field doublet corresponds to the methyl group which is coupled to the methine proton.

The chelate is stable from pH 0 to 9; precipitation occurs outside this pH range. No changes in the nmr spectrum are observed within the stability region of the chelate.

Consideration of molecular models indicates that two geometrical isomers are possible for the chelate, which are interconvertible by a slight twisting of the chelate
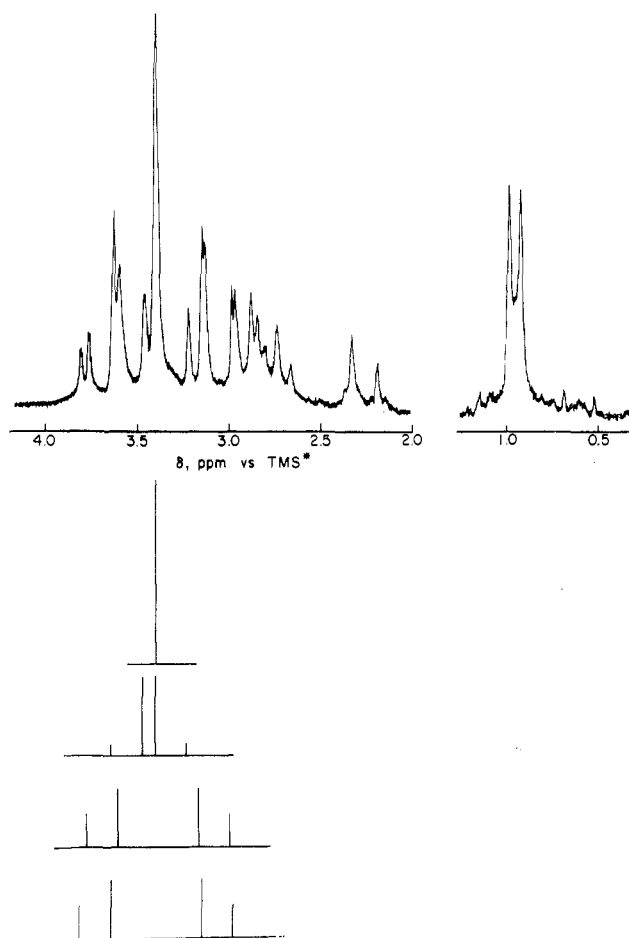
Figure 2.—Proton nmr spectrum (100 Mc) of Mo(V)–PDTA. Tentative line assignments of the four AB quartets are indicated. The chemical shifts (δ_{CH_2}), the coupling constants (J), and the chemical shift differences ($\delta_A - \delta_B$) for the four AB patterns are: (1) $\delta_{CH_2} = 3.41$ ppm, $\delta_A - \delta_B = 0$ ppm; (2) $\delta_{CH_2} = 3.44$ ppm, $J = 18.0$ cps, $\delta_A - \delta_B = 0.158$ ppm; (3) $\delta_{CH_2} = 3.37$ ppm, $J = 16.6$ cps, $\delta_A - \delta_B = 0.606$ ppm; (4) $\delta_{CH_2} = 3.40$ ppm, $J = 17.5$ cps, $\delta_A = \delta_B = 0.630$ ppm.

molecule. One isomer has the methyl group directed away from the plane of the dioxo bridge (equatorial methyl). The other isomer has the methyl group directed on an angle toward the plane of the dioxo bridge (axial methyl). In the latter case, a strong spatial interaction exists between the methyl group protons and the methylenic protons of the two adjacent acetate groups. Two methyl doublets should be observed when both isomers are present because the doublet arising from the axial methyl group would be in a different chemical environment than the doublet from the equatorial methyl of the other isomer.[25] Studies on the Co(III)–PDTA complex have shown no evidence for the formation of the more strained isomer with the axial methyl group.[25,26] A time-averaged spectrum exhibiting only one methyl doublet due to rapid interconversion between the two isomeric forms is not expected because of steric interactions. A temperature study of the nmr spectrum from 0 to 90° (which showed no significant changes) supports this conclusion. Thus,

the data are consistent with the formation of the equatorial methyl isomer.

trans-(1,2-Cyclohexylenedinitrilo)tetraacetate Complex of Molybdenum(V).—The nmr data give no evidence for the formation of a Mo(V)–CyDTA chelate from pH 0 to 12. This result is not surprising if the energetics of the cyclohexane ring in the free ligand and the complex are considered. The preferred conformation of the cyclohexane ring in the free ligand is the chair form with the two nitrogen atoms in the diaxial positions. However, on the basis of molecular model considerations, the two nitrogen atoms are required to be in either the equatorial–axial or diequatorial positions when the acetate groups are in the proper geometry to chelate the molybdenum(V) dimer. Thus, the energy gained in chelation apparently is not sufficient to force the cyclohexane ring and the two nitrogens into the less preferred forms.

Nitrilotriacetate Complex of Molybdenum(V).—The nmr spectrum of the synthesized Mo(V)–NTA chelate consists of two peaks. The smaller high-field peak (chemical shift, 3.77 ppm) is assigned to coprecipitated free NTA on the basis of pH studies and comparison to the free ligand nmr spectrum. The larger low-field peak (chemical shift, 4.35 ppm) is assigned to the molybdenum(V) chelate.

The chelate is stable from pH 1 to 8. The nmr peak is quite broad at low pH values ($W_{1/2} = 8$ cps at pH 1) but becomes sharper at higher pH values ($W_{1/2} = 4$ cps above pH 3). As the probe temperature is lowered from 38 to 10°, the nmr peak broadens significantly ($W_{1/2}$ changes from 4 to 14 cps); at temperatures above 38° the peak becomes slightly sharper. These facts indicate labile molybdenum–acetate bonding, allowing averaging of the chemical environments of the methylenic protons such that only one time-averaged nmr line is observed.[27] However, the appearance of separate resonance lines for the chelate and the free ligand indicates that the intermolecular exchange kinetics are slow with respect to the nmr time scale.

Establishing the Mo:NTA ratio by an nmr variation study (where the ratio of the metal to ligand is varied) has not been successful because of molybdenum precipitation. The available evidence (elemental carbon analysis) supports a 1:1 Mo:NTA ratio but is not conclusive. In the complex a molybdenum dimer unit is required to account for the diamagnetic properties. However, on the basis of the data, no conclusions can be made regarding the structure of the dimeric unit, *i.e.*, whether the dimer is dioxo-bridged or linear-bridged. Molecular models indicate that the two NTA groups of the dimer in the *trans* form should be stable relative to the *cis* form because of spatial interaction of the acetate groups when the ligands are in a *cis* configuration.

N-Methyliminodiacetate Complex of Molybdenum-(V).—Nmr spectral evidence for the formation of a Mo(V)–MIDA chelate is obtained when a series of

(25) R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).
(26) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
(27) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

nmr spectra are recorded as a function of pH. A simple two-lined nmr spectrum corresponding to the uncomplexed ligand is observed for the clear, dark, red-brown solution at pH 0. A heavy, light brown precipitate forms at pH 1. Between pH 3 and 4 the precipitate changes to a darker brown and partially dissolves; the intensities of the free-ligand nmr peaks decrease and several relatively broad peaks appear between pH 4 and 9. Above pH 9 further precipitation occurs and only the free ligand peaks are observed.

Determination of the stoichiometry of the chelate by nmr techniques is complicated by partial molybdenum precipitation in the pH region where complex formation occurs. Calculations based on molybdenum titration data and the nmr spectral integral imply a 1:1 metal: ligand ratio in the complex. Although both *cis* and *trans* isomers of the dimeric complex are possible, inspection of molecular models of the isomers indicates that the two MIDA groups in the *trans* position should be more stable because steric repulsions exist between the methyl groups when the ligands are arranged in the *cis* configuration.

A Kinetic and Equilibrium Study of the Reaction between Ethylenediaminetetraacetatomanganate(III) and Azide

By MARK A. SUWYN and RANDALL E. HAMM

Ethylenediaminetetraacetatomanganate(III), $[Mn^{III}EDTA(OH_2)]^-$, and azide were shown to react to form the complex azido(ethylenediaminetetraacetato)manganate(III), $[Mn^{III}EDTA(N_3)^{2-}]$, with a formal equilibrium constant of 32.1 at 25° and an ionic strength of 0.25. The potassium salt, $K_2[Mn^{III}EDTA(N_3)] \cdot H_2O$, was prepared and recovered for analysis. The infrared spectrum of the complex indicated that the compound was probably seven-coordinate. In solution this complex decomposed by an electron-transfer step to give ethylenediaminetetraacetatomanganate(II) and gaseous nitrogen. At $\mu = 0.25$ the kinetics of the formation of the azide complex and its decomposition were studied over the temperature range 6.5–30°. At all temperatures the ratio of the rate constants for the forward and backward reactions in the formation and decomposition of the azido complex was in good agreement with the equilibrium constant determined by an independent method.

Introduction

A few ethylenediaminetetraacetic acid (EDTA) type complexes of manganese(III) have recently been prepared.[1,2] They have been found to be quite stable in the crystalline form and to decompose only slowly in aqueous solution. These complexes are relatively strong oxidants and can be used to oxidize a variety of compounds. The mechanism of the oxidation of oxalate with *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) has been investigated and was found to involve the interaction of the oxalate species with the manganese(III) complex as the rate-determining step rather than the electron-transfer step.[3] The reaction of Mn^{III}EDTA with excess ligand has been studied[4] and it was found that the complex oxidizes the excess free ligand rather than the coordinated ligand. This is just the opposite of what has been reported for most reactions of manganese(III) complexes[5] where the

unimolecular decomposition of the complex is looked on as the rate-determining step.

The azide ion is quite unstable thermodynamically but is kinetically inert toward many oxidants. The azide ion is quantitatively oxidized by ceric ion to nitrogen gas,[6] while the reaction of azide with permanganate[7] is sluggish and gives a variety of products. Nitrous acid reacts with azide rapidly and completely to give nitrogen gas and nitrous oxide.[8]

Experimental Section

The EDTA was obtained from Geigy Chemical Corp. and was recrystallized twice from hot water and was air dried before use. Sodium azide from Eastman Organic Chemicals was used to prepare the stock solutions. The sodium azide was recrystallized and analyzed according to the methods given by Pepkowitz.[9] The recrystallized material was found to be 99.2% pure. Stock solutions of the sodium azide were prepared by adding weighed portions of sodium azide to distilled water and diluting to the mark in a volumetric flask.

The pH of solutions was adjusted with perchloric acid and carbonate-free sodium hydroxide solution. The ionic strength was

(1) Y. Yoshino, A. Ouchi, Y. Tsunoda, and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).
(2) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).
(3) M. A. Suwyn and R. E. Hamm, *ibid.*, **6**, 142 (1967).
(4) K. A. Schroeder and R. E. Hamm, *ibid.*, **3**, 391 (1964).
(5) W. A. Waters and J. S. Littler, "Oxidations in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 185–241.

(6) J. Martin, *J. Am. Chem. Soc.*, **49**, 2133 (1927).
(7) R. Dennis and D. Browne, *ibid.*, **26**, 577 (1904).
(8) G. Sommer, *Ber.*, **48**, 1843 (1915).
(9) L. P. Pepkowitz, *Anal. Chem.*, **24**, 900 (1952).