

- below that of the unsubstituted benzoato derivative.^{17b}
- (27) The several strongly absorbing species appearing during the course of the Cr(II) and Eu(II) reductions, which are taken to be radicals analogous to the nitro²² and nitroso⁴⁶ reduction products observed in nitrobenzoato systems, persist in solution, whereas the reactions yielding Co^{2+} are complete in a few seconds. The colored materials must therefore be secondary products, almost certainly from reduction of the liberated ligand, rather than intermediates in the primary electron-transfer sequence. Pigments of this type are obtained from the Eu(II) reduction of the 2,4, but not the 2,5, complex, suggesting that these result from reduction of the 4- NO_2 group, with the species first formed (λ_{max} 520 nm) a nitro

radical and that formed later in the addition sequence (λ_{max} 500 nm) a nitroso radical. Nitro (λ_{max} 503 nm) and nitroso (λ_{max} 475 nm) radicals appear to be formed also in the Cr(II) reduction sequences, but with this reductant, either the 2 substituent or the more distant substituent (or both) may be converted to a radical center. The pigments formed in the Cr(II) sequences appear to be much more intensely colored than those in the Eu(II) sequence, leading us to suspect that the former may be Cr(III)-bound radicals analogous to the Cu(III)-bound pyrazine radicals described by Wu and co-workers.

- (28) M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, **17**, 326 (1978).

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Intramolecular Exchange in the Molybdenum(VI) Complex with Nitrilotriacetate and a Comparison of the Labilities of the Molybdenum and Tungsten Complexes with Various Aminopolycarboxylates

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NMR spectra of $\text{MoO}_3\text{NTA}^{3-}$ in an organic solvent at a series of temperatures clearly indicate that the unbound glycinate arm of the ligand readily exchanges with the bound arms. Exchange is also induced by the introduction of water. A unique, plausible mechanism is suggested. The corresponding W(VI) complex is also fluxional but the activation energy is larger. A general comparison of the Mo(VI) and W(VI) complexes with various aminopolycarboxylates indicates a larger lability for the molybdenum complexes. It is also shown that the ^1H NMR spectra of several complexes of W(VI) were reported incorrectly.

Introduction

The ability of molybdenum to form stable chelates with the aminopolycarboxylates, ethylenediaminetetracetate (EDTA), methyliminodiacetate (MIDA), iminodiacetate (IDA), and nitrilotriacetate (NTA), has been established by ^1H NMR.¹⁻⁷ With the exception of the $\text{Mo}^{\text{VI}}\text{-NTA}$ complex, all the molybdenum(VI)-aminopolycarboxylate chelates display AB splitting in the resonances due to the methylene protons. To account for the singlet observed in the spectrum of $\text{MoO}_3\text{NTA}^{3-}$ it has been suggested that, in the absence of an exchange process, NTA could use all four donor sites to generate a seven-coordinate, capped octahedron with C_{3v} symmetry.^{1,8} However, the similarities which exist between $\text{MoO}_3\text{NTA}^{3-}$ and other aminopolycarboxylate complexes in terms of ligand donor atoms and stability constants⁹ suggest that all of these complexes should assume similar geometries. This expectation was confirmed, at least in the solid state, by the recent crystal structure of $\text{K}_3\text{MoO}_3\text{NTA}\cdot\text{H}_2\text{O}$.¹⁰ The structure has shown that the coordination number of molybdenum is six and that one of the glycinate arms is not bound to the metal atom.

We have reexamined the nature of the $\text{MoO}_3\text{NTA}^{3-}$ anion in solution in order to determine whether the magnetic equivalence of the methylene protons is the result of an exchange process, which is not accessible to the other aminopolycarboxylate complexes, or whether it reflects a geometry in solution which is different from that observed in the solid state. In addition, we have examined the congeneric $\text{W}^{\text{VI}}\text{-NTA}$ complex as well as other aminopolycarboxylate complexes with W(VI) in order to augment our comparison of the complexes derived from Mo(VI) and W(VI).⁴

Experimental Section

Reagents. Reagent grade chemicals were used without further purification. Enriched Na^{13}CN (90 atom %), CD_3OD (99.5 atom %), bis(triphenylphosphine)iminium chloride (PPNCl), and

$\text{Na}_3\text{NTA}\cdot\text{H}_2\text{O}$ were purchased from Merck Sharpe and Dohme Canada Ltd., Aldrich Chemical Co., Ventron Corp., and Sigma Chemical Corp., respectively.

Analysis. Microanalyses (C, H, N, and P) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Tungsten was analyzed gravimetrically by digesting the complex in HClO_4 , dissolving the resulting tungstic oxide in base, and precipitating the tungsten as the oxinate.¹¹

Synthesis of ^{13}C -Enriched Nitrilotriacetic Acid, $\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{*CO}_2\text{H})_2$. The acid form of the ligand, enriched in ^{13}C at two of the three carboxylate carbon atoms, was prepared by the carboxymethylation of glycine¹² using ^{13}C -enriched NaCN . Since we planned to achieve a total enrichment which was 3.4 times the ^{13}C content in natural abundance, a solution containing CN^- enriched in ^{13}C to 5.1 atom % was used. A moderate yield (55%) of the desired crystalline material was obtained. The synthesis was confirmed by comparisons of the melting point and infrared spectrum of the labeled compound with those of an authentic sample containing ^{13}C in natural abundance. The level of enrichment was confirmed by comparing ^{13}C NMR spectra of equimolar solutions of the labeled and unlabeled compounds. Careful integrations of the signals arising from the carboxylate carbon atoms indicated that the intensity of the signal from the enriched compound was greater than that from the compound containing ^{13}C in natural abundance by a factor of 3.48. The theoretical value is 3.42.

Synthesis of $(\text{PPN})_3(\text{MoO}_3\text{NTA})$. To prepare the bis(triphenylphosphine)iminium salt of $\text{MoO}_3\text{NTA}^{3-}$, the pH of a solution of $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (0.06 M) and $\text{Na}_3\text{NTA}\cdot\text{H}_2\text{O}$ (0.06 M) was adjusted to 7.5 with concentrated HCl. Twenty milliliters of the $\text{MoO}_3\text{NTA}^{3-}$ solution was added to 300 mL of a solution of PPNCl (0.012 M). Complete precipitation was accomplished by cooling for 6 h at 10°C . The white solid was recrystallized from ethanol through the addition of water. The solid was dried for 24 h under vacuum over P_2O_5 . An average yield of 55% was obtained. The analytical results indicate that the compound is probably hydrated, at least at the time of analysis. The extremely hygroscopic nature of this compound makes handling it difficult. Anal. Calcd for $(\text{PPN})_3\text{MoO}_3(\text{NTA})\cdot 4\text{H}_2\text{O}$: C, 67.7; H, 5.2; N, 2.8; P, 9.2. Found: C, 67.8; H, 5.6; N, 2.5; P, 9.4. The ^{13}C and ^1H NMR spectra

contained only small signals due to impurities, mainly free NTA.

The preparation of $(\text{PPN})_3\text{MoO}_3\text{NTA}$ with ^{13}C labeled H_3NTA required that the solution of H_3NTA be neutralized prior to addition of MoO_4^{2-} to prevent the polymerization of MoO_4^{2-} under acidic conditions.^{5,6,9}

Synthesis of $(\text{PPN})_3\text{WO}_3\text{NTA}$. The preparation of this compound was identical with that of the $\text{MoO}_3\text{NTA}^{3-}$ salt. Again, this compound is extremely hygroscopic making handling and analysis difficult. Unlike the molybdenum complex, the analytical results in this case agree best with an anhydrous compound. Anal. Calcd for $(\text{PPN})_3\text{WO}_3(\text{NTA})$: C, 67.2; H, 4.7; N, 2.8; P, 9.1. Found: C, 66.6; H, 5.4; N, 2.8; P, 9.1.

Synthesis of $(\text{PPN})_2\text{W}_6\text{O}_{19}$. The bis(triphenylphosphine)iminium salt of $\text{W}_6\text{O}_{19}^{2-}$ was prepared by two methods. When 1.0 g of $(\text{PPN})_3\text{WO}_3\text{NTA}$ was dissolved in 5 mL of CHCl_3 at room temperature, a white crystalline material formed slowly over a period of 3 days. After washing extensively with CHCl_3 the yield of $(\text{PPN})_2\text{W}_6\text{O}_{19}$ was 0.1 g. Alternatively, when 4.12 g of $(\text{PPN})_2\text{W}_6\text{O}_4$ was dissolved in 20 mL of CHCl_3 , 0.7 g of an identical crystalline material formed over a period of several days. Removal of the solid and the addition of fresh CHCl_3 resulted in the formation of additional product. The infrared spectra of the products prepared by either method were identical. Anal. Calcd for $(\text{PPN})_2\text{W}_6\text{O}_{19}$: C, 34.8; H, 2.4; N, 1.1; W, 44.4. Found: C, 34.7; H, 2.4; N, 1.2; W, 44.5. Two tungsten-oxygen stretching frequencies were observed for $(\text{PPN})_2\text{W}_6\text{O}_{19}$: a sharp band at 973 cm^{-1} and a broad absorption at 811 cm^{-1} . These values are in excellent agreement with those reported for the alkylammonium salts.¹³

Instrumental Analysis. All Fourier-transform ^{13}C NMR spectra were obtained with a Varian Associates XL-100-15 FT spectrometer operating at 25.196 MHz, externally locked on a hexafluorobenzene signal. Free induction decay was obtained using a 19- μs radio-frequency pulse and recycle times of 3–4 s. The data were accumulated as 8 K data points in the time domain, transformed as 16 K, and displayed as 8 K in the frequency domain. The temperature, accurate to $\pm 1^\circ\text{C}$, was maintained with a Varian variable-temperature controller. All proton NMR spectra were recorded on a Varian HR-220 spectrometer, with temperatures accurate to $\pm 2^\circ\text{C}$. All ^{13}C NMR samples were prepared in either CH_2Cl_2 , CHCl_3 , or H_2O using CH_3OH as an internal standard.¹⁴ Proton samples were prepared in either CD_3OD or D_2O , using Me_4Si or *tert*-butyl alcohol as an internal standard. Chemical shifts are reported relative to Me_4Si . Infrared spectra were recorded using a Perkin-Elmer 283 infrared spectrometer. The pH of solutions was measured with a Sargent pH meter, Model 7, equipped with a Corning 30070-1C electrode.

Analysis of ^{13}C Spectra. Line-shape analysis of the ^{13}C spectra was performed using Binsch's DNMR program¹⁵ for computation of exchange-broadened spectra and a CDC 6600 computer. The rearrangement process was treated as a three-spin, three-configuration exchange. The frequency separation observed between the two resonances and the overall line shapes were used as criteria for matching simulated and experimental spectra. A value of 0.12 s was used for the transverse relaxation time, T_2 . This value was obtained from the line width of the carboxylate signals in the absence of exchange at -20°C and was assumed to be constant over the range of temperatures examined.¹⁶

Results and Discussion

The ^1H or ^{13}C NMR spectra of aqueous $\text{MoO}_3\text{NTA}^{3-}$ in the presence of free NTA consists of sharp, well-resolved resonances for both the bound and the free ligand, which indicates that an intermolecular exchange of bound and free ligand is slow on a NMR time scale.¹⁷ However, the narrow line width of the signal due to bound NTA suggests that an intramolecular exchange process, if it exists, must be fast. Initially, it was thought that the inherently larger nature of ^{13}C chemical shifts would provide a method for distinguishing the bound and unbound carboxylate carbon atoms at temperatures accessible with aqueous solutions. Rapid conformeric changes for $(\text{MoO}_2)_2\text{EDTA}^{2-}$ have been successfully observed in aqueous solution in this manner.¹⁸ Unfortunately, only asymmetric broadening was found for the methylene and carboxylate carbons atoms at the low-temperature limit of a 1.0 M aqueous solution of $\text{MoO}_3\text{NTA}^{3-}$. It was therefore

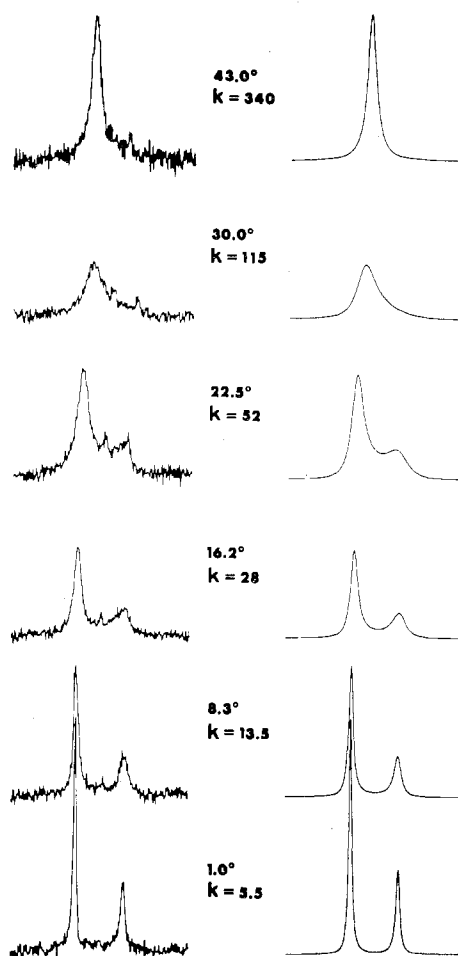


Figure 1. Observed and calculated ^{13}C NMR spectra of the carboxylate carbon atoms of $\text{MoO}_3\text{NTA}^{3-}$ at various temperatures in a 3:1 mixture of CH_2Cl_2 - CH_3OH .

necessary to use organic solvents to achieve a larger working temperature range. The bis(triphenylphosphine)iminium salt of $\text{MoO}_3\text{NTA}^{3-}$ was conveniently synthesized and provided the necessary solubility although the hygroscopic nature of this compound made it difficult to handle. To enhance the detection of the NTA carbon atom resonances in the presence of strong signals from the phenyl carbon atoms of the counterion, two of the three carboxylate carbon atoms of NTA were enriched in ^{13}C .

A series of temperature-dependent ^{13}C NMR spectra obtained from a 0.2 M solution of enriched $(\text{PPN})_3\text{MoO}_3(\text{NTA})$ is given in Figure 1. Only the resonances arising from the carboxylate carbon atoms are shown. The solvent was a 3:1 mixture of CH_2Cl_2 and CH_3OH . The corresponding computer-simulated spectra and calculated rate constants are also provided. In the slow-exchange region which occurs near and below 1° , a 2:1 pattern is observed in agreement with the structure found in the solid state. At the highest temperature conveniently accessible with this solvent (43°C), a broad resonance appears with the expected average chemical shift. The chemical shifts in the slow-exchange region for the bound and unbound carboxylate carbon atoms are 220.0 and 216.4 ppm downfield from Me_4Si while the coalesced peak occurs at 218.7 ppm. The activation parameters for the intramolecular process which were determined from an Eyring plot are $\Delta H^* = 16.4 \pm 0.9\text{ kcal mol}^{-1}$ and $\Delta S^* = 5 \pm 1\text{ eu}$. Since the exchange is accelerated in the presence of water (see below) and since this compound is probably hydrated (see Experimental Section), the activation barrier described by these values is undoubtedly somewhat less than that which could

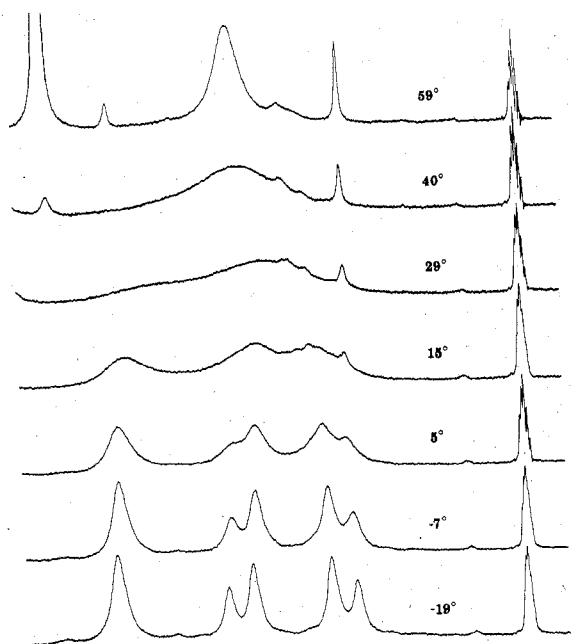


Figure 2. The temperature dependence of the 220-MHz ^1H NMR spectra of $\text{MoO}_3\text{NTA}^{3-}$ in CD_3OD . The upfield signal found in all of the spectra is due to residual methyl protons from the solvent. The temperature-dependent signal which appears furthest downfield in the spectrum at 59°C is due to residual hydroxyl protons. This signal is followed by a sideband and signals due to the complex, an impurity, and some free NTA.

be obtained in a perfectly anhydrous medium.

These results point to a structure, at least in the organic solvent, in which two of the three arms of the ligand are bound to the metal in agreement with the gross features of the crystal structure.¹⁰ Although the bound arms are not strictly equivalent in the solid state,¹⁰ molecular models do not indicate any steric interactions which would prevent their equivalency. The most probable explanation lies in packing effects within the lattice. Assuming this is the case, equivalence in solution is not surprising. The intramolecular exchange process is then identified as the exchange of bound and unbound arms of the ligand.

These spectra also suggested that the intramolecular process in organic solvents would be slow enough to be examined by ^1H NMR spectroscopy at 220 MHz. Figure 2 contains a series of temperature-dependent ^1H NMR spectra for a concentrated solution of $(\text{PPN})_3\text{MoO}_3\text{NTA}$ in CD_3OD . A singlet and an AB pattern (intensity ratio 2:4) are observed at 4.51 and 3.98 ppm, respectively, at -19°C . As predicted by the crystal structure, the singlet corresponds to the equivalent protons of the uncoordinated glycinate arm and the AB pattern arises from the inequivalent protons of the coordinated glycinate arms. A value of 17 Hz was found for the AB coupling constant. This value is consistent with the values reported for the IDA, MIDA, and EDTA complexes.¹⁶ As the temperature increases the peaks coalesce to a singlet at 4.15 ppm.

To further evaluate the effect of solvent on the rearrangement of $\text{MoO}_3\text{NTA}^{3-}$, D_2O was added in increments of $100\ \mu\text{L}$ to $0.5\ \text{mL}$ of a $0.25\ \text{M}$ solution of $(\text{PPN})_3\text{MoO}_3\text{NTA}$ in CD_3OD . The 220-MHz spectrum was recorded at -5°C after each addition. The results, displayed in Figure 3, show that the initial spectrum first broadens and then sharpens into a singlet as more D_2O is added. Sufficient D_2O could not be added to induce rapid exchange, due to precipitation of the complex. The final spectrum does not lie at the center of gravity expected from the chemical shifts of the singlet and AB pattern observed in the initial spectrum. This is the result of an overall solvent dependence in the chemical shifts which

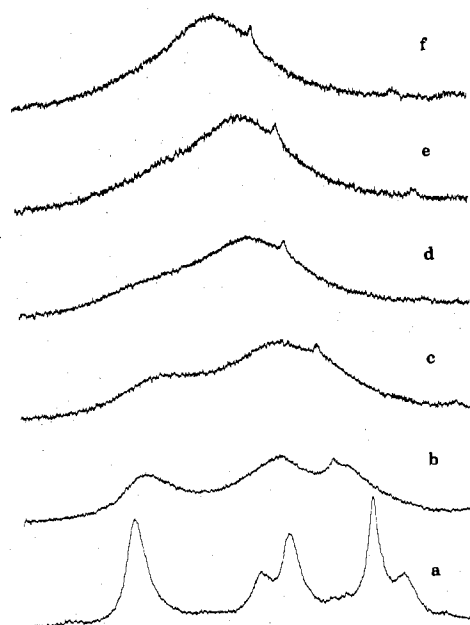


Figure 3. The 220-MHz ^1H NMR spectrum of $\text{MoO}_3\text{NTA}^{3-}$ in CD_3OD at -5°C (a) and spectra showing the effect of incremental additions of $100\ \mu\text{L}$ of D_2O (b-f). The initial concentration and volume were $0.25\ \text{M}$ and $0.5\ \text{mL}$.

also affects the smaller peak due to free NTA. Nevertheless, the overall result is that interconversion of the bound and unbound glycinate groups can be initiated by the addition of D_2O at -5°C , just as it can be initiated at elevated temperatures. Similar activity has been observed in aqueous solutions of CdEDTA^{2-} , where the addition of NH_3 will enhance the rate of the exchange process by assisting the cleavage of the cadmium-carboxylate bond.¹⁹

A salient feature of the exchange process is the occurrence of slow exchange in nonaqueous solvents at temperatures where rapid exchange appears to occur in pure aqueous solution. Since incremental additions of water to an organic solvent cause an increased rate of exchange, rapid exchange is undoubtedly occurring in aqueous solution due to an extensive solvent dependence. Consequently, the structure of the complex is probably similar in both aqueous and nonaqueous solvents and at least grossly similar to that found in the crystal structure. Although the infrared spectrum of aqueous $\text{MoO}_3\text{NTA}^{3-}$ has not been described in detail,¹⁰ it would also seem to be in accord with this conclusion.

Previous NMR studies^{19,20} of aminopolycarboxylate complexes of $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ have established the minimum requirements for averaging the environments of the methylene protons of a bound glycinate arm: consecutive dissociation of the metal-carboxylate and metal-nitrogen bonds followed by inversion of the configuration around the nitrogen atom. The absence of either of the dissociative steps is believed to preclude inversion. Since the ^1H NMR spectra of the $\text{Mo}(\text{VI})$ complexes of MIDA and EDTA contain AB patterns due to the methylene protons, inversion does not occur and at least one of the dissociative steps must be absent. The ABX pattern in the spectrum of $\text{MoO}_3\text{IDA}^{2-}$ indicates a similar dissociative inertness and provides additional insight concerning the lability of the molybdenum-carboxylate bond.⁶ The lifetime of that bond must be sufficiently long to preserve the distinctly different coupling constants between the imino proton and the pair of methylene protons. These coupling constants would be approximately averaged if dissociation of the molybdenum-carboxylate bond allowed rotation about the $\text{CH}_2\text{-N}$ bond. A similar inertness can be safely assumed for the molybdenum-carboxylate bonds in the MIDA and EDTA

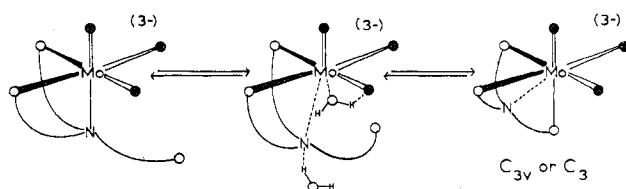


Figure 4. The proposed mechanism for the rearrangement of $\text{MoO}_3\text{NTA}^{3-}$. The central structure shows two ways by which water could assist the intramolecular exchange but no implication of the actual molecularity is intended.

complexes as well as $\text{MoO}_3\text{NTA}^{3-}$. There is no experimental evidence regarding the lability of the Mo–N bond on the NMR time scale but at least a lability on the chemical time scale can be safely inferred.²¹

A mechanism which requires that the Mo–N bond is at least somewhat labile but preserves the inertness of the molybdenum–carboxylate bonds in the ground state is depicted in Figure 4. Beginning with the known structure of $\text{MoO}_3\text{NTA}^{3-}$, the first step is partial or complete dissociation of the Mo–N bond followed by coordination of the previously unbound glycinate group. An examination of molecular models suggests that these steps must be consecutive and not simultaneous. An internal S_N2 reaction would require rotation of the unbound arm and consequent steric interactions between the carboxylate oxygen atoms and the oxo ligands. Consequently, extensive dissociation of the nitrogen atom appears to be a necessary precursor to coordination of the unbound carboxylate group. The lability of the Mo–N bond may also be enhanced by an inductive effect due to the presence of the third carboxylate group. Once coordination of the third carboxylate group is complete, the complex will have a structure of intermediate stability which will equilibrate the glycinate carbon atoms. The methylene protons will also be equilibrated in the intermediate if the resultant structure has true C_{3v} symmetry. The requirements for full C_{3v} symmetry are planar glycinate rings which require an exceptionally long Mo–N distance.⁸ This is conceivable if the nitrogen atom undergoes total inversion. However, if any significant interaction between the molybdenum and nitrogen atoms remains, then a puckering of the rings will be required to accommodate the shortened Mo–N bond distance. The intermediate structure will then have C_3 symmetry and will require a rapid interconversion of a pair of enantiomers to complete the averaging of the methylene protons. Regardless of the exact nature of the intermediate, the methylene protons will be averaged by cycling through this process. Dissociation of one of three equivalent glycinate arms and complete reformation of the Mo–N bond will regenerate the structure found in the ground state. Both of the bound glycinate arms will be in rapid exchange with the uncoordinated arm, where both protons are equivalent. The averaging of the methylene protons in $\text{MoO}_3\text{NTA}^{3-}$ by this mechanism is unique in that it does not require the prior dissociation of a molybdenum–carboxylate bond to achieve rearrangement and only some degree of inversion of the configuration about the nitrogen

atom. This mechanism is not available to the other aminopolycarboxylate complexes of Mo(VI) since inversion and the exchange of the environments of the methylene protons could only occur after dissociation of a molybdenum–carboxylate bond, a bond which is believed to be inert on the NMR time scale.

The energy required to partially or completely rupture the Mo–N bond and open up the coordination site by bending back the two metal–glycinate ring systems would certainly account for the observed value of ΔH^* which was obtained in the organic solvent. The positive value observed for ΔS^* in the organic solvent strongly suggests a net decrease in the bonding interactions on approaching the transition state, a situation which would occur in the absence of extensive solvent participation. Furthermore, the increase in vibrational freedom experienced by the chelate ligand during Mo–N bond cleavage will also contribute to this value. Finally, before the unbound glycinate arm can interact with the metal, any weakly bound organic solvent or counterion molecules will have to be released.

The intermediate structure in Figure 4 also depicts the manner in which water could interact specifically to influence the activation energy of this rearrangement. Water is shown interacting with the metal center to facilitate the dissociation of the nitrogen. Hydrogen bonding to the oxo ligands may play a significant role by favorably positioning the water molecules to interact with the metal. Once solvent is bound to the metal, it would be expected to inhibit the recoordination of the nitrogen atom prior to rearrangement. Water may also stabilize the dissociated nitrogen atom and assist in its subsequent inversion. Methanol would clearly be inferior to water in all aspects of these solvent interactions. In addition to these specific effects, nonspecific effects can arise through the formation of an ion pair between the PPN^+ cation and negatively charged, uncoordinated glycinate arm. The strength of the interaction between the cation and the uncoordinated glycinate arm, which will be dependent upon the dielectric constant of the solvent, could markedly influence the rate of the exchange process. Both specific and nonspecific effects may be contributing to the overall rate.

An alternative mechanism, which is capable of providing a pathway for rearrangement and which does not require Mo–N bond rupture, is displayed in Figure 5. The known structure of $\text{MoO}_3\text{NTA}^{3-}$ is illustrated at both ends of the scheme, and the carboxylate oxygen atoms are labeled to simplify following the rearrangement process. Cleavage of one of the molybdenum–carboxylate bonds, followed by rotation about the Mo–N bond and subsequent coordination of the previously unbound glycinate arm, will lead to a different isomeric form of $\text{MoO}_3\text{NTA}^{3-}$. After the rearrangement, the free glycinate arm is now positioned on the side of the molecule opposite to the mutually cis oxo ligands. Conformational changes in the glycinate rings are also evident. Although rapid cycling through this process will provide for the averaging of inequivalent sites, there are sufficient reasons to suspect that this mechanism is unlikely. Rotation of the Mo–N bond, necessary to isomerize the complex, leads to severe distortion

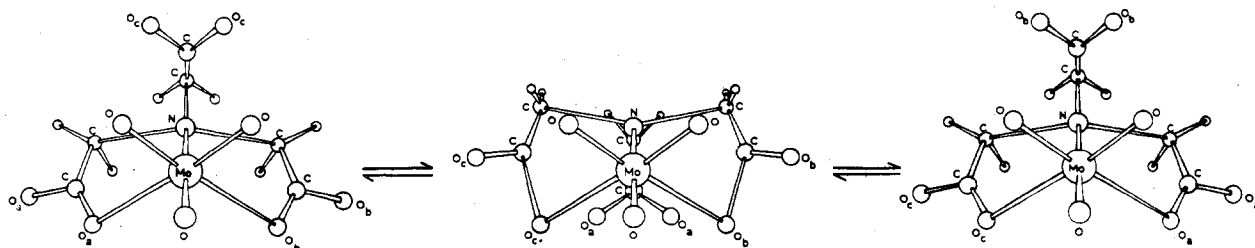


Figure 5. An alternative mechanism for the rearrangement of $\text{MoO}_3\text{NTA}^{3-}$.

from tetrahedral geometry about the nitrogen atom as well as distortion of the bound glycinate rings. In addition, this mechanism involves the dissociation of a molybdenum-carboxylate bond which is believed to be relatively inert. Although it does not necessarily invalidate this mechanism, evidence for a second isomer has never been detected in any spectra of the $\text{MoO}_3\text{NTA}^{3-}$ complex.

Aminopolycarboxylate Complexes of W(VI). The formation constants for aminopolycarboxylate complexes of molybdenum and tungsten are nearly identical.^{4,9} This and other aspects of the chemistries of molybdenum and tungsten have been examined in terms of nature's almost exclusive selection of molybdenum over tungsten in biological systems.⁴ A natural extension of the previous work was the investigation of $\text{WO}_3\text{NTA}^{3-}$. This complex was expected to display fluxional behavior at lower temperatures than for the $\text{MoO}_3\text{NTA}^{3-}$ complex, since it was previously reported that the tungsten complexes of EDTA and MIDA are fluxional but the analogous molybdenum complexes are not.^{4,22} However, no evidence for an exchange process was found in the NMR spectrum of a 0.2 M solution of $(\text{PPN})_3\text{WO}_3\text{NTA}$ in a 3:1 mixture of CH_2Cl_2 and CH_3OH at 30 °C. The molybdenum complex undergoes exchange under similar conditions with a rate constant of $\sim 10^2 \text{ s}^{-1}$. The chemical shifts for the bound and unbound carboxylate carbon atoms in $(\text{PPN})_3\text{WO}_3\text{NTA}$ are 220.9 and 216.3 ppm, respectively. The ^1H NMR at 220 MHz in CD_3OD confirms that $(\text{PPN})_3\text{WO}_3\text{NTA}$ is static under conditions where $(\text{PPN})_3\text{MoO}_3\text{NTA}$ is fluxional. At 20 °C the unbound methylene protons appear as a singlet at 4.48 ppm; the bound methylene protons appear as an AB pattern centered at 4.09 ppm. The AB coupling constant is 17 Hz. However, elevation of the temperature to 60 °C or addition of D_2O to the point of precipitation of the complex leads to spectra which are qualitatively similar to that obtained at only 15 °C with the molybdenum complex (see Figure 2). The ^1H NMR spectrum of the W(VI) complex in D_2O alone at 17 °C consists of only a single averaged resonance. The line width is 4.2 Hz whereas the line width of the resonance obtained from the molybdenum complex in the same solvent and at the same temperature is only 2.8 Hz. However, equivalent line widths occur at 78 °C. All of these observations indicate that the exchange process occurs with greater facility in the molybdenum complex, a behavior which is in direct contrast with previous reports that tungsten complexes of aminopolycarboxylates are more labile.^{4,9,22}

Because of this conflict, the ^1H NMR spectra of the IDA, MIDA, and EDTA complexes of W(VI) were reexamined in aqueous solution at 220 MHz. Each spectrum contained an AB pattern which indicates absence of rapid intramolecular exchange. It was found that $J_{\text{AB}} = 17 \pm 0.3 \text{ Hz}$ in each case which is in agreement with the values of J_{AB} found for the molybdenum complexes. The spectra of equimolar solutions of $\text{MoO}_3\text{IDA}^{2-}$ and $\text{WO}_3\text{IDA}^{2-}$ in addition to equimolar solutions of $\text{MoO}_3\text{MIDA}^{2-}$ and $\text{WO}_3\text{MIDA}^{2-}$, obtained at 17 °C in D_2O , are shown in Figure 6. Part of the problem experienced in the previous interpretation of the spectrum of WO_3MIDA results from the relatively weak wing lines of the AB pattern and the complete overlap of the intense resonance due to free MIDA with one of the central lines of the AB pattern. However, when the temperature is increased to 50 °C, this central line becomes evident as shown in Figure 6. This resolution is possible because the increase in temperature causes the chemical shift difference between the A and B protons to enlarge. A comparison of the spectra obtained at 50 and 17 °C indicates that the upfield peaks of the AB pattern are shifted upfield approximately twice as much as the downfield resonances. A temperature-dependent interaction with the solvent is presumed to be responsible.²⁸ No

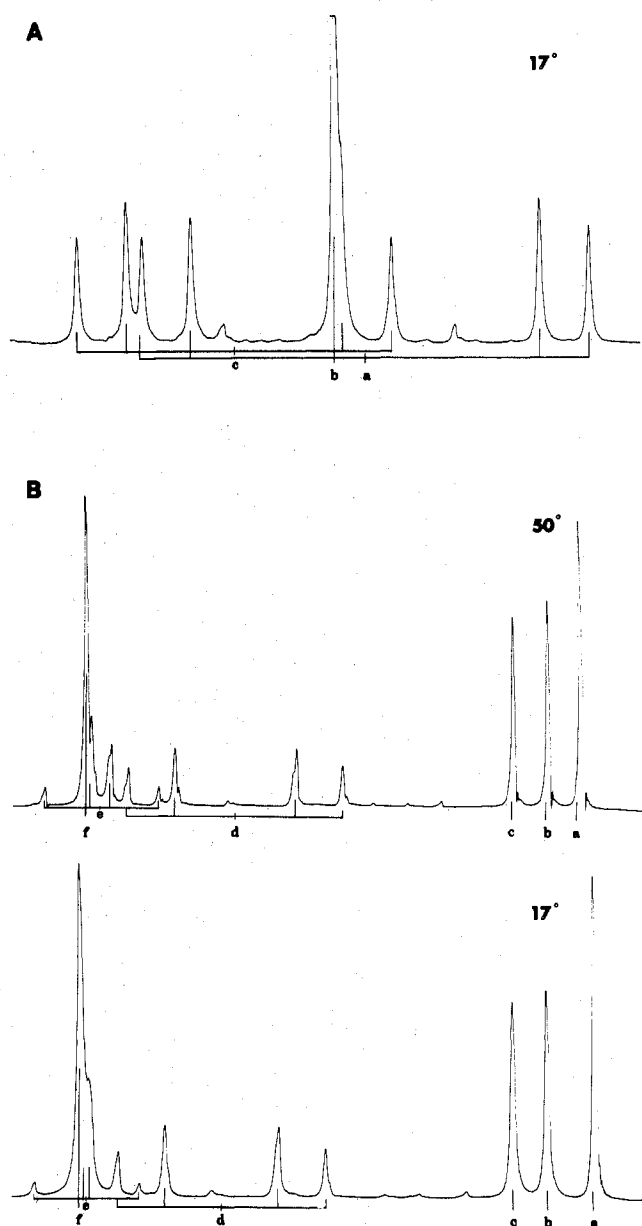


Figure 6. The ^1H NMR spectra of (A) an equimolar solution of $\text{MoO}_3\text{IDA}^{2-}$ and $\text{WO}_3\text{IDA}^{2-}$ and (B) an equimolar solution of $\text{MoO}_3\text{MIDA}^{2-}$ and $\text{WO}_3\text{MIDA}^{2-}$. In (A), the AB patterns centered at a and c are due to methylene protons of $\text{MoO}_3\text{IDA}^{2-}$ and $\text{WO}_3\text{IDA}^{2-}$, respectively, while free IDA appears at b. In (B), the methyl protons of free MIDA, the molybdenum complex, and the tungsten complex appear at a, b, and c, respectively. The resonances due to the methylene protons of $\text{MoO}_3\text{MIDA}^{2-}$ and $\text{WO}_3\text{MIDA}^{2-}$ appear at d and e while the signal due to these protons in free MIDA occurs at f. All spectra were obtained at 220 MHz in D_2O at pD 8.0.

change in J_{AB} occurs upon altering the temperature, however.

When the temperature of an equimolar solution of $\text{MoO}_3\text{MIDA}^{2-}$ and $\text{WO}_3\text{MIDA}^{2-}$ (also containing free MIDA) was increased to 78 °C, there was no evidence for either intramolecular or intermolecular exchange. In contrast, $\text{MoO}_3\text{IDA}^{2-}$ is known to undergo an intermolecular exchange⁶ which can be accelerated by increasing the temperature or the pH. The rate of this interchange is reflected in the line widths observed for the AB pattern. When NMR spectra of the Mo(VI) and W(VI) complexes of IDA were compared, the molybdenum complex showed consistently larger line widths as the temperature or the pH was increased. These results suggest that $\text{MoO}_3\text{IDA}^{2-}$ is more labile than $\text{WO}_3\text{IDA}^{2-}$.

toward this interchange process.

Our observations, then, indicate that the molybdenum complexes are generally more labile than the tungsten complexes. These observations are in line with the general trend toward increasing inertness of the heavier transition metals of any group. Good illustrations of this trend are provided by the acid or base hydrolysis of octahedral complexes²³ and the intramolecular, metal-centered inversion of dithiocarbamate complexes.²⁴

Although it has been argued that nature's selection of molybdenum in enzymes with the virtual exclusion of tungsten^{22,25} arises from differences in the redox properties of these two metals,⁴ the differences in the lability of simple molybdenum and tungsten complexes suggest that there may also be a kinetic factor which would make molybdenum a more favorable choice. If dissociation of water or a portion of the peptide chain must occur to provide a coordination site for substrate interaction, molybdenum would be preferred over tungsten based on its more labile nature. Any internal rearrangement of donor atoms during catalysis would similarly occur more readily with molybdenum. The loss or absence of catalytic activity associated with the replacement of molybdenum by tungsten in enzymes may then reflect the kinetic inertness of tungsten as well as its poorer oxidizing strength.

An Additional Observation. It was also found that a rather interesting reaction occurs when solutions of $(PPN)_3WO_3NTA$ in $CHCl_3$ are heated or allowed to stand for several days at room temperature. Large, colorless crystals of $(PPN)_2W_6O_{19}$ are obtained by either method. The same compound is also obtained when $(PPN)_2WO_4$ is allowed to stand in $CHCl_3$. Presumably, traces of water are responsible for the polymerization in each case. Neither $(PPN)_3MoO_3NTA$ nor $(PPN)_2MoO_4$ displays a tendency to polymerize under similar conditions. These observations accord with the well-known, increased susceptibility of W(VI) toward hydrolytic polymerization relative to Mo(VI). Since the reason for this increased susceptibility undoubtedly lies within the province of thermodynamics and not kinetics, no contradictions need occur between these observations and those cited in reference to the dynamics of aminopolycarboxylate complexes of Mo(VI) and W(VI) in solution.

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Registry No. $(PPN)_3(MoO_3NTA)$, 67316-59-0; $(PPN)_3(WO_3NTA)$, 67316-61-4; $(PPN)_2W_6O_{19}$, 67316-62-5; MoO_3IDA^{2-} , 19709-67-2; WO_3IDA^{2-} , 67316-63-6; MoO_3MIDA^{2-} , 67316-64-7; WO_3MIDA^{2-} , 67316-65-8.

References and Notes

- S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Am. Chem. Soc.*, **86**, 377 (1964).
- R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).
- L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, **6**, 2146 (1967).
- G. E. Callis and R. A. D. Wentworth, *Bioinorg. Chem.*, **7**, 57 (1976).
- R. J. Kula, *Anal. Chem.*, **38**, 1382 (1966).
- R. J. Kula, *Anal. Chem.*, **39**, 1171 (1967).
- R. J. Kula, *Anal. Chem.*, **38**, 1581 (1966).
- J. J. Park, M. D. Glick, and J. L. Hoard, *J. Am. Chem. Soc.*, **91**, 301 (1969).
- R. J. Kula and D. L. Rabenstein, *Anal. Chem.*, **38**, 1934 (1966).
- R. J. Butcher and B. R. Penfold, *J. Cryst. Mol. Struct.*, **6**, 13 (1976).
- A. I. Vogel, "Quantitative Inorganic Analysis", Longmans, Green and Co., London, 1955.
- A. E. Martell and F. C. Bersworth, *J. Org. Chem.*, **15**, 46 (1950).
- K. F. Jahr, J. Fuchs, and R. Oberhauser, *Chem. Ber.*, **101**, 477 (1968).
- The chemical shift used for CH_3OH was 49.3 ppm downfield from Me_4Si . J. B. Strothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
- Quantum Chemistry Exchange Program, Indiana University.
- The line width for the methyl protons of CH_3OH in the sample varied no more than 1.8 Hz over the temperature range examined.
- Although intermolecular exchange is slow on an NMR time scale, experiments with labeled NTA have shown that intermolecular exchange does occur and that it is fast on a chemical time scale.
- G. L. Blackmer, K. J. Johnson, and R. L. Roberts, *Inorg. Chem.*, **15**, 596 (1976).
- R. J. Day and C. N. Reilly, *Anal. Chem.*, **36**, 1073 (1964).
- D. L. Rabenstein and B. J. Fuhr, *Inorg. Chem.*, **11**, 2430 (1972).
- For example, there is no evidence that the tridentate ligand in $MoO_3(dien)$ remains bonded to the metal in aqueous solution. R. S. Taylor, P. Gans, P. F. Knowles, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 24 (1972).
- R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).
- F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1967.
- L. H. Pignolet, *Top. Current Chem.*, **56**, 91 (1975).
- E. I. Stiefel, W. E. Newton, G. D. Watt, and K. C. Hadfield, *Adv. Chem. Ser.*, No. 162, 353 (1977).

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Equilibrium Constants for the Aqueated Iron(II) Cation

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Ferrous ion was generated coulometrically in aqueous HCl from vacuum-annealed iron electrodes of 99.999% spectroscopic purity in a closed titration cell quite free of oxygen. At 25 °C the first acid constant of the aquated ferrous ion is $pK_a = 9.2 \pm 0.1$. The solubility product of $Fe(OH)_2(ppt)$ at 25 °C is $pK_{sp} = 14.39 \pm 0.05$. Additional measurements at 1 and 40 °C yielded the heat of acid dissociation of Fe^{2+}_{aq} as $\Delta H = +8.5 \pm 1.2$ kcal/mol and the heat of dissolution of the hydroxide to ions as $\Delta H = +4.7 \pm 0.4$ kcal/mol. Ferrous hydroxide as ordinarily precipitated was found to be amorphous by X-ray diffraction. Measurements of the ion-pair association constant of $FeHCO_3^+$ place this constant, if it pertains, in the range 10–30 at 25 °C. Directly observed potentials Fe^{2+}/Fe^0 were independent of pH above pH 6 and under these conditions lay between the two values -0.409 and -0.440 V compiled in standard sources.

Introduction

Values of equilibrium constants for several simple but important reactions of the aquated ferrous ion Fe^{2+}_{aq} have never been established with certainty. For the solubility product of ferrous hydroxide, for example, numbers ranging from 10^{-16} to 10^{-13} can be found. The acid dissociation constant of the aquated ion was determined by a reliable method in 1 M $NaClO_4$ after a number of determinations by

incorrect methods; only one thermodynamic value referred to infinite dilution has been available.¹⁰ The potential of the couple Fe^{2+}/Fe^0 has been reported from -0.467 to -0.409 V on the standard hydrogen scale, and the uncertainty in this value appears to affect seriously thermochemical tabulations for many iron-containing species. Although the solubility product of $FeCO_3$ (siderite) is known with good precision, little else is understood concerning the geochemically important