crossing competing with quartet vibrational relaxation (case IV, alternative A). Since $^2E_g \rightarrow {}^4T_{2g}$ back-ISC proceeds with near unit efficiency,[1,6] 0.57 and 0.38 are then the corresponding quantum yields for $^4T_{2g} \rightarrow {}^2E_g$ ISC for irradiation above and below, respectively, the surface crossing point. Thus, 0.38 represents the efficiency for ISC out of the vibrationally equilibrated $^4T_{2g}$ state. If this analysis is correct, independent experimental support should be forthcoming from the relative phosphorescence intensity studies at these wavelengths. The data in Table I are again in excellent agreement with this expectation. The ratio of the phosphorescence yields at 514 and 436 nm (0.63) matches closely the corresponding reaction quenching ratio (0.65). In addition, the 514-nm vs. 436-nm phosphorescence ratio reported here (0.63) is identical with that observed by Balzani et al.[2] for biacetyl-sensitized vs. direct emission for $Cr(en)_3^{3+}$. This information provides further evidence for the near-energetic equivalence of the biacetyl triplet and the Thexi $^4T_{2g}$ level.[10,26] The agreement between the phosphorescence and percent reaction quenching data in Table I is especially pleasing, in view of the clear-cut conclusions which can be drawn from the former. The higher phosphorescence yield associated with 436-nm irradiation clearly indicates a higher resultant doublet population to that obtained on 514-nm excitation. Although wavelength dependence studies of Cr(III) phosphorescence have been reported previously,[28] the present investigation appears to be the first in which yields have been compared across a common absorption band.

Although Beattie and co-workers[29,30] have demonstrated that ISC can be a rapid process, the present results are to our knowledge the first experimental evidence in Cr(III) systems for the step proceeding at a comparable rate to vibrational relaxation in aqueous solution at 25 °C. It has been argued by Adamson et al.[9,10] that a similar situation exists for most Cr(III) complexes at very low temperatures up to the solvent glass point region. The spin-multiplicity restrictions associated with organic photochemistry clearly do not apply rigidly to Cr(III) species, an observation consistent with substantial spin–orbit coupling.

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Registry No. (+)D-$Cr(en)_3^{3+}$, 41509-53-9; OH^-, 14280-30-9.

References and Notes

(1) N. A. P. Kane-Maguire and C. H. Langford, *Chem. Commun.*, 895 (1971).
(2) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *J. Am. Chem. Soc.*, **93**, 339 (1971).
(3) C. H. Langford and L. Tipping, *Can. J. Chem.*, **50**, 887 (1972).
(4) N. A. P. Kane-Maguire and C. H. Langford, *J. Am. Chem. Soc.*, **94**, 2125 (1972).
(5) H. F. Wasgestian, *J. Phys. Chem.*, **76**, 1947 (1972).
(6) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, **77**, 2947 (1973).
(7) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
(8) G. B. Porter, S. N. Chen, H. L. Schlafer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).
(9) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(10) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Prog. Inorg. Chem.*, **17**, 1 (1972).
(11) R. D. Gillard and P. R. Mitchell, *Inorg. Synth.*, **13**, 184 (1972).
(12) F. Galsbol, *Inorg. Synth.*, **12**, 269 (1970).
(13) H. L. Schlafer and O. Kling, *Z. Phys. Chem. (Frankfurt am Main)*, **16**, 14 (1958).
(14) E. Jorgensen and J. Bjerrum, *Acta Chem. Scand.*, **13**, 2075 (1959).
(15) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(16) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(17) D. Banerjea and B. Chakravarty, *J. Inorg. Nucl. Chem.*, **26**, 1233 (1954).
(18) L. E. Erickson, *J. Am. Chem. Soc.*, **91**, 6284 (1969).
(19) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, p 33.
(20) C. S. Garner and D. A. House, *Transition Met. Chem.*, **7**, 59 (1970).
(21) C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 518 (1956).
(22) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
(23) S. N. Chen and G. B. Porter, Abstracts, of the Xth Informal Conference on Photochemistry, Stillwater, Okla., May 1972, p 155.
(24) S. Chen and G. B. Porter, *J. Am. Chem. Soc.*, **92**, 2189 (1970).
(25) N. A. P. Kane-Maguire, J. Conaway, and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 801 (1974).
(26) It is our view that it should be possible to duplicate the essential features of the biacetyl-sensitization study by direct $Cr(en)_3^{3+}$ excitation at 514.5 nm. However, in contrast to our observed value of $\phi_{rac} = 0.40$ (514.5 nm), Balzani et al.[2] reported a limit-sensitized hydrolysis yield of 0.8. These contradictory findings are discussed elsewhere.[27]
(27) N. A. P. Kane-Maguire and D. E. Richardson, in preparation.
(28) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1687 (1963).
(29) J. T. Yardley and J. K. Beattie, *J. Am. Chem. Soc.*, **94**, 8925 (1972).
(30) J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *J. Am. Chem. Soc.*, **95**, 2052 (1973).

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Conformational Dynamics of Dioxodi-μ-oxo-aminopolycarboxylatodimolybdate(V) Complexes by Carbon-13 Nuclear Magnetic Resonance

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Carbon-13 nuclear magnetic resonance spectroscopy was employed to study the kinetic processes associated with the conformational interconversions of two isomeric forms of a molybdenum(V) complex of ethylenediaminetetraacetic acid, $(MoO_2)_2EDTA^{2-}$. The ^{13}C NMR spectra of the molybdenum(V) complex of *dl*-1,2-propylenediaminetetraacetic acid, $(MoO_2)_2PDTA^{2-}$, and a recently synthesized Mo(V) complex of *trans*-1,2-cyclohexanediaminetetraacetic acid, $(MoO_2)_2CyDTA^{2-}$, are also reported. The latter two complexes were found to be conformationally rigid over the temperature range studied (0–95 °C). Kinetic data for the $(MoO_2)_2EDTA^{2-}$ complex were collected and both rate constants and the corresponding activation parameters were determined by least-squares techniques.

Introduction

X-ray crystallographic studies[1] have established that the ethylenediaminetetraacetic acid (EDTA) complex of molybdenum(V) contains the dioxo-bridged Mo_2O_4 unit. The diamagnetism of the dioxo-bridged species is believed to be a consequence of either spin pairing through the oxo bridges or the formation of a direct metal–metal bond.[2-6] Since many complexes of molybdenum(V) exhibit diamagnetic charac-

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teristics, they may be conveniently studied by conventional NMR techniques for the elucidation of structures, stabilities, and dynamics of these chelates in solution. Further, since molybdenum has been shown to participate in a host of biochemical reactions,[7-9] considerable interest has developed regarding the role of molybdenum complexes in biological processes.

In the study reported here, a chelate of molybdenum(V), dioxodi-μ-oxo-ethylenediaminetetraacetatodimolybdate(V), $(MoO_2)_2EDTA^{2-}$, illustrates the dynamics of conformational interconversions of coordination complexes as a function of temperature. This compound interconverts between two conformers of equal energy, populations, and lifetimes.

We also report the synthesis and ^{13}C and ^1H NMR spectra of a new complex of Mo(V) that is structurally similar to the $(MoO_2)_2EDTA^{2-}$ species but conformationally "rigid". This complex, $(MoO_2)_2CyDTA^{2-}$, contains *trans*-1,2-cyclohexanediaminetetraacetic acid as a chelating agent and the complex was found to exhibit conformational rigidity similar to that observed for the *dl*-1,2-propylenediaminetetraacetic acid complex, $(MoO_2)_2PDTA^{2-}$.

Experimental Section

The natural-abundance ^{13}C Fourier transform spectra were recorded on a Varian Associates XL-100 NMR spectrometer equipped with a 15-in. magnet (operating at 25.2 MHz in the ^{13}C mode), pulse unit, broad-band random-noise ^1H decoupler, variable-temperature controller, and an external ^{19}F lock. In ~1 h 1000 pulses of 120-μs duration were applied with a 2.0-s accumulation time and 0.1-s delay between pulses. The range of 1000 Hz was covered by 4096 addresses in the Fourier transform spectrum. All spectra were taken after the sample had been allowed to equilibrate for ~30 min at the new probe temperature. All spectral assignments (^{13}C and ^1H) were made using 3-(trimethylsilyl)propanesulfonic acid, sodium salt (NaDSS), as an internal reference. The NaDSS was obtained from Thompson-Packard, Inc. The D_2O solvent was obtained from Stohler Isotope Chemicals and was used without further purification.

Preparation of $Na_2[(MoO_2)_2EDTA]$. The complex was synthesized by the method of Haynes and Sawyer and produced the $Na_2[(MoO_2)_2EDTA]$ complex in good yields with the reported purity.[10]

Preparation of $Na_2[(MoO_2)_2PDTA]$. This complex was synthesized by the method of Callahan and Wing.[2]

Preparation of $Na_2[(MoO_2)_2CyDTA]$. H_4CyDTA (2.77 g) was dissolved in a 1.4 N solution of sodium hydroxide. To this solution was added, with good stirring, 33 ml of 0.5 *F* Mo(V) solution (prepared by reduction of a Mo(VI) in 3 M hydrochloric acid with mercury). The resultant solution was brought to a final pH of ~6.5 by the addition of a few drops of saturated sodium hydroxide solution. Ethanol (95%) was added until a persistent cloudiness was obtained. Cooling at 10 °C for several weeks yielded red-brown crystals. Recrystallization was achieved from a water–ethanol mixture (yield 1.3 g). The results of elemental analysis indicate a molecular formula $Na_2Mo_2O_{24}H_{42}C_{14}N_2$. Anal. Calcd for $Na_2[(MoO_2)_2CyDTA]\cdot 12H_2O$: Mo, 22.28; C, 19.53; H, 4.93; N, 3.25. Found: Mo, 22.30; C, 19.48; H, 4.26; N, 3.10.

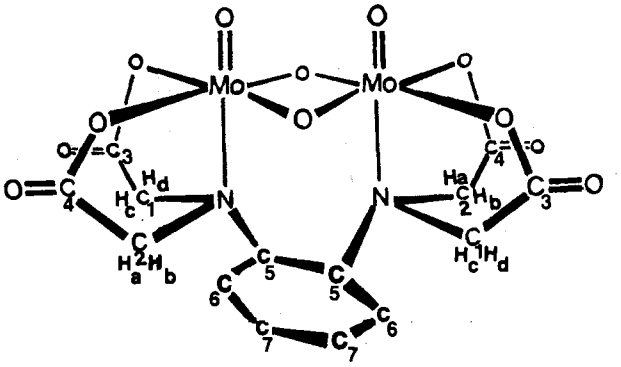
Mo^VCyDTA

Previous attempts to prepare the CyDTA chelate complex of molybdenum(V) in the crystalline form failed.[10] In fact, no evidence of Mo^VCyDTA chelate formation was observed from NMR data over the pH range 0–12. We have reexamined this system and have found that indeed a CyDTA complex containing the molybdenum dimer unit $(MoO_2)_2CyDTA^{2-}$ does form and can be obtained in the crystalline state (see Experimental Section). An x-ray crystallographic study of this complex is currently being conducted in our laboratory to confirm the NMR structural data given below. Chelate formation of this product was found, however, to be somewhat restricted as crystallization only occurs on long standing. Several weeks was required to achieve product formation.

Figure 1 shows the glycinate portion of the 100-MHz proton NMR spectrum of $(MoO_2)_2CyDTA^{2-}$ as consisting of two

Figure 1. ^1H NMR spectrum of $(MoO_2)_2CyDTA^{2-}$ in D_2O at 100 MHz. For AB-one, average chemical shift (δ_{av}) relative to DSS is 3.50 ppm, J_{AB} = 16 Hz; for AB-two, δ_{av} = 3.36 ppm, J_{AB} = 18 Hz.

overlapping AB patterns corresponding to the two sets of nonequivalent glycinate protons; see I. Tentative line as-



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signments of the two AB patterns are shown in the figure. The AB pattern labeled AB-one (J = ~16 Hz) is assigned to protons H_c and H_d (in I) on the basis of chemical shifts induced by the C–N bond anisotropy of the backbone ring.[11] The AB-two pattern (J = ~18 Hz) is similarily assigned to H_a and H_b. Coupling constants of 16 and 18 Hz are commonly observed for metal ion complexes of aminocarboxylates and have been cited as being a measure of the degree-of-planarity of the chelate rings.[12,13] Further, glycinate rings having a high degree of planarity were observed to undergo deuterium exchange with greater ease than those being less planar. These arguments would suggest, therefore, that the high-field protons H_a and H_b (J = ~18 Hz) should undergo deuterium exchange with greater ease than H_c and H_d in this type of complex. Indeed, this was found to be the case in the $(MoO_2)_2EDTA^{2-}$ complex as will be pointed out later.

The compound $(MoO_2)_2CyDTA^{2-}$ was initially chosen for this study on the premise that the bulky cyclohexane ring on the N–C–C–N backbone ring of the CyDTA ligand, in I, would increase the barrier to ring inversion to such a degree as to render the complex conformationally inert. Failing to detect any change in the proton NMR spectrum of this

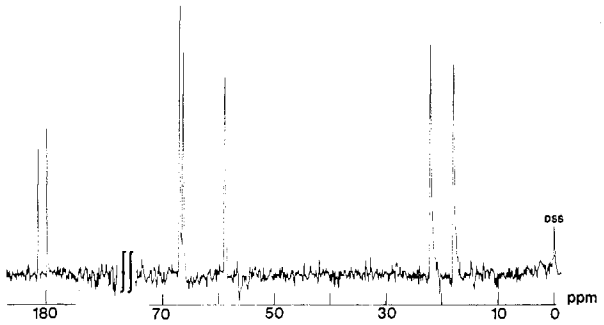


Figure 2. Natural-abundance ^{13}C Fourier transform NMR spectrum of $(MoO_2)_2CyDTA^{2-}$ in H_2O.

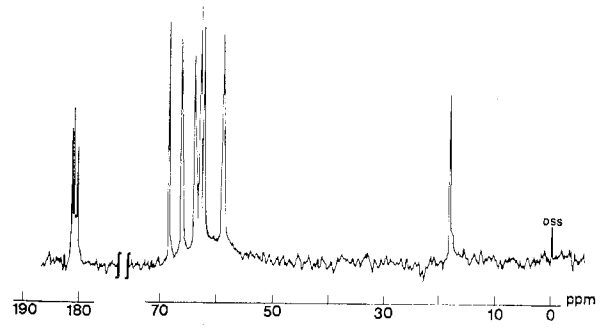


Figure 3. Natural-abundance ^{13}C Fourier transform NMR spectrum of $(MoO_2)_2PDTA^{2-}$ in H_2O.

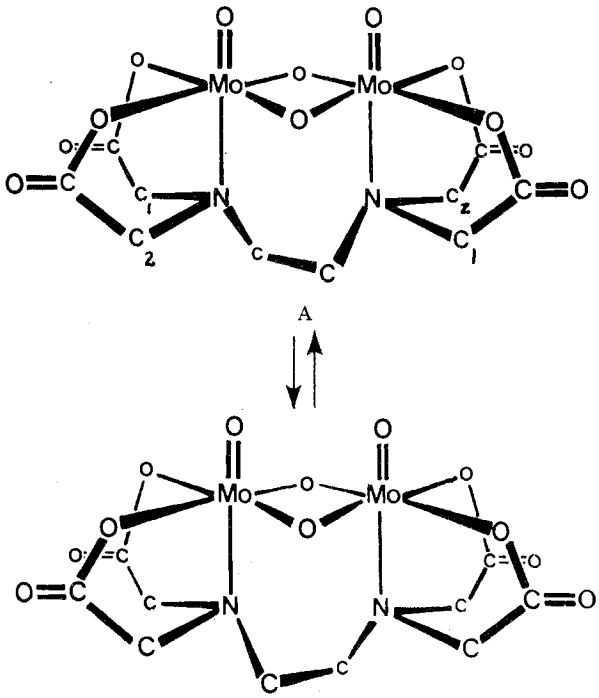
complex (over the temperature range 0–95 °C), the compound was studied by ^{13}C NMR where minor changes in structure or conformation are more easily detected. Figure 2 shows the natural-abundance proton-decoupled ^{13}C Fourier transform of the $Mo^{V}CyDTA$ complex at 0 °C. The two extremely sharp low-field resonances occurring at 180 and 181 ppm vs. NaDSS are assigned to the two types of carbonyl carbons C_3 and C_4 in I (again resulting from the C–N bond anisotropy). The two high-field resonances (18.3 and 22.2 ppm) are assigned to carbon atoms C_6 and C_7 of the cyclohexane ring, in I. The resonance at 67.1 ppm is tentatively assigned to the ring (C_5) carbons between the two nitrogens of the backbone. The glycinate carbon atoms C_1 and C_2 were assigned to the resonances occurring at 66.3 and 58.7 ppm, respectively. These tentative assignments were made in part by deuterium-exchange studies and in part by analogy to previously studied complexes of the CyDTA ligand.[14] The decrease in intensity of the C_1 signal and concomitant increase in its multiplicity are indicative of the fact that the spin-decoupled protons, originally bound to the C_1 carbon, have been (at least in part) replaced by deuterium atoms (in D_2O) which resonate outside of the spin-decoupling frequency range employed to decouple protons.

When the $(MoO_2)_2CyDTA^{2-}$ complex was dissolved in water and heated to 95 °C, no spectral changes were observed. Thus, the bulky cyclohexane ring renders the CyDTA complex of Mo(V) conformationally rigid.

$Mo^{V}PDTA$

The PDTA complex of molybdenum(V) is similar in structure to both the CyDTA (I) and EDTA (II) complexes. In the PDTA complex, however, a methyl group is substituted on the ethylenic N–C–C–N backbone and thus removes the C_2 axis of symmetry common to the other two species. Thus, the NMR spectrum of $(MoO_2)_2PDTA^{2-}$ is complicated dramatically. A previous proton NMR study of this compound from 0 to 90 °C indicated no evidence that the complex underwent conformation inversion.[10] Our ^{13}C NMR studies, given below, support this contention. The backbone methyl group of one isomer (presumably the more stable) is directed away from the plane of the dioxo–molybdenum bridge whereas the methyl group of the second isomer is directed more toward this plane. The latter geometric isomer would contain a highly strained "axial" methyl group.[15,16] The only metal ion complex of PDTA reported to date containing the methyl group in the axial position was that of Rh(III).[17] The axial isomer of this complex could only be obtained in small yields upon strong uv irradiation.

Figure 3 shows the ^{13}C NMR spectrum of $(MoO_2)_2PDTA^{2-}$ in aqueous solution. The four low-field resonances between 180 and 181 ppm are typical of those arising from the carbonyl carbons. The high-field peak at 18.7 ppm was assigned to the methyl group of the PDTA backbone by off-resonance decoupling. Specific assignments of the four glycinate carbon resonances and the two backbone carbon resonances (68.3–58.7 ppm) were not attempted but presumably would be analogous to those reported for $Co^{III}PDTA$.[14] The ^{13}C spectrum of $(MoO_2)_2PDTA^{2-}$ remained unchanged over the temperature range 0–95 °C indicating that no conformational changes occur in this molecule.



$Mo^{V}EDTA$

The ^{1}H NMR spectrum of $(MoO_2)_2EDTA^{2-}$ was previously reported as consisting of a broad AB quartet, presumably arising from the glycinate protons of the EDTA chelate rings, and a rather broad singlet of the EDTA backbone.[10] This spectral pattern was interpreted as being consistent with the rapid interconversion between two isomeric forms of the chelate complex, II, in solution. If the complex existed permanently in either of the two configurations (i.e., a rigid structure), a far more complicated spectral pattern would be expected (two glycinate proton AB quartets and a complex A_2B_2 pattern arising from the ethylenediamine backbone). Previous attempts to study the dynamics of chelate interconversions of the $Mo^{V}EDTA$ complex by proton NMR were unsuccessful.[10] Aside from some broadening at very low temperatures, ^{1}H NMR spectral changes were not sufficiently dramatic to allow kinetic interpretation.

The larger chemical shifts inherent in ^{13}C NMR, however, furnish a marked advantage over ^{1}H NMR in that coalescence of ^{13}C resonances is reached at considerably higher tem-

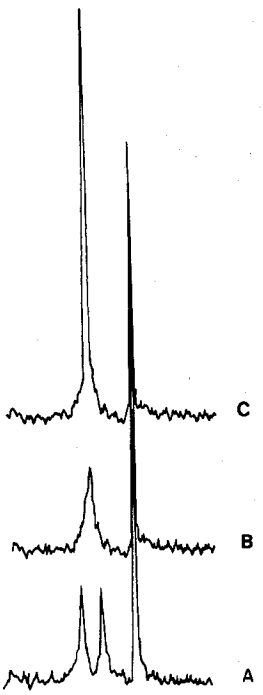


Figure 4. Natural abundance ^{13}C Fourier transform NMR spectrum[18] of $(MoO_2)_2EDTA^{2-}$ in H_2O at (A) 0 °C, (B) 15 °C, and (C) 40 °C.

perature than was observed in the proton case. Thus, the temperature range of greatest interest (which would have been well below the freezing point of the solvent in the ^1H NMR study[10]) was readily accessible by ^{13}C NMR.

Spectral Analysis

Figure 4A shows a partial[18] 25.2-MHz ^{13}C NMR spectrum of $(MoO_2)_2EDTA^{2-}$ at 0 °C in H_2O. The spectrum consists of two distinct signals at $\nu_1 = 64.0$ and $\nu_2 = 68.3$ ppm, the resonant frequencies of the glycinate carbon atoms C_1 and C_2 (in II) when the complex is not undergoing inversion. In this slow-exchange region the lifetimes τ_A and τ_B of the two conformers, in II, are large compared to the inverse of the separation of the frequencies $(\nu_2 - \nu_1)^{-1}$.

The low-field doublet (area ~4) is very slightly unsymmetrical due to the greater spin coupling of the molybdenum isotopes ^{95}Mo ($I = 5/2$, 15.78% abundant) and ^{97}Mo ($I = 5/2$, 9.60% abundant) to the high-field carbon atom, C_1, than to the low-field carbon, C_2. The rather sharp singlet (area ~2) occurring at 58.0 ppm represents the ethylenic carbons of the EDTA backbone. A C_2 axis of symmetry bisects the carbon–carbon bond of the EDTA backbone; thus these atoms remain magnetically equivalent regardless of conformer. Since this resonance remains virtually unchanged throughout the range studied, any temperature-dependent paramagnetic effect is precluded. Although spin decoupling of ^{95}Mo and ^{97}Mo would be highly desirable for resolution enhancement, it was not available in the present instrumentation. Fortunately, these molybdenum nuclei have rather low magnetic moments (−0.9099 and −0.9290, respectively) and have no quadrupole moment, so the amount of line broadening imparted by these isotopes is quite small and may be ignored. Selective spin coupling of metal ions to ligand nuclei, of the type observed here, has previously been reported for complexes of Co(III),[19] Pt(II),[20] and Rh(III)[21] where greater spin coupling was observed for equatorial protons than for axial.

When the $(MoO_2)_2EDTA^{2-}$ complex was dissolved in D_2O (rather than H_2O) at 0 °C and its ^{13}C NMR spectrum recorded, the high-field carbon resonance was so severely broadened that any spectral analytical data obtained was deemed unreliable. This severe broadening was evidently caused by ^{13}C–D coupling as a result of stereospecific deuterium–proton exchange of the glycinate protons of the chelate rings. Such stereospecificity is routinely observed in metal ion complexes of aminopolycarboxylic acids.[12,22,23]

Table I. Calculated Conformational Parameters[a] for $(MoO_2)_2EDTA^{2-}$

T, °C	$10^3\tau$, s	C	σ^2
0	10.0 ± 0.2	510 ± 5	1.1
5	7.4 ± 0.2	520 ± 6	1.4
10	4.9 ± 0.1	495 ± 5	1.3
15	2.5 ± 0.05	550 ± 6	1.9
20	1.3 ± 0.03	430 ± 7	2.1
25	0.99 ± 0.02	466 ± 8	2.9
30	0.72 ± 0.02	417 ± 6	2.5
35	0.63 ± 0.01	410 ± 5	4.7
40	0.44 ± 0.01	413 ± 6	3.5

[a] For all cases $\nu_1 \approx 1610$ Hz and $\nu_2 \approx 1720$ Hz.

Figure 4B shows the spectrum of the $(MoO_2)_2EDTA^{2-}$ complex recorded at a temperature (~15 °C) where the lifetimes τ_A and τ_B are on the order of $(\nu_2 - \nu_1)^{-1}$. Figure 4C shows the spectrum of $(MoO_2)_2EDTA^{2-}$ above 40 °C. In the limit of rapid exchange, τ_A and τ_B are small and the central portion of the signal will be centered on $(\nu_2 + \nu_1)/2$ and appears at 66.0 ppm.

In addition to the cases shown in Figures 4A, B, and C, spectra were obtained for several other cases as given in Table I.

All spectra were analyzed by a nonlinear least-squares computer program utilizing the Marquardt algorithm.[24,25] The effect of the molybdenum spin coupling was ignored. The experimental spectra were manually digitized (40–150 points). The fitting function[26] used was

$$I_{calcd}(\nu) = \frac{C\tau(\nu_2 - \nu_1)^2}{[^1/_2(\nu_1 + \nu_2) - \nu]^2 + 4\pi^2\tau^2(\nu_1 - \nu)^2(\nu_2 - \nu)^2}$$

Here $I_{calcd}(\nu)$ is the calculated intensity at the frequency ν, C is a scaling factor which is not involved in the final activation parameter calculations, τ is the relaxation time, and ν_1 and ν_2 are the transition frequencies in the limit of slow conformational inversion. The fitting function assumes $1/T_2 \ll 1/\tau$. The goodness of fit was indicated by the standard deviation of the parameters (C, τ, ν_1, ν_2) and the variance of the fit, σ^2, where

$$\sigma^2 = \frac{\sum_{i=1}^{N} [I_{obsd}(\nu_i) - I_{calcd}(\nu_i)]^2}{N - m - 2}$$

Here $I_{obsd}(\nu_i)$ and $I_{calcd}(\nu_i)$ are the observed and calculated intensities, N is the number of experimental points, and m is the number of variable parameters (2 or 4). Figures 5 and 6 illustrate the goodness of fit for the slow conformational inversion (0 °C) and rapid conformational inversion (40 °C). The chemical shift did not change over this temperature range. The calculated parameters for the nine spectra analyzed are given in Table I.

A transmission coefficient, κ, was assigned a value of 0.5 since the ethylenediamine backbone of the EDTA complex has an equal probability of returning to its original conformation or continuing the inversion process to achieve the new conformational form after reaching a planar intermediate. Thus, the rate constant, k_R, is given by $2/\tau$, and the enthalpy, $\Delta H^\ddagger$, and the entropy, $\Delta S^\ddagger$, of activation are derived from the Eyring equation of absolute reaction rate theory

$$k_R = (KT/h)\exp(\Delta S^\ddagger/R)\exp(-\Delta H^\ddagger/RT)$$

Therefore, $\ln(2/\tau T)$ was plotted against $10^3/T$, and the slope

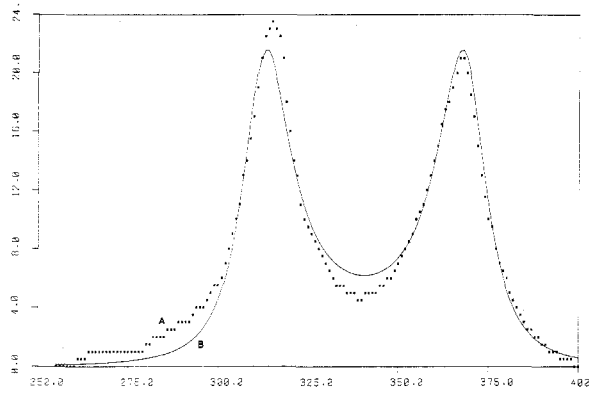


Figure 5. (A) Observed ^{13}C Fourier transform NMR spectrum of $(MoO_2)_2EDTA^{2-}$ in H_2O at 0 °C. (B) Calculated spectrum.

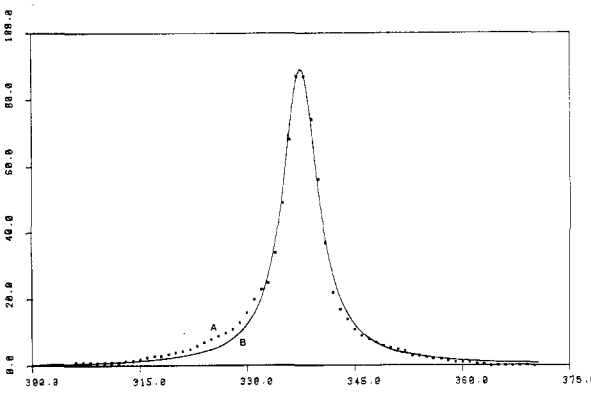


Figure 6. (A) Observed ^{13}C Fourier transform NMR spectrum of $(MoO_2)_2EDTA^{2-}$ in H_2O at 40 °C. (B) Calculated spectrum.

and intercept yielded $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Their actual values were calculated by a linear least-squares analysis of the data as plotted in Figure 7. The results of this analysis gave results of $\Delta H^{\ddagger} = 13 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = 0.2 \pm 0.04$ eu for the conformational inversion process. The standard deviation corresponds to 2.5σ (99% confidence interval). It is assumed that any systematic error associated with the approximation $1/T_2 \ll 1/\tau$ is included in these error limits. The relatively low entropy of activation seems consistent with the degree of freedom apparently available for the proposed ring inversion in the transition state. The enthalpy of activation of this compound, however, is somewhat higher than one might predict from a superficial observation of the geometry of the molecule. Assuming the molecule remains completely intact during the inversion process, the nitrogen atom is forced to go through a nearly trigional-planar geometry during the transition state of the inversion process due to the semirigid nature of the glycinate chelate rings. This would logically impart a larger degree of torsional distortion to the ring undergoing inversion and increase significantly its inversion barrier. It might be expected that the energy barrier to inversion studied here, would not be unlike that of the cyclohexane series where the transition state is presumably a half-chair with four carbon atoms in a near-planar configuration, C_1–C_2–C_3–C_4. The analogy to the ethylenediamine backbone of the $(MoO_2)_2EDTA^{2-}$ complex can easily be drawn, N_1–C_2–C_3–N_4. In the latter case, however, additional rigidity is supplied to the terminal nitrogen atoms through coordination to the molybdenum atoms as well as the glycinate rings. In a study of conformational inversion rates of cyclohexane derivatives and cis decalins by ^{13}C NMR, Grant et al.[27] reported an average enthalpy of activation of 11.5 kcal/mol for six such compounds. An average $\Delta H^{\ddagger}$ of 13.9 kcal/mol was also calculated from the data of Gerig and

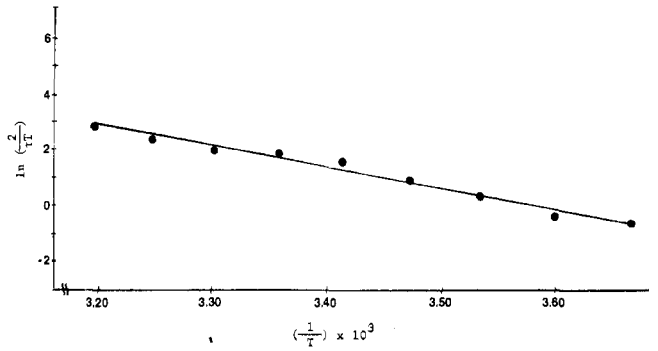


Figure 7. Logarithmic vs. $1/T$ plot for the determination of activation parameters for the $(MoO_2)_2EDTA^{2-}$ inversion process.

Roberts[28] for similar compounds. Hendrickson[29] made an estimate of 12.7 kcal/mol for the inversion barrier of cyclohexane due largely to torsional distortions within the molecule.

It can only be concluded, therefore, lacking appropriate potential energy calculations on the $(MoO_2)_2EDTA^{2-}$ species, that the rather high barrier found for this compound, in agreement with the other similar evidence cited above, is a result of the ring–ring interactions that occur as a result of chelation. These interactions, coupled with the additional stabilizing effects imposed by backbone substitution (PDTA and CyDTA), increase the ring inversion barrier of $(MoO_2)_2PDTA^{2-}$ and $(MoO_2)_2CyDTA^{2-}$ to such a point as to render them conformationally inert (rigid).

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References and Notes

(1) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 2303 (1969).
(2) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).
(3) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960.
(4) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).
(5) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1963).
(6) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).
(7) G. Palmer, R. C. Bray, and H. Beinert, *J. Biol. Chem.*, **239**, 2657 (1964).
(8) D. I. Arnon in "Trace Elements in Plant Physiology", IUBS Colloquia Series No. 1, Chronica Botamica Co., Waltham, Mass., 1950, p 31.
(9) R. H. Burris in "Annual Reports on Plant Physiology", Vol. 17, L. Machlis, Ed., Annual Reviews, Inc., Palo Alto, Calf., 1966, p 155.
(10) L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, **6**, 2146 (1967).
(11) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).
(12) J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10**, 90 (1971).
(13) G. L. Blackmer and J. L. Sudmeier, *Inorg. Chem.*, **10**, 2019 (1971).
(14) G. L. Blackmer and T. M. Vickrey, *J. Coord. Chem.*, **3**, 225 (1973).
(15) R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).
(16) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
(17) G. L. Blackmer, J. L. Sudmeier, R. N. Thibedeau, and R. M. Wing, *Inorg. Chem.*, **11**, 189 (1972).
(18) Carbonyl resonances (two, below coalescence temperature) occurring at very low fields (~180 ppm vs. NaDSS) have been omitted. They are extemely sharp lines (as a result of long carbonyl relaxation times), essentially devoid of NOE, and offer little additional kinetic information. These can, of course, be used to obtain kinetic parameters but, due to NOE differences vs. the reference peak, were undesirable for use in this study.
(19) J. L. Sudmeier and G. L. Blackmer, *J. Am. Chem. Soc.*, **92**, 5238 (1970).
(20) L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Am. Chem. Soc.*, **90**, 6371 (1968).
(21) J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, **10**, 2010 (1971).
(22) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).
(23) J. L. Sudmeier and G. Occupati, *Inorg. Chem.*, **7**, 2524 (1968).
(24) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N.Y., 1969.
(25) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
(26) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw Hill, New York, N.Y., 1959.

(27) D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Am. Chem. Soc.*, **93**, 3678 (1971).
(28) J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2791 (1966).
(29) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

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Tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron(0). Fluxional Pathways

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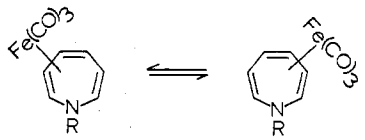
The synthesis and characterization of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron(0) and the related complexes tricarbonyl(4–7-η-3-methyl-1(1*H*),2-diazepine)iron(0) and tricarbonyl(4–7-η-1-methyl-1(1*H*),2-diazepine)iron(0) are described. Solvent- and concentration-dependent ^{1}H NMR and ir studies of the fluxional parent complex tricarbonyl(4–7-η-1-(1*H*),2-diazepine)iron(0) indicate that the fluxional pathway involves intermolecular proton transfer. The fluxional process is strongly acid catalyzed and proceeds through a fluxional η^4 imminium ion complex which can be directly observed in the ^{1}H NMR spectrum. A crystalline trifluoroacetate salt of this η^4 imminium ion has been isolated and structurally characterized. Protonation of nonfluxional diazepine derivatives leads to static N_2-protonated η^4 imminium ion complexes. Tricarbonyl(4–7-η-1-methyl-1(1*H*),2-diazepine)iron protonates with rearrangement to give the same ion as that obtained from reaction of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron with methyl fluorosulfonate.

Introduction

Substituted 1(1*H*),2-diazepines,[1–3] like other seven-membered rings[4–8] with three sites of unsaturation, readily form η^4 tricarbonyliron complexes. Crystallographic evidence indicates that a change from a "tub" to a folded "envelope" conformation is a common feature accompanying complexation (cf. Figure 1). In spite of the fairly extensive geometrical reorganization required, processes leading to a time-averaged symmetry plane can occur and both tricarbonyl(4–7-η-*N*-ethoxycarbonyl-1*H*-azepine)iron **2c** (R = CO_2Et)[5,6] and tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron **2d** (R = H)[3] are fluxional on the ^{1}H NMR time scale at or near room temperature.[1,2] Fluxional pathways[5,6] leading to the time-averaged symmetry plane for the azepine complexes **2c** require a simple shift of the $Fe(CO)_3$ moiety to an alternate η^4 bonding site (**3** ⇄ **3'**) in a fashion similar to that found for tricarbonyl-(1–4-η-cyclooctatetraene)iron[15] and characteristic of cycloolefin complexes in general. The nature of the N substituent appears to have little effect on the fluxional character although this aspect has not been studied in detail.[5,6] A different situation persists for the 1(1*H*),2-diazepine complexes **2d** for which a time-averaged symmetry plane cannot be achieved via a simple $Fe(CO)_3$ migration. The fluxional behavior observed[3] for **2d** (R = H) must involve prototropy as well as valence isomerization. The as yet unknown and potentially antiaromatic 1(1*H*),2-diazepine **1d** (R = H) bears a vinylogous relationship to pyrazole which also shows a ^{1}H NMR spectrum characteristic of a symmetrical structure resulting from rapid valence tautomerism.[16] In the case of the N-substituted 1(1*H*),2-diazepine(tricarbonyl)iron complexes (**2d**, R = alkyl, acyl), prototropy is impossible and static structures result.[1–3] Analogous pyrazole complexes are not available for comparison.[17]

We were interested in obtaining more detailed information concerning the nature of the fluxional process described by **4** ⇄ **4'**. In particular we wished to establish (i) whether the prototropy required in the fluxional process was *inter-* or *intra*molecular and (ii) the effects of protonation. Presently we report findings relevant to (i) and (ii) together with details of some of our previous results.[3]



3 **3'**

Results and Discussion

The synthesis of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron (**2d**, R = H) in high yield was accomplished via sodium ethoxide promoted deacetylation of tricarbonyl(4–7-η-1-acetyl-1(1*H*),2-diazepine) (**2d**, R = $COCH_3$). A similar reaction afforded complex **11** in good yield from tricarbonyl(4–7-η-1-acetyl-3-methyl-1(1*H*),2-diazepine)iron. The *N*-methyl complex **7** was prepared from **4** by treatment with methyl bromide in the presence of sodium carbonate.[18]

The infrared spectrum of **2d** in the carbonyl region in the solid state and in solution shows three bands characteristic of a diene(tricarbonyl)iron complex with an overall molecular symmetry lower than C_{3v}.[2] The molecule fragments as expected in the mass spectrometer, consecutive loss of three molecules of CO giving the base ion $(C_5H_6N_2)Fe^+$. A significant feature of the mass spectrum is the ion at *m/e* 94 which was unequivocally identified by accurate mass measurements as the molecular ion of the unknown parent 1-(1*H*),2-diazepine. The stability of this ion in the mass spectrometer is notable, considering the likelihood that the neutral molecule possesses antiaromatic properties. Analytical, infrared, and mass spectrometric data for complexes **7** and **11** confirm their identity as typical η^4-diene(tricarbonyl)iron derivatives.

The novel fluxional properties of **2d** were described in a preliminary communication.[3] Further information concerning the fluxional process **4** ⇄ **4'** was obtained from detailed ir and ^{1}H NMR studies. Figure 2 shows the results of a concentration-dependent infrared study of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron (**4**) in carbon tetrachloride. Saturated solutions (ca. 0.1 M) in CCl_4 showed a sharp ν(N–H) absorption at 3418 cm^{-1} assigned to free N–H as well as broad bands at 3280 and 3180 cm^{-1} characteristic of