bridging mandelate ligands present. The absorption centered on 2600 cm^{-1} can be assigned, as in the case of **B**, to intramolecular hydrogen bonds involving the oxygens of chelated bidentate ligands. Dimerization of the **A** species produces the **B′** species, which is identical with the aqueous **B** product. Thus **A** may be considered an isomer of the aqueous product **B**. This brings us to the question of the nature of the yellow **A′** species. A methanol solution of this product, for which a visible–ultraviolet spectrum was taken, showed a featureless Laporte allowed transition tailing off at about 490 nm and going off scale at 364 nm which is attributed to chlorozirconium transition. Since the metal-bound chloride is clearly seen in the infrared spectrum and the rest of the spectrum is very similar to that of **A**, the structure of **A′** is envisioned to be the same as **A**, except that the monodentate mandelate is replaced by a chloride.

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Proton Nuclear Magnetic Resonance Studies of Several Polyaminocarboxylic Acid Complexes of Vanadium(V)

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The solution structures and equilibria of the vanadium(V) complexes formed by ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate (EDTA), ethylenediamine-*N*,*N′*-diacetate (EDDA), and *N*,*N′*-dimethylethylenediamine-*N*,*N′*-diacetate (DMEDDA) have been studied by proton nuclear magnetic resonance spectroscopy. All three complexes have the formula $[VO_2Y]$, where Y represents EDTA, EDDA, or DMEDDA, and have been isolated as the sodium or potassium salts. Infrared spectra indicate that the oxygen atoms in the VO_2 unit have a cis conformation. Structures are proposed for all three complexes on the basis of the nmr and infrared data. The EDTA and DMEDDA complexes appear to form a single isomer (α-cis), while the EDDA complex forms both α-cis and β-cis isomers. The β-cis $\rightleftarrows$ α-cis equilibrium has been studied at several temperatures to evaluate the thermodynamic parameters.

Proton nuclear magnetic resonance (nmr) has proven useful for the study of numerous metal ion complexes with polyaminocarboxylic acids such as ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA).[1–7] If the metal–ligand bonds are long-lived compared to the nmr time scale, considerable information about the solution structures of these compounds can be obtained. For such conditions the methylenic protons of the acetate group become chemically nonequivalent, due to the asymmetric bonded nitrogen atom, giving rise to an AB spin–spin splitting pattern.[1] From the coupling constant and chemical shift difference between the two protons, the environment of the acetate group and its position relative to the N–metal–N plane can be determined.[1,3–6]

Vanadium(V) (d^0 electronic configuration) normally forms octahedral complexes.[8] The solution equilibria of the vanadium(V) complex with EDTA have been studied; the one-to-one complex has a log K_{stab} value of 15.55.[9] The present investigation has been undertaken to study the solution structures of the chelates of vanadium(V) with EDTA, ethylenediamine-*N*,*N′*-diacetic acid (EDDA), and *N*,*N′*-dimethylethylenediamine-*N*,*N′*-diacetic acid (DMEDDA) by means of proton nmr and infrared spectroscopy.

Experimental Section

The nmr spectra were recorded with a Varian HA-100 high-resolution spectrometer equipped with a variable temperature probe and operating at 100 MHz; the ambient probe temperature was 32°. Varian precision-bore nmr tubes were used for all measurements. Two small drops of reagent-grade *tert*-butyl alcohol were added to each sample to serve as the lock signal and internal reference. Deuterium oxide was used as the solvent. The concentration of complex in each sample was ~ 0.7 *F*. All chemical shift values are referenced to TMS. Peaks were integrated by use of a compensating polar planimeter. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer, with the samples dispersed in KBr disks.

Measurements of pH were made with a Leeds and Northrup Model 7664 line-operated pH meter equipped with micro electrodes, which were standardized against Leeds and Northrup buffer solutions; data were obtained at 25°.

Disodium ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate dihydrate and vanadium pentoxide (assay 100.0%) were obtained from J. T. Baker Co., and ethylenediamine-*N*,*N′*-diacetic acid (assay 98+%) was obtained from Aldrich Chemical Co.; these materials were used without further purification. Deuterium oxide (isotopic purity 99.8%) and reagent grade *tert*-butyl alcohol were supplied by Mallinckrodt Chemical Works.

Ammonium metavandate was prepared and purified by the method of Baker, *et al.*;[10] its infrared spectrum coincided exactly with that reported by Miller and Wilkins.[11] Barium *N*,*N′*-dimethylethylenediamine-*N*,*N′*-diacetate was prepared by the method of Legg and Cooke;[5] no nmr-detectable impurities were

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[1] R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

[2] L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, **6**, 2146 (1967).

[3] Y. O. Aochi and D. T. Sawyer, *ibid.*, **5**, 2085 (1966).

[4] J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *ibid.*, **10**, 90 (1971).

[5] J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).

[6] J. I. Legg and D. W. Cooke, *ibid.*, **5**, 594 (1966).

[7] P. F. Coleman, J. I. Legg, and J. Steele, *ibid.*, **9**, 937 (1970).

[8] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley, New York, N. Y., 1962, pp 808–818.

[9] L. Przyborowski, G. Schwarzenbach, and Th. Zimmerman, *Helv. Chim. Acta*, **48**, 1556 (1965).

[10] R. H. Baker, H. Zimmerman, and R. N. Maxson, *Inorg. Syn.*, **3**, 117 (1950).

[11] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

TABLE I

NMR COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR THE VANADIUM(V) COMPLEXES[a]

A. Spin–Spin Splitting Patterns for the Methylenic Protons of the Acetate Groups

Complex	$J_{A,B}$	δ_A	δ_B	$\delta_A - \delta_B$	$\bar{\delta}_{A,B}$	$\bar{\delta}_X$
$[VO_2EDTA]^{3-}$	17.2	4.12	3.58	0.54	3.85	3.89
$[VO_2DMEDDA]^-$	17.0	3.80	3.32	0.48	3.56	
α-*cis*-$[VO_2EDDA]^-$	17.9	4.12	3.24	0.88	3.68	
β-*cis*-$[VO_2EDDA]^-$	17.0	3.93	3.38	0.55	3.65	
	16.3	3.85	3.39	0.46	3.62	

B. C_2D_2 Spin–Spin Splitting Patterns for Ethylenic Protons (Computer Analysis)

Complex	δ_C	δ_D	$\delta_C - \delta_D$	$\bar{\delta}_{C,D}$	$J_{CC'}$	J_{CD}	J_{CD}	$J_{DD'}$
$[VO_2EDTA]^{3-}$	3.185	2.835	0.349	3.01	10.3	−14.6	3.7	5.2
α-*cis*-$[VO_2EDDA]^-$	3.043	2.717	0.326	2.88	13.4	−13.1	4.1	2.2

[a] δ in ppm from TMS; *J* in Hz.

found. All other chemicals were reagent grade and were used without further purification.

All the compounds isolated as solids were analyzed for carbon and hydrogen by Elek Microanalytical Laboratories, Los Angeles, Calif. Vanadium was determined by a procedure based on the method of Kolthoff and Elving.[12] The sample was combusted in a platinum crucible over a Meeker burner. The fine ash was dissolved in 10% H_2SO_4 and transferred quantitatively to the titration vessel. The vanadium(V) was reduced to blue VO^{2+} ion by excess $Fe(NH_4)_2(SO_4)_2$. After adding 3–4 ml of H_3PO_4, the excess Fe^{2+} and the VO^{2+} were titrated potentiometrically with a standard ceric solution at 70–75°.

Preparation of Trisodium Dioxo(ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetato)vanadium(V).—To a rapidly stirred suspension of 11.17 g (30 mmol) of $Na_2H_2EDTA \cdot 2H_2O$ in 30 ml of water was added 3.51 g (30 mmol) of NH_4VO_3. A nearly clear yellow solution resulted after 1 hr; concentrated HCl or a strong NaOH solution was added dropwise as needed to maintain the solution acidity between pH 6 and 7. The solution was filtered through a fine-pore sintered glass filter and then passed through a 40-mequiv column of Dowex 50W-X8 (50–100 mesh) cation-exchange resin in the sodium form at a rate of 2 ml/min to exchange Na^+ for NH_4^+. The yellow fraction was then evaporated to a hydrous mass under a stream of dry air. Water was added to bring the volume to 40 ml; the solution was stirred for 1 hr and filtered, and 95% ethanol added until a permanent turbidity was obtained that did not disappear with vigorous stirring. The vessel was sealed and allowed to stand for five days, during which time the complex crystallized as shiny yellow plates, leaving a nearly colorless supernate. The crystals were collected on a filter, washed once with ice-cold water and then with 95% ethanol, and air-dried. The product was recrystallized three times from water with ethanol to give an overall yield of 6.8 g (43%). Analysis indicated that the complex was isolated as $Na_3[VO_2EDTA] \cdot 4H_2O$. *Anal.* Calcd for $Na_3VC_{10}H_{20}N_2O_{14}$: C, 23.44; H, 3.91; V, 9.96. Found: C, 23.67; H, 4.13; V, 9.82.

Preparation of Potassium Dioxo(*N*,*N′*-dimethylethylenediamine-*N*,*N′*-diacetato)vanadium(V).—Ba(DMEDDA) (3.39 g, 10 mmol) was placed in 20 ml of water which had been previously boiled and allowed to cool while sealed. Concentrated HCl was added dropwise as necessary to dissolve the solid and maintain the solution acidity between pH 6 and 7. To the clear solution 1.17 g (10 mmol) of NH_4VO_3 was added gradually; the pH was kept between pH 6 and 7 by addition of 12 *F* HCl. The yellow solution was stirred overnight, then filtered through a fine-pore sintered glass filter. To exchange K^+ for Ba^{2+} and NH_4^+, the solution was passed slowly through a column of Dowex 50W-X8 cation-exchange resin in the K^+ form, which had been rinsed with 1.5 l. of preboiled water. The yellow fraction was evaporated to dryness under a stream of dry air. The resulting solids were dissolved in 15 ml of preboiled water, yielding a green solution. Slow addition of 95% ethanol caused precipitation of KCl, which was filtered off. More ethanol was added to the filtrate until a permanent turbidity was obtained. The vessel was sealed and allowed to stand for three days, during which time shiny yellow crystals appeared, leaving a blue supernate. The crystals were collected on a filter, washed with 95% ethanol, and air-dried. The product was recrystallized twice from water with ethanol to give an overall yield of 1.41 g (41%). Analysis indicated that the complex was isolated as $K[VO_2DMEDDA] \cdot H_2O$. *Anal.* Calcd for $KVC_8H_{16}N_2O_7$: C, 28.07; H, 4.68; V, 14.91. Found: C, 27.92; H, 4.87; V, 14.65.

Preparation of Potassium Dioxo(ethylenediamine-*N*,*N′*-diacetato)vanadium(V).—To a rapidly stirred suspension of 2.34 g (20 mmol) of NH_4VO_3 in 50 ml of water was added gradually 3.52 g (20 mmol) of H_2EDDA, such that the solution acidity stayed above pH 6.0. Three drops of fresh 10% H_2O_2 was added to inhibit reduction of vanadium(V). The nearly clear yellow-green solution was filtered through a fine-pore sintered glass filter and then passed through the column of Dowex 50W-X8 cation-exchange resin in the potassium form. The yellow and green fractions were collected together, and the pH was adjusted, if necessary, to pH 6.5. The solution was then dried overnight under a stream of dry air to a hydrous green mass. This was stirred with 20 ml of water to give a dark green solution, to which 95% ethanol was added until the first permanent turbidity was obtained. The vessel was covered and allowed to stand overnight. The solid that was obtained, composed of orange and green shiny flakes, was a mixture of V(V) and V(IV) decomposition products and was collected on a filter and discarded. The filtrate was made turbid once again with 95% ethanol, covered, and allowed to stand overnight. Filtration yielded a yellow solid with green surface impurities and a dark blue filtrate, which was discarded. Generous washing with 95% ethanol removed all of the green impurities from the solid. This initial yield was dissolved in 20 ml of water and precipitated with 95% ethanol. After filtering, the green filtrate was made turbid again with ethanol to give a further yield of the yellow product. The two yields were combined and recrystallized twice from 10 ml of water with 95% ethanol. This complex crystallized as a dull yellow powder to give an overall yield of 2.34 g (50%). Analysis indicated that the complex was isolated as $K[VO_2EDDA] \cdot H_2O$. *Anal.* Calcd for $KVC_6H_{12}N_2O_7$: C, 22.93; H, 3.82; V, 16.24. Found: C, 23.15; H, 3.74; V, 16.61.

Line spectra for the C_2D_2 patterns and the spectral parameters in Table I were calculated using the LAOCOON III computer program[13] on an IBM 360/50 computer; spectra were plotted by a Calcomp plotter.

Results

The three vanadium(V) complexes are stable from pH 4 to pH 9, as indicated by the lack of change in their nmr spectra. Above pH 9, the solutions become colorless as V(V) polymerizes to give uncomplexed ligand. Below pH 4, the compounds readily decompose to give a paramagnetic blue VO^{2+} species.

The nmr spectrum of the $[VO_2EDTA]^{3-}$ chelate (Figure 1) exhibits two AB splitting patterns, one of which is very nearly collapsed, and a C_2D_2 pattern. The AB patterns, with average chemical shifts of 3.85 and 3.89 ppm, are assigned to the protons on the acetate groups of the ligand. The C_2D_2 pattern, centered at 3.01 ppm, arises from the protons on the ethylenic backbone of the ligand. Although ^{51}V has a nuclear moment of $^7/_2$, no coupling was observed between the metal and the ligand protons in any of the complexes

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[12] I. M. Kolthoff and P. J. Elving, Ed., *Treatise Anal. Chem.*, **8**, 223 (1963).

[13] D. F. De Tar, "Computer Programs for Chemistry," Vol. I, W. A. Benjamin, New York, N. Y., 1968, pp 10–53.

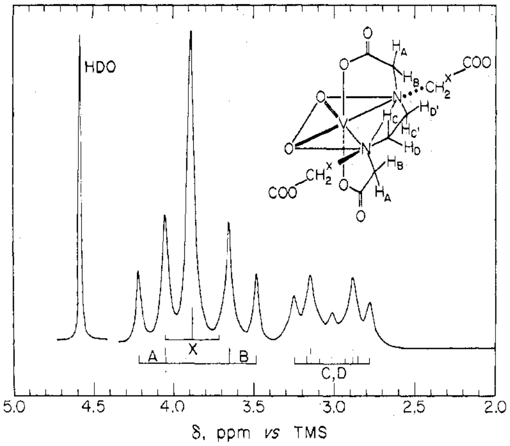

Figure 1.—Nmr spectrum (100 MHz) and proposed structure for the $[VO_2EDTA]^{3-}$ complex anion.

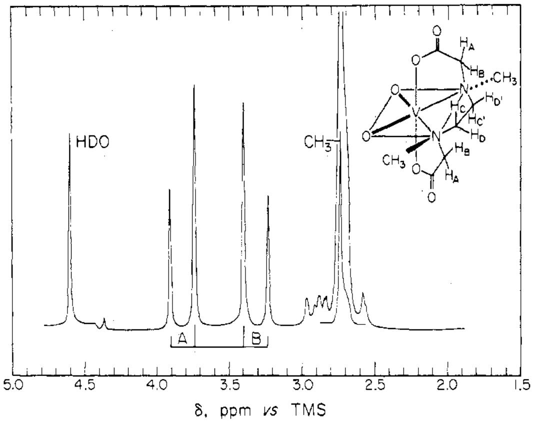

Figure 2.—Nmr spectrum (100 MHz) and proposed structure for the $[VO_2DMEDDA]^-$ complex anion.

studied. The coupling constants and chemical shifts for the three complexes are summarized in Table I.

The spectrum of $[VO_2DMEDDA]^-$, shown in Figure 2, consists of only one AB pattern, centered at 3.56 ppm, and what may be a C_2D_2 pattern, centered at 2.75 ppm, that is obscured by the large CH_3 singlet. The AB pattern is assigned to the acetate group protons, and the higher field resonances are assigned to the ethylenic backbone and methyl groups.

The nmr spectrum of $[VO_2EDDA]$ is illustrated by Figure 3. The acetate group resonances consist of three AB patterns; one pattern is noticeably more intense than the other two, which have equal intensities. Peaks have been assigned to particular AB patterns by use of standard spin-tickling techniques.[4] The overlapping peaks also have been resolved by recording the spectrum at 220 MHz. The C_2D_2 pattern, centered at 2.88 ppm, has about the same intensity as the large AB pattern. In the region from 3.2 to 3.5 ppm, after subtracting the contributions from the AB patterns, the remaining intensity is nearly equal to the summed intensities of the two small AB patterns. This hidden pattern, the fine structure of which is unknown, is assigned to the ethylenic backbone protons of the species associated with the two small acetate AB patterns. The symmetrical C_2D_2 pattern is assigned to the backbone protons of the species having the large AB pattern for its acetate resonance. The amine protons in the EDDA complex are not observed in the nmr spectrum, presumably because of solvent exchange.

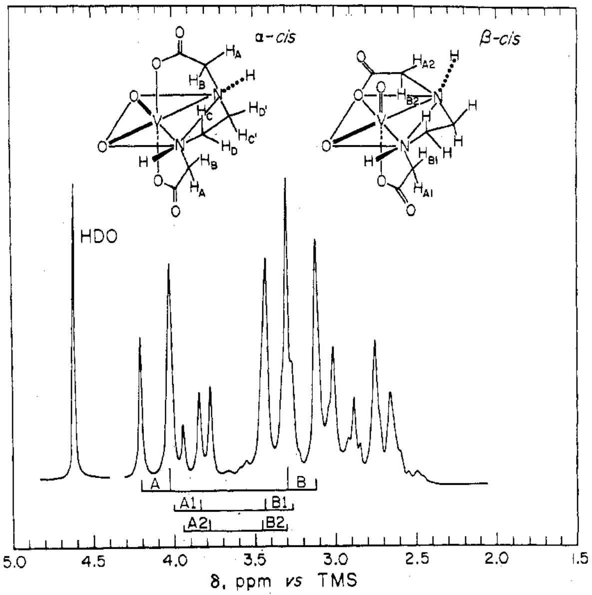

Figure 3.—Nmr spectrum (100 MHz) and proposed structures for the isomers of $[VO_2EDDA]^-$.

Infrared spectra of the isolated vanadium(V) complexes have been recorded to ascertain the positions of the oxygens in the VO_2 moiety. All three complexes exhibit three strong bands in the region 950–850 cm^{-1}. One band is assigned to the COO^- groups on the ligands;[14,15] the respective frequencies for the EDTA, DMEDDA, and EDDA complexes are 925, 910, and 890 cm^{-1}. The remaining two bands result from the vanadium–oxygen bonds of the VO_2 group; the respective frequencies for the EDTA, DMEDDA, and EDDA complexes are 935, 895; 935, 900; and 905, 865 cm^{-1}.

The EDDA complex is by far the least stable of those investigated with respect to reduction of V(V) to V(IV). Aqueous solutions of the EDTA and DMEDDA complexes of V(V) retain their initial yellow color for about two months before taking on a green tint. The EDDA analog, however, becomes slightly green almost immediately upon dissolving; after standing for 1 or 2 days, reduction to V(IV) is so extensive that the solution must be discarded.

Discussion and Conclusions

The infrared data indicate that the oxygen atoms of the VO_2 moiety in the complexes are cis with respect to one another. The appearance of two metal–oxygen stretch bands in the infrared corresponds to C_2 symmetry, the two bands being the symmetric and asymmetric stretch modes. If the VO_2 oxygens were trans, only one band would appear in the infrared.[16,17] Infrared and Raman evidence for cis oxygens in the VO_2 units of $[VO_2F_4]^{3-}$ and $[VO_2(C_2O_4)_2]^{3-}$ has been found previously by Griffith and Wickins.[16]

$[VO_2EDTA]^{3-}$.—Vanadium(V), with two of its coordination sites occupied by oxygen atoms, probably has an octahedral configuration with four available coordination sites. Hence, the donor groups of a hexa-

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(14) D. T. Sawyer and P. J. Paulsen, *J. Amer. Chem. Soc.*, **81**, 816 (1959).

(15) D. T. Sawyer, *Ann. N. Y. Acad. Sci.*, **88**, 307 (1960).

(16) W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 400 (1968).

(17) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).

dentate ligand, such as EDTA, will compete for these bonding sites. The nmr results support this conclusion. In the spectrum of $[VO_2EDTA]^{3-}$, the wide AB pattern arises from two acetate groups that are bonded to the metal; the lifetime of the bond is long compared to the nmr time scale, which causes the two methylene protons on each bonded acetate group to be nonequivalent. The coupling constant of 17.2 Hz indicates that the acetates bond out of the N–V–N plane; if they bonded in the N–V–N plane, a coupling constant of 15–16 Hz would be expected.[3,4]

Thus, the four available coordination sites of the VO_2^+ ion are occupied by two nitrogen and two acetate oxygen atoms of EDTA; the two other acetate groups are not bonded to the metal and are free to rotate about the C–N bond. Because the bonded nitrogen is asymmetric, the methylene protons on a nonbonded acetate group are nonequivalent.[1] Hence, an AB splitting pattern is expected for the nonbonded as well as for the bonded acetate groups. For the present case, the AB pattern for the nonbonded acetates is nearly collapsed, which indicates a very small chemical shift difference between the protons.

The C_2D_2 pattern, which is exhibited by the ethylenic backbone portion of the ligand, indicates that the V–N–C–C–N ring is locked in one conformation, at least on the nmr time scale. If the ring inverted rapidly, the fine structure would degenerate into a singlet because the environments of the CH_2CH_2 protons would become averaged. Chemical shifts and coupling constants for the backbone patterns are given in Table I.

The structure proposed for the $[VO_2EDTA]^{3-}$ complex is illustrated in Figure 1; the molecule has a C_2 axis of symmetry passing through the vanadium atom and the center of the backbone. To conform with the terminology suggested by Legg, *et al.*,[18] the structure is denoted as the α-cis isomer; cis refers to the oxygens in the VO_2 unit and α indicates that the bonded acetate oxygens are trans to one another.

From consideration of the magnetic anisotropies of C-N bonds, the AB patterns that result from the bonded acetate group protons can be completely assigned.[4,5] One proton lies over the center of the C–N bond, and thus is shielded, while the other proton is along the axis of, and away from, the C–N bond and is deshielded. For each H_A–H_B pair shown in the illustrations, H_A is the proton which resonates at lower field (higher δ). No attempt has been made to assign the protons of the unbonded acetates in the EDTA complex.

Further evidence for the proposed structure is provided by its ^{13}C nmr spectrum. Five peaks of equal intensity are observed; four are assigned to the C atoms of the bonded and unbonded acetate groups, and one is assigned to the C atoms of the ethylenic backbone.

$[VO_2DMEDDA]^-$.—The nmr spectrum of this complex also is consistent with the α-cis structure. The single AB pattern for the two acetate groups, with a J_{AB} value of 17.0 Hz, indicates a twofold axis of symmetry with the acetate oxygens bonded out of the N–V–N plane. That the ethylenic backbone is held in a rigid conformation is indicated by the partially visible C_2D_2 pattern. The proposed structure for the $[VO_2DMEDDA]^-$ complex anion is illustrated in Figure 2.

$[VO_2EDDA]^-$.—The nmr spectrum of the EDDA chelate has characteristics indicative of a mixture of isomers (see Figure 3). Of the three AB patterns, one is much more intense than the other two, which exhibit equal intensities. Furthermore, the C_2D_2 pattern, centered at 2.88 ppm, has nearly the same intensity as the large AB pattern. Therefore, the large AB pattern and the C_2D_2 pattern are assigned to one isomer. The coupling constant of 17.9 Hz indicates that the acetates are bonded out of the N–V–N plane. The structure appears to be similar to the EDTA and DMEDDA complexes with an α-cis configuration.

The small AB patterns have J_{AB} values of 17.0 and 16.3 Hz, and their intensities are equal. This implies that they are due to the acetate groups of a second complex. Because each acetate group of this isomer exhibits a different pattern, the isomer apparently lacks an axis of symmetry. Furthermore, one acetate group is bonded out of the N–V–N plane (J_{AB}, 17.0 Hz), while the other probably is bonded in that plane (J_{AB}, 16.3 Hz). The structure that is consistent with these conditions is the β-cis isomer, in which both the VO_2 oxygens and the bonded acetate oxygens are cis. For such a structure, without an axis of symmetry passing through the center of the ethylenic backbone, a CDEF pattern should result from the protons of the backbone. The resonances associated with these protons are assigned mainly to the hidden intensity between 3.2 and 3.5 ppm; the fine structure of the pattern is unknown and no attempt has been made to determine the chemical shifts and coupling constants for it. The structures proposed for the $[VO_2EDDA]^-$ chelates are illustrated in Figure 3.

Isomerization of metal–EDDA complexes between the α-cis and β-cis conformations has been observed by Legg, *et al.*,[5,7,18] for the $[Co^{III}(L)EDDA]$ system, where L represents ethylenediamine, oxalate, malonate, and carbonate. The bidentate ligands, L, can complex only in the cis configuration and are analogous to the cis VO_2 oxygens in the present study. Legg only observed the α-cis isomer when using DMEDDA or DEEDDA (*N,N'*-diethyl-EDDA), instead of EDDA, as the tetradentate ligand.

Thermodynamics of the $[VO_2EDDA]^-$ System.—The nmr spectrum of the $[VO_2EDDA]^-$ complex at ambient probe temperature indicates nearly equal concentrations of the α-cis and β-cis isomers. This has led to a temperature study, which confirms that the α-cis and β-cis isomers are in dynamic equilibrium. The equilibrium is fully established in the time required to thermally equilibrate the probe, tune the instrument, and obtain the spectrum (approximately 15 min). At each temperature studied, the relative amount of each isomer has been obtained by integrating the downfield halves of the three AB patterns. Figure 4 summarizes the change in relative concentrations as a function of temperature for the equilibrium

$$\beta\text{-cis} \rightleftharpoons \alpha\text{-cis}, K \qquad (1)$$

Analysis of the slope ($-\Delta H°/R$) and the intercept ($\Delta S°/R$) of this graph yields the thermodynamic parameters for the isomerization equilibrium: $\Delta H°$, 2.2 kcal/mol; $\Delta S°$, 7.8 cal/(mol deg); and $\Delta G°_{298}$, -0.090 kcal/mol.

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(18) P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).

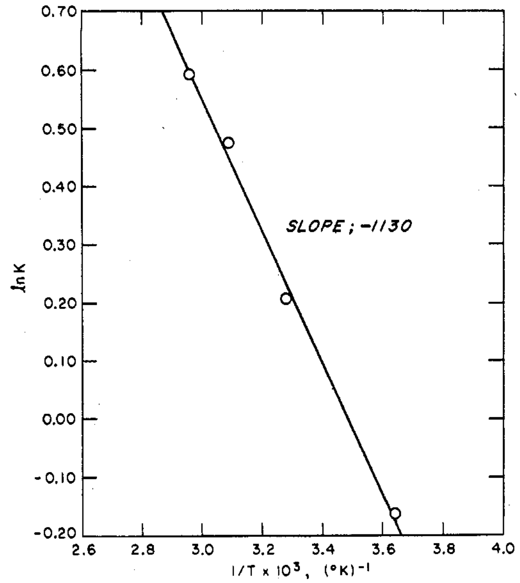

Figure 4.—Plot of ln K *vs.* $1/T$, where $K = [\alpha\text{-cis}]/[\beta\text{-cis}]$, for the $[VO_2EDDA]^-$ system. Intercept for $1/T = 0$ is 3.94.

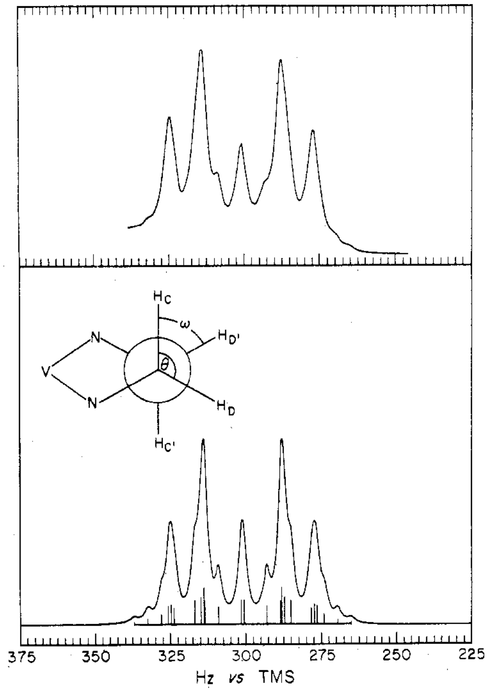

Figure 5.—Observed (top) and calculated C_2D_2 splitting patterns for $[VO_2EDTA]^{3-}$ at 100 MHz. Newman projection of backbone structure, looking along the C–C bond.

The small free energy difference between the isomers of the EDDA chelate indicates the effect of substitution at the nitrogens in the ligand. A negligible amount of β-cis isomer is formed upon replacing the amine hydrogens in EDDA with methyl groups (*i.e.*, by going to the DMEDDA complex). The absence of the β-cis isomer in the nmr spectrum of the DMEDDA complex (less than 3%) indicates that the free energy difference between α-*cis*- and β-*cis*-$[VO_2DMEDDA]^-$ is at least 2.1 kcal/mol compared to the 0.09 kcal/mol found for the unsubstituted EDDA complex.

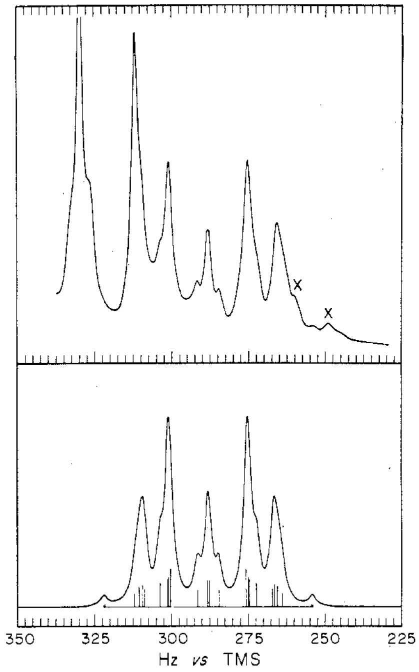

Figure 6.—Observed (top) and calculated C_2D_2 splitting patterns for α-*cis*-$[VO_2EDDA]^-$ at 100 MHz. Only the upfield half (≤288 Hz from TMS) was used for the calculation. The peak and shoulder marked X result from the backbone protons of the β-cis isomer.

An interesting result is the positive $\Delta S°$ value for the equilibrium reaction (eq 1), which indicates that the symmetric α-cis isomer has a greater absolute entropy than the unsymmetric β-cis form. One explanation is that the two isomers have different solvation spheres.

Ethylenic Backbone Structures.—By analyzing the chemical shifts and proton–proton coupling constants of the C_2D_2 splitting patterns, insight can be obtained into the structures of the rigid ethylenic backbones of the complexes (Figures 5 and 6). Of the complexes studied, only the symmetric α-*cis*-$[VO_2EDTA]^{3-}$ and α-*cis*-$[VO_2EDDA]^-$ chelates yield such patterns. For the symmetric DMEDDA complex, the C_2D_2 pattern is obscured by the large methyl singlet; the β-cis isomer of $[VO_2EDDA]^-$ yields a poorly resolved, unsymmetric CDEF pattern.

Only the upfield half of the C_2D_2 pattern of α-*cis*-$[VO_2EDDA]^-$ has been employed in the analysis; the downfield half is obscured by the acetate AB resonances (see Figure 6). The two peaks marked by an X in this figure are believed to be outlying peaks of the CDEF pattern for the β-cis isomer. The calculated pattern can be refined to match the observed pattern only if these two peaks are ignored. The chemical shifts and coupling constants are summarized in Table I; the observed and calculated C_2D_2 splitting patterns for the EDTA and EDDA complexes are illustrated by Figures 5 and 6, respectively.

The positions of the protons on rigid ethylenic backbones can be envisioned easily by drawing Newman projections looking along the carbon–carbon bond (see Figure 5). Because the C_2 symmetry axis passes through the center of the C–C bond, protons H_C and $H_{C'}$ are magnetically equivalent, as are protons H_D and $H_{D'}$. The H–C–C–H dihedral angle, φ, between two vicinal protons can be related to their coupling constant by Karplus equations of the forms[19,20]

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[19] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[20] W. A. Thomas, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **1**, 72 (1968).

$$J = A_1 \cos^2 \varphi, \quad 0° \leqslant \varphi \leqslant 90° \qquad (2)$$

$$J = A_2 \cos^2 \varphi, \quad 90° \leqslant \varphi \leqslant 180° \qquad (3)$$

where A_1 and A_2 are constants. Using the projected H–C–H geminal angle, θ, and the smaller vicinal angle, ω, the Karplus relations can be rewritten for the EDTA backbone pattern as

$$J_{\mathrm{CC'}}{}^{\mathrm{EDTA}} = A_2 \cos^2 (\theta_{\mathrm{T}} + \omega_{\mathrm{T}}) \qquad (4)$$

$$J_{\mathrm{CD'}}{}^{\mathrm{EDTA}} = A_1 \cos^2 \omega_{\mathrm{T}} \qquad (5)$$

$$J_{\mathrm{DD'}}{}^{\mathrm{EDTA}} = A_1 \cos^2 (\theta_{\mathrm{T}} - \omega_{\mathrm{T}}) \qquad (6)$$

Similarly, for the EDDA analog (α-cis isomer)

$$J_{\mathrm{CC'}}{}^{\mathrm{EDDA}} = A_2 \cos^2 (\theta_{\mathrm{D}} + \omega_{\mathrm{D}}) \qquad (7)$$

$$J_{\mathrm{CD'}}{}^{\mathrm{EDDA}} = A_1 \cos^2 \omega_{\mathrm{D}} \qquad (8)$$

$$J_{\mathrm{DD'}}{}^{\mathrm{EDDA}} = A_1 \cos^2 (\theta_{\mathrm{D}} - \omega_{\mathrm{D}}) \qquad (9)$$

These relations have been used to calculate the values of ω_{T}, θ_{T}, ω_{D}, and θ_{D}, where the subscripts T and D refer to the backbone structures of the EDTA and EDDA complexes, respectively. The resulting values are ω_{T}, 52; θ_{T}, 95; ω_{D}, 50; and θ_{D}, 113°.

The method of calculation is a simple iterative process. A reasonable value of ω_{T} is assumed; from eq 5, a value of A_1 is calculated and used in eq 6 to find $(\theta_{\mathrm{T}} - \omega_{\mathrm{T}})$. From ω_{T} and $(\theta_{\mathrm{T}} - \omega_{\mathrm{T}})$, the value of $(\theta_{\mathrm{T}} + \omega_{\mathrm{T}})$ is found and used in eq 4 to calculate A_2. The process is repeated for several values of ω_{T} between 40 and 70°. Any ω_{T} which results in $(\theta_{\mathrm{T}} + \omega_{\mathrm{T}}) > 180°$ is discarded. Also rejected are ω_{T} values which yield $A_2 < J_{\mathrm{CC'}}{}^{\mathrm{EDDA}}$ (if $A_2 < J_{\mathrm{CC'}}{}^{\mathrm{EDDA}}$, then eq 7 yields $\cos^2 (\theta_{\mathrm{D}} + \omega_{\mathrm{D}}) > 1$, which is meaningless). As a result of these two restrictions, $\omega_{\mathrm{T}} < 55°$.

The A_2 values are used in eq 7 to calculate $(\theta_{\mathrm{D}} + \omega_{\mathrm{D}})$, and the A_1 values are used in eq 8 to calculate ω_{D}. Knowing $(\theta_{\mathrm{D}} + \omega_{\mathrm{D}})$ and ω_{D}, then θ_{D} and $(\theta_{\mathrm{D}} - \omega_{\mathrm{D}})$ are obtained by subtraction. As a final check, $(\theta_{\mathrm{D}} - \omega_{\mathrm{D}})$ is calculated by putting the A_1 value into eq 9. The discrepancy between the $(\theta_{\mathrm{D}} - \omega_{\mathrm{D}})$ values obtained by subtraction and those from eq 9 is an indication of the correctness of the initial ω_{T} value.

Comparison of the two structures indicates that the protons on the $[\mathrm{VO_2EDTA}]^{3-}$ backbone are more compressed than those in the EDDA complex. The compression is attributed to crowding of the ethylenic backbone by the unbonded acetate groups of EDTA. Replacement of these acetates with hydrogen atoms yields the EDDA complex; the crowding is minimized and the backbone protons are able to spread further apart. However, the $[\mathrm{VO_2EDDA}]^-$ backbone does not attain the "perfect" nonstrained configuration with $\theta = 120°$ and $\omega = 60°$. The proton–proton angles are still slightly compressed, probably due to some strain in the five-membered V–N–C–C–N ring.

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Niobium(IV) and Tantalum(V) Pseudohalide Complexes with Nitrogen Donor Ligands

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Complexes of the type $\mathrm{NbX_4L_2}$ and $\mathrm{TaX_5}$(2,2′-bipyridine) (X = $\mathrm{NCS^-}$ or $\mathrm{NCSe^-}$, L = 2,2′-bipyridine or 4,4′-dimethyl-2-2′-bipyridine) have been prepared by the reaction of the hexaisothiocyanate or hexaisoselenocyanate complexes with the organic ligand under anhydrous conditions. $\mathrm{Nb(NCS)_4(C_{10}H_8N_2)_2}$ and $\mathrm{Nb(NCSe)_4(C_{10}H_8N_2)_2}$ were also prepared by the reduction of the hexaisothiocyanate and hexaisoselenocyanate complexes of Nb(V). The niobium complexes appear to be eight-coordinate. The pyridine complexes, $\mathrm{Nb(NCS)_4(py)_2}$ and $\mathrm{Ta(NCS)_5(py)}$, were prepared in an analogous manner. The mode of bonding in the thiocyanate and selenocyanate moiety has been investigated using infrared spectra. In all cases these ambidentate ligands are N-bonded and corresponding shifts in the C–N, C–S or C–Se, M–N stretching and N–C–S or N–C–Se bending regions are observed. The ultraviolet–visible spectra and magnetic susceptibility data are also discussed.

Introduction

The product obtained from the reaction of niobium(IV) or tantalum(V) halides with various nitrogen donor ligands is critically dependent upon the reaction conditions, *e.g.*, whether the reaction is carried out under an inert atmosphere or under high vacuum, the temperature, and the solvent employed.[1] Depending on the conditions, both the 5+ and 4+ metal halides give rise to complexes with pyridine which are of the type $\mathrm{MX_4(C_5H_5N)_2}$ (M = Nb, Ta; X = Cl, Br, I).[1–5] 2,2′-Bipyridine reacts with the tetrahalides to yield the

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(1) C. Djordjevic and V. Katovic, *J. Chem. Soc. A*, 3382 (1970).

(2) R. E. McCarley, B. G. Hughes, J. C. Boatman, and B. A. Torp, *Advan. Chem. Ser.*, **No. 37**, 243 (1963).

(3) M. Allbutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, **6**, 299 (1964).

(4) R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **2**, 547 (1963).

(5) R. E. McCarley and B. A. Torp, *ibid.*, **2**, 540 (1963).