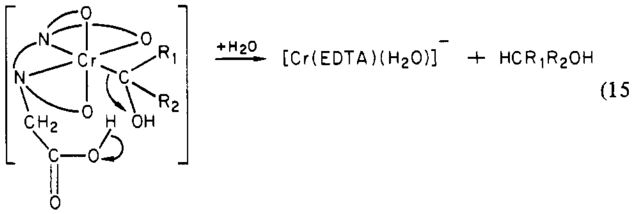
systems are very similar to each other. The large difference between the k_1 values of $[CrR(EDTA)]^{2-}$ and $[CrR(H_2O)_5]^{2+}$ may suggest that the k_c path predominates over the k_b path in the reaction of $[CrR(EDTA)]^{2-}$. The intimate mechanism of the k_c path would be expressed as eq 15. In this mechanism, the uncoordinated CH_2COOH group acts as an internal electrophile to the chromium-bound carbon atom and supplies the proton to the hydroxyalkyl ligand in the same complex.



(15)

Registry No. $[Cr(CH_2OH)(EDTA)]^{2-}$, 79391-91-6; $[Cr(CH(CH_3)OH)(EDTA)]^{2-}$, 79391-92-7; $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$, 79391-93-8.

Supplementary Material Available: Table II (kinetic data for $[Cr(CH_2OH)(EDTA)]^{2-}$), Table III (kinetic data for $[Cr(CH(CH_3)OH)(EDTA)]^{2-}$), Table IV (kinetic data for $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$), Figure 2 (plots of ln $|A_t - A_\infty|$ vs. t at different concentrations of $[[Cr(CH_2OH)(EDTA)]^{2-}]_0$), Figure 3 (relation between k_{obsd} and $[H^+]$ for the $[Cr(CH_2OH)(EDTA)]^{2-}$ system), Figure 4 (relation between k_{obsd} and $[H^+]$ for the $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$ system), and the Appendix (procedure for the determination of the Q, k_0, and k_1 values) (7 pages). Ordering information is given on any current masthead page.

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Ligand Substitution of (Ethylenediaminediacetato)vanadium(V) with Nitrilotriacetate Ions

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Kinetics studies of ligand substitution of ethylenediaminetetraacetate (EDTA) or ethylenediaminediacetate (EDDA) by nitrilotriacetate ions (NTA) in vanadium(V) complexes have been carried out by stopped-flow spectrophotometry in solution at pH 4–6, $\mu = 3$ ($NaClO_4$), and 25 °C. We took into account that the general mechanism of reaction could proceed, for each chelate, by three paths: direct, H^+-induced dissociation followed by formation of the NTA chelate, and direct attacks by NTA species. The results show that there is no reaction via the direct dissociative path, only via the H^+-induced dissociative path; there exist possibilities of direct attacks of VO_2EDTA^{3-} by $H(NTA)^{2-}$, of VO_2EDTA^{3-} by H_2NTA^-, of $VO_2H(EDTA)^{2-}$ by $H(NTA)^{2-}$, of VO_2EDDA^- by $H(NTA)^{2-}$, and of VO_2EDDA^- by H_2NTA^-. The direct attacks of the NTA species would be fast formations of outer-sphere complexes followed by aminocarboxylate ligand interchanges, which are the rate-determining steps. This mechanism differs from the generally proposed one in the fact that there is no inner water molecule bonded to the metal in the reactant chelates.

Many studies have reported on kinetic mechanisms of substitution of metal chelates with multidentate aminocarboxylate ligands in aqueous solutions.[1-11] In these papers, one multidentate ligand displaces another from a metal ion, usually Ni^{2+}, Cu^{2+}, Co^{2+}, or Zn^{2+}. The proposed mechanism of the exchange reactions shows the substitution proceeding through an intermediate in which the metal atom is bonded with both the leaving and the entering multidentate ligands. The complete displacement is then obtained by a "chain of reactions" with bond ruptures between the metal and the leaving ligand and bond formations between the metal and the entering ligand. The first attack of the entering multidentate ligand can occur either by displacement of water molecules bonded to the metal or by displacement of one of the very weak bonds of the leaving ligand. Thence we can distinguish between the chelates with a multidentate ligand, which has a number of chelating groups inferior to the number of the available coordination sites of the metal, and the chelates without such a ligand. In the first case the metal is simultaneously bonded to chelating groups and water molecules. In the second case some of the chelating groups of the multidentate ligand could be either very weakly bonded to the metal or not bonded and replaced by water molecules. Conformational and steric effects also lead to this hypothesis, which explains the formation of an inner mixed complex during the reactions of substitution of one multidentate ligand by another, which have been studied.

The present paper describes ligand-exchange reactions (eq 1 and 2) with vanadium(V) as the metal (previous results have shown the complexation of VO_2^+ as the central ion[15]), where

$$\sum_{i=0}^{2} VO_2H_iEDTA^{(3-i)-} + \sum_{j=0}^{4} H_jNTA^{(3-j)-} \rightarrow VO_2NTA^{2-} + \sum_{k=0}^{6} H_kEDTA^{(4-k)-} \quad (1)$$

$$VO_2EDDA^- + \sum_{i=0}^{4} H_iNTA^{(3-i)-} \rightarrow VO_2NTA^{2-} + \sum_{j=0}^{4} H_jEDDA^{(2-j)-} \quad (2)$$

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Table I. Pseudo-First-Order Rate Constants for the Ligand Substitution Reaction of the Vanadium(V)-Ethylenediamine-*N,N,N',N'*-tetraacetate Complex with Nitrilotriacetic Acid[a]

	$[NTA]_T$/mol dm^{-3}				
pH	0.30	0.20	0.10	0.08	0.05
4.00	0.219 ± 0.003	0.192 ± 0.002	0.155 ± 0.002	0.146 ± 0.003	0.126 ± 0.002
	0.216 ± 0.002	0.194 ± 0.004	0.156 ± 0.003	0.147 ± 0.003	0.130 ± 0.002
	(0.222)	(0.199)	(0.163)	(0.153)	(0.137)
4.25	0.190 ± 0.004	0.168 ± 0.002	0.133 ± 0.002	0.126 ± 0.002	0.112 ± 0.002
	0.186 ± 0.003	0.169 ± 0.003	0.135 ± 0.002	0.127 ± 0.003	0.111 ± 0.001
	(0.187)	(0.168)	(0.137)	(0.129)	(0.113)
4.50	0.165 ± 0.002	0.142 ± 0.003	0.124 ± 0.003	0.102 ± 0.002	0.0871 ± 0.002
	0.164 ± 0.002	0.144 ± 0.002	0.126 ± 0.002	0.107 ± 0.002	0.0881 ± 0.002
	(0.155)	(0.139)	(0.112)	(0.104)	(0.0903)
4.75	0.137 ± 0.002	0.120 ± 0.002	0.0923 ± 0.002	0.0869 ± 0.002	0.0717 ± 0.002
	0.140 ± 0.003	0.119 ± 0.002	0.0953 ± 0.001	0.0884 ± 0.001	0.0715 ± 0.002
	(0.130)	(0.116)	(0.0911)	(0.0840)	(0.0708)
5.00	0.109 ± 0.002	0.0956 ± 0.002	0.0712 ± 0.002	0.0671 ± 0.001	0.0546 ± 0.001
	0.105 ± 0.002	0.0983 ± 0.002	0.0707 ± 0.002	0.0673 ± 0.002	0.0542 ± 0.002
	(0.113)	(0.0995)	(0.0760)	(0.0690)	(0.0562)

[a] The given k_{obsd} values, in s^{-1}, are experimental ones; the values in parentheses (k_{calcd}) are calculated from the functions f_1, f_2, and f_3. All concentrations are given at the initial time after mixing. The reactions were followed at 275 nm: $[V(V)] = 2 \times 10^{-4}$ mol dm^{-3}; $[EDTA] = 2 \times 10^{-3}$ mol dm^{-3}; $[CH_3COOH] = 5 \times 10^{-2}$ mol dm^{-3}.

ethylenediamine-*N,N,N',N'*-tetraacetic acid, nitrilotriacetic acid, and ethylenediamine-*N,N'*-diacetic acid are abbreviated as H_4EDTA (hexadentate), H_3NTA (tetradentate), and H_2EDDA (tetradentate), respectively.

In EDTA or EDDA complexes, the four available coordination sites of the VO_2^+ ion are occupied by two nitrogen and two acetate oxygen atoms of the multidentate ligands. So, we see that in both these complexes no water molecule is bonded to the central metal and there is no metal–ligand bond that is very weak. Thus, we must propose a special mechanism to explain the multidentate ligand exchange for reactions with VO_2^+ as the central complexed group. We suggest the fast formation of an outer-sphere complex followed by a rate-determining step, which seems to be a ligand interchange.

Experimental Conditions

Reagents. Sodium perchlorate, sodium monovanadate, sodium acetate, acetic acid, perchloric acid, sodium hydroxide, H_2Na_2EDTA, and H_3NTA were obtained from Merck. The chemicals were analytical reagent grade and were used without any purification. H_2EDDA purchased from Fluka was recrystallized twice from distilled water. Its concentration was checked by pH titration. Vanadium(V) solutions were standardized by titration against a standard iron(II) sulfate solution.[14] NTA solutions were standardized complexometrically with an excess of zinc sulfate against a standard sodium hydroxide solution. EDTA solutions were standardized with zinc sulfate in ammonia buffered solution.

Measurements. All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 3 mol dm^{-3} with sodium perchlorate. All the solutions were buffered with 5×10^{-2} mol dm^{-3} CH_3COO^-/CH_3COOH and then adjusted to pH 4–6 by dropwise addition of carbonate-free sodium hydroxide or perchloric acid in a nitrogen atmosphere. A Tacussel Aries 20000 pH meter and a Tacussel "high alkalinity" glass electrode were used for pH measurements. Equilibrium spectrophotometric measurements were performed, with quartz cells, on a Jobin Yvon Duospac spectrophotometer.

For kinetic measurements a stopped-flow spectrophotometer, of the type Durrum 131, was used. It was equipped with a Datalab DL 905 transient recorder interfaced to an Olivetti P652 microcomputer. This system and the computer programs used for data treatment have been previously described.[16,17]

Results and Discussion

(1) Experimental Rate Law of the Ligand Exchange. To study reactions 1 and 2, we performed series of kinetic runs by stopped-flow spectrophotometry at various pHs and various concentrations of entering group and of reacting chelates.

In all kinetic studies, the solutions of aminocarboxylate complex at a given pH contained chelating agent in sufficient excess to ensure that only the 1:1 complexes were entirely formed,[15] i.e., VO_2EDTA^{3-}, $VO_2H(EDTA)^{2-}$, $VO_2H_2EDTA^-$, or VO_2EDDA^-. With a large excess of NTA, the equilibria (1) at pH <5.5 and (2) at pH <6.5 lie far to the right.[15] The substitution reactions of vanadium(V)–EDTA and –EDDA complexes with NTA are complete, and reverse reactions may be omitted in the kinetic study. Each observed reaction was found to be first order with respect to the reacting chelate over 95% of the reaction. The values of k_{obsd}, the pseudo-first-order rate constant, presented in Tables I and II are the average of at least three determinations. The values of k_{obsd} are independent of the concentrations of the buffer and of the excess free leaving ligand (EDTA or EDDA). But k_{obsd} increases with decreasing pH and increasing concentration of the entering group (NTA). At constant pH, k_{obsd} is a hyperbolic function of the total concentration of the entering group ($[NTA]_T$) and may be written as

$$k_{obsd} = \frac{A + B[NTA]_T}{1 + C[NTA]_T} \tag{3}$$

Experimental results allow us to calculate the parameters *A*, *B*, and *C* using a linear least-squares method as explained in a previous paper.[18] Table III gives the values of *A*, *B*, and *C* as a function of pH.

(2) Proposed Reaction Routes and Mechanism. Several paths might be proposed in reactions of replacement of one multidentate ligand by another:[1] on one hand, a displacement of a multidentate ligand by solvent, or its conjugate acid or base, followed by fast formation of the new chelate; on the other hand, direct ligand–ligand replacement.

For the systems studied here, previous works have been done: hydrolysis of the V(V)–EDTA and V(V)–EDDA complexes by OH^- [18] and by H^+ [20] and formation of the V(V)–NTA complex from the free ligand and VO_2^+ ion.[16] At pH <6 the rate of hydrolysis of the reacting complexes by OH^- is negligible compared with the H^+-induced hydrolysis rate. If the ligand substitution occurs via a dissociative path, which can

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Table II. Pseudo-First-Order Rate Constants for the Ligand Substitution Reaction of the Vanadium(V)-Ethylenediamine-*N,N'*-diacetate Complex with Nitrilotriacetic Acid[a]

	$[NTA]_T$/mol dm^{-3}			
pH	0.050	0.040	0.025	0.015
5.00	0.0765 ± 0.0046 0.0775 ± 0.0048 (0.0765)	0.0711 ± 0.0050 0.0703 ± 0.0046 (0.0716)	0.0586 ± 0.0052 0.0594 ± 0.0052 (0.0607)	0.0501 ± 0.0034 0.0489 ± 0.0027 (0.0492)
5.10	0.0707 ± 0.0050 0.0691 ± 0.0050 (0.0702)	0.0662 ± 0.0040 0.0651 ± 0.0048 (0.0651)	0.0550 ± 0.0032 0.0555 ± 0.0038 (0.0542)	0.0427 ± 0.0033 0.0421 ± 0.0019 (0.0430)
5.25	0.0607 ± 0.0054 0.0620 ± 0.0051 (0.0615)	0.0560 ± 0.0050 0.0558 ± 0.0048 (0.0564)	0.0460 ± 0.0057 0.0462 ± 0.0048 (0.0458)	0.0356 ± 0.0030 0.0343 ± 0.0035 (0.0354)
5.50	0.0481 ± 0.0050 0.0477 ± 0.0057 (0.0501)	0.0443 ± 0.0040 0.0447 ± 0.0058 (0.0453)	0.0332 ± 0.0039 0.0338 ± 0.0034 (0.0355)	0.0252 ± 0.0028 0.0252 ± 0.0024 (0.0263)
6.00	0.0388 ± 0.0037 0.0383 ± 0.0042 (0.0375)	0.0324 ± 0.0037 0.0331 ± 0.0040 (0.0331)	0.0243 ± 0.0029 0.0247 ± 0.0029 (0.0248)	0.0177 ± 0.0025 0.0200 ± 0.0030 (0.0174)

[a] The given k_{obsd} values, in s^{-1}, are experimental ones; the values in parentheses (k_{calcd}) are calculated from the functions g_1, g_2, and g_3. All concentrations are given at the initial time after mixing. The reactions were followed at 320 nm: $[V(V)] = 2 \times 10^{-4}$ mol dm^{-3}; $[EDDA] = 2.5 \times 10^{-3}$ mol dm^{-3}; $[CH_3COOH] = 5 \times 10^{-2}$ mol dm^{-3}.

Table III. Determination of $k_{obsd} = (A + B[NTA]_T)/(1 + C[NTA]_T)$

reacn	pH	A/s^{-1}	B/mol^{-1} dm^3 s^{-1}	C/mol^{-1} dm^3
V^VEDTA + NTA	4.00	0.0900	1.24	3.75
	4.25	0.0750	1.19	4.34
	4.50	0.0600	1.12	4.96
	4.75	0.0375	1.08	5.48
	5.00	0.0250	0.904	5.83
V^VEDDA + NTA	5.00	0.0166	3.89	35.3
	5.10	0.0132	3.41	31.8
	5.25	0.0093	2.63	26.0
	5.50	0.0052	1.86	20.6
	6.00	0.0017	1.40	17.5

be H^+ induced, the formation of the NTA chelate from decomplexed vanadium and free NTA is a fast step of the substitution under our experimental conditions. Calculations show that a reaction scheme taking into account only direct and H^+-induced dissociation of the V(V)–EDTA (or V(V)–EDDA) chelate followed by the fast formation of the V(V)–NTA complex cannot explain the experimental results; then we must also consider direct ligand–ligand replacements.

In many cases, direct ligand–ligand replacement proceeds through the formation of an intermediate, a mixed complex with both ligands simultaneously coordinated to the metal. The existence of this intermediate is generally shown by thermodynamic or kinetic measurements. Formation of a stable mixed complex[1,2] has been studied thermodynamically in some cases. Either an experimental curve indicative of two consecutive reactions[2,6] or a difference between the absorbance measured by extrapolation of the stopped-flow data to zero time and the calculated absorbance[2] indicates the formation of an intermediate.

We showed that no mixed complex of V(V)–EDTA–NTA or V(V)–EDDA–NTA was stable, as a final product. We verified this spectrophotometrically using two tandem cells. We prepared the following three solutions at pH 5: 1, 4×10^{-4} M V(V) + 8×10^{-2} M H_3NTA; 2, 5×10^{-3} M EDDA; 3, mixture of equal volumes of solutions 1 and 2. The tandem matched quartz cells were filled with the solutions 1, 2 and 3 as follows: reference cell, |1|2|; measurement cell, |3|3|. The difference spectrum was recorded between 220 and 400 nm, and the measured absorbance was always less than 0.002. Our other experimental conditions were similarly studied and gave the same result, indicating no stable mixed complex formation. These experiments were also performed with EDTA instead of EDDA and led to the same conclusion.

For the kinetic experiments, at constant pH, the k_{obsd} (=f(entering group)) functions are of the hyperbolic type and seem to be almost independent of the concentration of the entering group above a certain limit. This kinetic result is also observed for the complexation reaction of pervanadyl ion with EDTA or NTA[16,19] and for the decomplexation reaction of vanadium(V) aminocarboxylate by hydroxide ions or hydronium ions.[18,20] We can explain this observation by proposing that there is a fast preequilibrium step leading to the formation of an outer-sphere-type complex.[6,16,18–20] For each kinetic experiment, we calculated the absorbance corresponding to time zero by addition of the absorbances for each of the reactants. No significant difference between this calculated value and the experimental absorbance was observed for wavelengths varying from 220 to 400 nm. This result seems to show that the formation of an outer-sphere complex is more probable than that of an inner-sphere complex. The rearrangement of the outer-sphere complex gives the final product of the reaction. Since the formation of the outer-sphere complex is a very fast reaction (half-life of reaction 10^{-9}–10^{-10} s), the rate-determining step in the ligand-exchange reaction is probably a ligand interchange in the outer-sphere complex between chelating groups of the entering ligand and the chelating groups of the leaving ligand bonded to the metal. This step should be first order as the reaction occurs in an outer-sphere complex and does not involve direct attack of an external species.

Thus, in the following interpretation of our data we shall consider three parallel routes of reactions: direct dissociation of the chelates followed by fast formation of a V(V)–NTA complex, H^+-induced dissociation of the chelates followed by fast formation of a V(V)–NTA complex, and direct attacks of the chelates by NTA-dominant species. In order to simplify the rate law relating to these three parallel routes of reactions, we will take into account only the dominant species in solution between pH 4 and 6: VO_2EDTA^{3-}, $VO_2H(EDTA)^{2-}$, $VO_2H_2EDTA^-$, VO_2EDDA^-, VO_2NTA^{2-}, $H(EDTA)^{3-}$, H_2EDTA^{2-}, H_3EDTA^-, $H(EDDA)^-$, H_2EDDA, H_3EDDA^+, $H(NTA)^{2-}$, and H_2NTA^-.

A complete calculation with all the species would lead to the same conclusions as those given below.

(3) Calculation. (a) The V^V–EDTA/NTA Exchange. Three complexes of V–EDTA are known:[15]

$$\begin{gathered} VO_2EDTA^{3-} + H^+ \overset{K_0}{\rightleftharpoons} VO_2H(EDTA)^{2-} \\ VO_2H(EDTA)^{2-} + H^+ \overset{K_1}{\rightleftharpoons} VO_2H_2EDTA^- \end{gathered} \qquad (4)$$

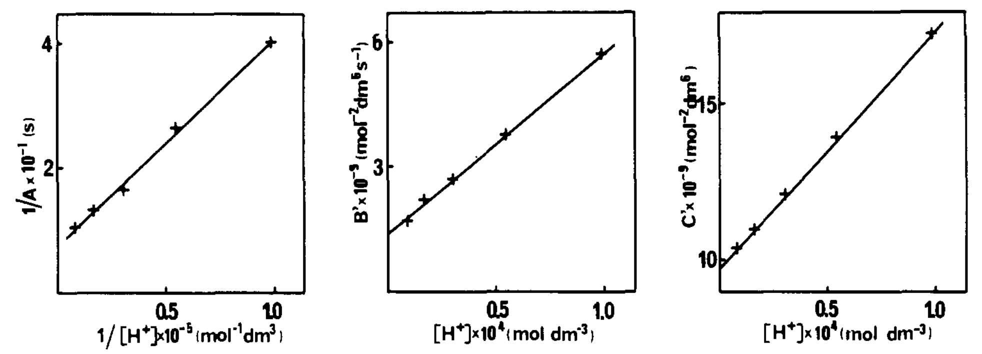

Figure 1. Determination of the kinetic parameters of ligand exchange of vanadium(V)-EDTA complexes with NTA ions.

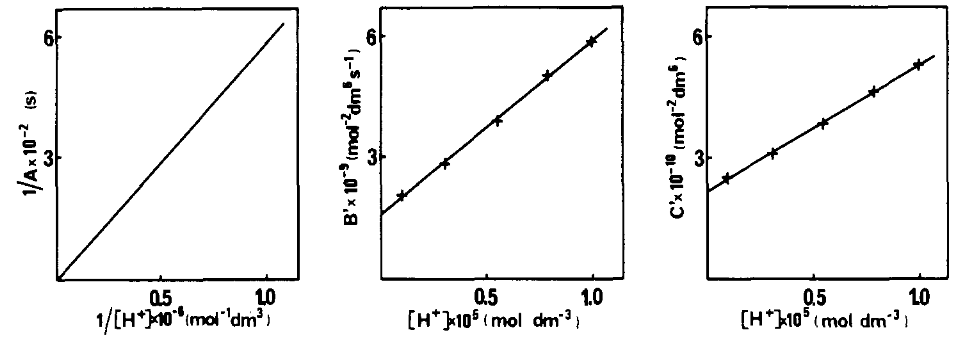

Figure 2. Determination of the kinetic parameters of ligand exchange of the vanadium(V)-EDDA complex with NTA ions.

with $K_0 = 1.26 \times 10^4$ mol^{-1} dm^3 and $K_1 = 1.99 \times 10^3$ mol^{-1} dm^3.

The possible parallel routes of reaction can be written, with $\sum_0^2 VO_2H_iEDTA^{(3-i)-}$ representing the three complexes of V(V)-EDTA instantaneously in equilibrium, as shown in Scheme I.

Scheme I

direct and H⁺-induced dissociative paths

$$\sum_0^2 VO_2H_iEDTA^{(3-i)-} \xrightarrow{k_{i\mathrm{D}}} V(OH)_4{}^+ + \sum_1^3 H_jEDTA^{(4-j)-}$$

$$\sum_0^2 VO_2H_iEDTA^{(3-i)-} + H^+ \overset{K_{i\mathrm{H}}}{\rightleftarrows} \sum_0^2 (VO_2H_iEDTA,H)^{(2-i)-} \xrightarrow{k_{i\mathrm{H}}} V(OH)_4{}^+ + \sum_1^3 H_jEDTA^{(4-j)-}$$

$$V(OH)_4{}^+ + \sum_1^2 H_jNTA^{(3-j)-} \xrightarrow{\text{fast}} \text{products}$$

direct attack of chelates by NTA-*dominant* species

$$\sum_0^2 VO_2H_iEDTA^{(3-i)-} + \sum_1^2 H_jNTA^{(3-j)-} \overset{K_{ij}}{\rightleftarrows} \sum_{i,j} (VO_2H_iEDTA,\ H_jNTA)^{(6-i-j)-} \xrightarrow{k_{ij}} VO_2NTA^{2-} + \sum_1^3 H_lEDTA^{(4-l)-}$$

The mechanism leads to eq 5, which fits the observed kinetic

$$v = \frac{f_1([H^+]) + f_2([H^+])[NTA]_T}{1 + f_3([H^+])[NTA]_T}[\text{chelate}]_T \qquad (5)$$

behavior, where $[\text{chelate}]_T$ represents the sum of the concentrations of all the V(V) chelates instantaneously in equilibrium (eq 6).

$$[\text{chelate}]_T = \sum_{i,j}([VO_2H_iEDTA^{(3-i)-}] + [(VO_2H_iEDTA,H)^{(2-i)-}] + [(VO_2H_iEDTA,H_jNTA)^{(6-i-j)-}]) \qquad (6)$$

The functions f_1, f_2, and f_3 can be expressed by eq 7–9. In

$$f_1([H^+]) = \{k_{0\mathrm{D}} + (k_{1\mathrm{D}}K_0 + k_{0\mathrm{H}}K_{0\mathrm{H}})[H^+] + (k_{2\mathrm{D}}K_0K_1 + k_{1\mathrm{H}}K_{1\mathrm{H}}K_0)[H^+]^2 + k_{2\mathrm{H}}K_{2\mathrm{H}}K_0K_1[H^+]^3\}/\{1 + (K_0 + K_{0\mathrm{H}})[H^+] + (K_0K_1 + K_0K_{1\mathrm{H}})[H^+]^2 + K_0K_1K_{2\mathrm{H}}[H^+]^3\} \qquad (7)$$

$$f_2([H^+]) = \{k_{01}K_{01}\beta_1 + (k_{11}K_{11}K_0\beta_1 + k_{02}K_{02}\beta_2) \times [H^+] + (k_{21}K_{21}K_0K_1\beta_1 + k_{12}K_{12}K_0\beta_2)[H^+]^2 + k_{22}K_{22}K_0K_1\beta_2[H^+]^3\}/\{(\beta_1 + \beta_2[H^+])(1 + (K_0 + K_{0\mathrm{H}}) \times [H^+] + (K_0K_1 + K_0K_{1\mathrm{H}})[H^+]^2 + K_0K_1K_{2\mathrm{H}}[H^+]^3)\} \qquad (8)$$

$$f_3([H^+]) = \{K_{01}\beta_1 + (K_{11}K_0\beta_1 + K_{02}\beta_2) \times [H^+] + (K_{21}K_0K_1\beta_1 + K_{12}K_0\beta_2)[H^+]^2 + K_{22}K_0K_1\beta_2[H^+]^3\}/\{(\beta_1 + \beta_2[H^+])(1 + (K_0 + K_{0\mathrm{H}})[H^+] + (K_0K_1 + K_0K_{1\mathrm{H}})[H^+]^2 + K_0K_1K_{2\mathrm{H}}[H^+]^3)\} \qquad (9)$$

these functions β_1 and β_2 are the global protonation constants of NTA.$^{3-}$ Their logarithmic values are 9.17 and 11.80, respectively.[15]

f_1 Function Treatment. The A values are the experimental values of the f_1 function. The plot of $1/A$ against $1/[H^+]$ is a straight line (Figure 1). This result suggests that $k_{0\mathrm{D}} = 0$ and that the $[H^+]^2$ and $[H^+]^3$ terms are negligible in the f_1 function. In the H⁺-induced hydrolysis of V(V)-EDTA chelate, $k_{2\mathrm{D}}$ has been found equal to zero. As there is no direct dissociative path for $VO_2H_2EDTA^-$ and VO_2EDTA^{3-} complexes, we should reasonably assume that there is also no direct dissociative path for the $VO_2H(EDTA)^{2-}$ complex ($k_{1\mathrm{D}} = 0$). The f_1 function may be written

$$f_1([H^+]) = \frac{k_{0\mathrm{H}}K_{0\mathrm{H}}[H^+]}{1 + (K_0 + K_{0\mathrm{H}})[H^+]} \qquad (10)$$

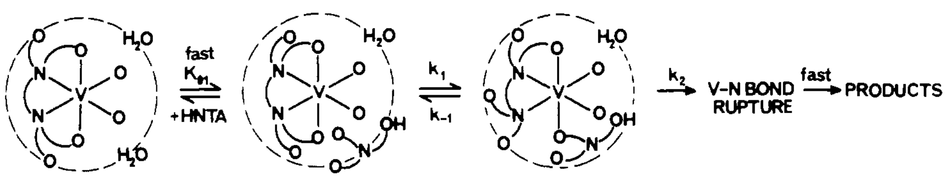

Figure 3. Ligand-exchange reaction between VO_2EDTA^{3-} and $H(NTA)^{2-}$. The calculation gives $k_{01} = k_1k_2/(k_2 + k_{-1})$.

Using a linear least-squares method, we calculate the intercept and the slope of the $1/A = f(1/H^+])$ function and we obtain $K_{0H} = 7.2 \times 10^3$ mol^{-1} dm^3 and $k_{0H} = 0.42$ s^{-1}, which are the parameters of the H^+-induced route of the VO_2EDTA^{3-} decomplexation.

f_2 Function Treatment. The B values are the experimental values of the f_2 function. Using the results obtained in the f_1 function treatment, we can define new experimental values B' for each studied pH (eq 11). This can be compared to the

$$B' = B(\beta_1 + \beta_2[H^+])(1 + (K_0 + K_{0H})[H^+]) \qquad (11)$$

numerator of the f_2 function, which is a polynomial of the third degree in $[H^+]$. B' vs. $[H^+]$ shown in Figure 1 is a straight line. The $[H^+]^2$ and $[H^+]^3$ terms can be neglected, and $B' = k_{01}K_{01}\beta_1 + (k_{11}K_{11}K_0\beta_1 + k_{02}K_{02}\beta_2)[H^+]$.

By linear regression analysis of B' vs. $[H^+]$ we can determine $k_{01}K_{01}\beta_1 = 12.6 \times 10^8$ mol^{-2} dm^6 s^{-1} and $k_{11}K_{11}K_0\beta_1 + k_{02}K_{02}\beta_2 = 4.44 \times 10^{13}$ mol^{-3} dm^9 s^{-1}.

f_3 Function Treatment. The C values are the experimental values of the f_3 function. We can define new experimental values C' for each studied pH (eq 12). C' is a linear function

$$C' = C(\beta_1 + \beta_2[H^+])(1 + (K_0 + K_{0H})[H^+]) \qquad (12)$$

of $[H^+]$ (Figure 1) with $K_{01}\beta_1 = 9.7 \times 10^9$ mol^{-2} dm^6 and $K_{11}K_0\beta_1 + K_{02}\beta_2 = 7.55 \times 10^{13}$ mol^{-3} dm^9.

From the results of f_2 and f_3, we calculate $K_{01} = 6.5$ mol^{-1} dm^3 and $k_{01} = 0.13$ s^{-1}, which are the kinetic parameters of the attack of VO_2EDTA^{3-} by $H(NTA)^{2-}$. Unfortunately we cannot exactly determine the parameters of the attack of $VO_2H(EDTA)^{2-}$ by $H(NTA)^{2-}$ (K_{11}, k_{11}) nor of the attack of VO_2EDTA^{3-} by H_2NTA^- (K_{02}, k_{02}). We obtain the sums

$$(1.9 \times 10^{13})K_{11} + (6.3 \times 10^{11})K_{02} = 7.55 \times 10^{13} \qquad (13)$$

$$(1.9 \times 10^{13})k_{11}K_{11} + (6.3 \times 10^{11})k_{02}K_{02} = 4.44 \times 10^{13} \qquad (14)$$

The ratio between the coefficients, $(1.9 \times 10^{13})/(6.3 \times 10^{11}) \approx 30$, shows that we cannot reasonably neglect these two reaction paths. Approximate values of k_{11} and k_{02} could be calculated if we suppose that both the interchange rate constants are of the same order of magnitude. This hypothesis is confirmed by the results obtained in the V^VEDDA/NTA exchange reaction studied next. Thus we can reasonably estimate 0.1 s^{-1} $< k_{11} \approx k_{02} < 0.6$ s^{-1}.

(b) The V^VEDDA/NTA Exchange. The H^+-induced hydrolysis of the VO_2EDDA^- species has been previously determined;[20] there is no direct dissociative path, only an H^+-induced dissociative path:

$$VO_2EDDA^- + H^+ \overset{K_H}{\rightleftarrows} (VO_2EDDA,H) \xrightarrow{k_H} V(OH)_4^+ + \sum_0^4 H_iEDDA^{(2-i)-} \qquad (15)$$

with $K_H = 3.9$ mol dm^{-3} and $k_H = 425$ s^{-1}.

Thus the parallel reaction routes for the ligand substitution V^VEDDA/NTA are as shown in Scheme II.

Scheme II

H^+-induced dissociative path followed by

$$V(OH)_4^+ + \sum_1^2 H_iNTA^{(3-i)-} \xrightarrow{\text{fast}} \text{products}$$

direct attack of chelate by NTA-*dominant* species

$$VO_2EDDA^- + \sum_1^2 H_iNTA^{(3-i)-} \overset{K_i}{\rightleftarrows} \sum_1^2 (VO_2EDDA,H_iNTA)^{(4-i)-} \xrightarrow{k_i} VO_2NTA^- + \sum_1^3 H_jEDDA^{(2-j)-}$$

Then we obtain eq 16, where $[\text{chelate}]_T$ represents the sum

$$v = \frac{g_1([H^+]) + g_2([H^+])[NTA]_T}{1 + g_3([H^+])[NTA]_T}[\text{chelate}]_T \qquad (16)$$

of the concentrations of all the V(V) chelates instantaneously in equilibrium (eq 17). The calculation gives eq 18–20. The

$$[\text{chelate}]_T = [VO_2EDDA^-] + [(VO_2EDDA,H)] + \sum_1^2 [(VO_2EDDA,H_iNTA)^{(4-i)-}] \qquad (17)$$

$$g_1 = \frac{k_HK_H[H^+]}{1 + K_H[H^+]} \qquad (18)$$

$$g_2 = \frac{k_1K_1\beta_1 + k_2K_2\beta_2[H^+]}{(\beta_1 + \beta_2[H^+])(1 + K_H[H^+])} \qquad (19)$$

$$g_3 = \frac{k_1\beta_1 + K_2\beta_2[H^+]}{(\beta_1 + \beta_2[H^+])(1 + K_H[H^+])} \qquad (20)$$

treatments of the functions g_2 and g_3 are analogous to those of f_2 and f_3. The graphs leading to the appropriate parameters for the functions g_2 and g_3 are given in Figure 2.

We have calculated the kinetic parameters $K_1 = 15$ mol^{-1} dm^3 and $k_1 = 0.072$ s^{-1} corresponding to the attack of VO_2EDDA^- by $H(NTA)^{2-}$ and $K_2 = 4.9 \times 10^3$ mol^{-1} dm^3 and $k_2 = 0.14$ s^{-1} corresponding to the attack of VO_2EDDA^- by H_2NTA^-.

(4) Conclusions. From the former calculations and from the rate constants and preequilibrium constants that we have already determined, we can recalculate the pseudo-first-order rate constants k_{obsd}, which have been experimentally measured. Tables I and II give these values (k_{calcd}) in parentheses. The calculated and the experimental values of k_{obsd} are in good agreement, showing the consistency of our hypotheses. We can summarize the results as follows: there is no reaction via the direct dissociative path, only via the H^+-induced dissociative path of VO_2EDTA^{3-} and VO_2EDDA^-; there exist possibilities of fast formation of outer-sphere complexes followed by aminocarboxylate ligand interchange between VO_2EDTA^{3-} and $H(NTA)^{2-}$, VO_2EDTA^{3-} and H_2NTA^-, and VO_2H-

$(EDTA)^{2-}$ and $H(NTA)^{2-}$ and also between VO_2EDDA^- and $H(NTA)^{2-}$ and between VO_2EDDA^- and H_2NTA^-.

There exist several paths of reaction via the formation of outer-sphere complexes between the reacting chelates and the entering aminocarboxylate ligands. These reactions are followed by ligand interchanges, which are the limiting steps of the reactions. For example, we propose, in Figure 3, a scheme for the ligand-exchange reaction between VO_2EDTA^{3-} and $H(NTA)^{2-}$. The first step is a fast formation of an outer-sphere preequilibrium complex. The structure of the VO_2EDTA^{3-} complex, with no water bonded to the vanadium and no very weak vanadium–ligand bond, and the lack of significant variation of the spectrum between 220 and 400 nm during this first step lead us to postulate the formation of this outer-sphere complex. The following steps might be reactions of interchange between one chelating group of EDTA bonded to the metal and one entering chelating group of NTA. The cleavage of a metal–EDTA nitrogen bond must be the key process. All these interchange reactions between chelating groups of the leaving ligand and chelating groups of the entering ligand are apparently first order as the reactions occur in outer-sphere complexes and do not involve direct attack of external species. Thus the rate constants of the ligand-interchange reactions must be of the same order of magnitude (0.1–$0.6\ s^{-1}$) as we have experimentally shown. This is due to the fact that in all reactions, the broken and new bonds are almost the same.

In conclusion, the results presented above show that the mechanism of chelating group exchange reactions depends on whether the central metal is or is not bonded to water molecules.

Registry No. VO_2EDTA^{3-}, 68907-94-8; VO_2EDDA^-, 38868-05-2; H_3NTA, 139-13-9.

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4:1 Lewis Base Adducts of Palladium Bis(hexafluoroacetylacetonate). The Structure of $(4\text{-}ClC_5H_4N)_4Pd(C_5HF_6O_2)_2$

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Palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, reacts with a wide variety of Lewis bases to form 4:1 adducts of the type $(L_4Pd_2)(F_6acac)_2$ where L includes $(CH_3)_2NH$, CH_3NH_2, NH_3, C_5H_5N, imidazole, 3,5-$(CH_3)_2$-pyrazole, t-C_4H_9NC, Ph_3Sb, benzothiazole, and 1,3-dithiolene-2-thione and the chelating bidentate ligands $Ph_2PC_2H_4PPh_2$, $Ph_2PCH_2PPh_2$, $Ph_2AsC_2H_4AsPh_2$, and 1,4-$C_4H_8S_2$. Metathesis with NH_4PF_6 yields $(L_4Pd)(PF_6)_2$. These compounds were characterized by conductivity and spectroscopic measurements. The 4-chloropyridine adduct $(4\text{-}ClC_5H_4N)_4Pd(F_6acac)_2$ was characterized by single-crystal X-ray diffraction. Crystal data: space group $P2_1/c$, $a = 19.356$ (3) Å, $b = 18.902$ (3) Å, $c = 10.636$ (2) Å, $\beta = 100.12°$, $V = 3831$ Å^3. There are two crystallographically independent molecules per unit cell. Both F_6acac groups have been displaced, and the pyridine rings in the $(4\text{-}ClC_5H_4N)_4Pd$ group are mutually perpendicular and $d(Pd\text{–}N)_{av}$ in the planar PdN_4 unit is 2.029 Å. Two oxygens, one from each F_6acac, occupy axial positions with $d(Pd\text{–}O) = 3.02$ Å.

Introduction

The chemistry of palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, is extensive in scope. It is a strong Lewis acid and with molecular bases forms adducts of the general formula $Pd(F_6acac)_2(ligand)_n$ where $n = 1, 2, 3$, or 4. Previous papers from these laboratories have characterized the $n = 1$ and 2 classes of adducts[2] and their role in ortho metalation[3] and β-diketonate transfer reactions[4] as well as acid–base surface complexes formed with use of metal oxides as condensed-phase donors.[5,6] This paper describes the synthesis and properties of the $n = 4$ class, $Pd(F_6acac)_2(ligand)_4$, and reports the crystal structure of a representative member, $Pd(F_6acac)_2(4\text{-}ClC_5H_4N)_4$.[7]

Synthesis and Properties of 4:1 Adducts

Addition of Lewis bases to solutions of $Pd(F_6acac)_2$ in solvents of low dielectric constant such as chloroform, toluene, or pentane results in successive displacement of the F_6acac groups[8] to yield $Pd(F_6acac)_2(base)$ ($n = 1, 2, 3, 4$). The stoichiometry of the materials isolated appears to be a function of the steric and electronic properties of the donor molecule. When the base is a strong σ donor and not highly hindered, these reactions go to completion to yield only $Pd(F_6acac)_2(ligand)_4$. Examples of such bases include ammonia and methylamine. The 4:1 adducts usually have low solubility in nonpolar solvents and separate from the reaction mixtures in analytical purity. Dimethylamine is a more hindered donor and generates both 1:1 and 2:1 adducts when a deficiency of amine is employed but, in the presence of excess amine, provides $Pd(F_6acac)_2[(CH_3)_2NH]_4$ (**1**). Heterocyclic nitrogen-containing donors such as pyridine, imidazole, and 3,5-dimethylpyrazole all afford 4:1 adducts in nearly quantitative yield. Analytical and spectroscopic data for these and other new compounds prepared are given in Tables S1–4 (supplementary material).

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