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Spectral Properties of Oxovanadium(IV) Complexes. II. Bistrifluoroacetylacetoneethylenediimine

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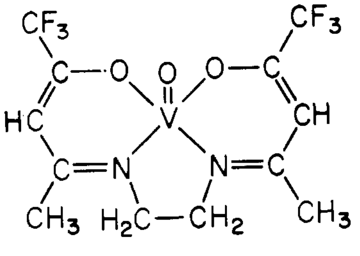
In a previous communication we reported the spectral properties of some β-ketimine complexes of the oxovanadium(IV) ion.[1] Although we were able to obtain the complexes of the quadridentate ligands bisacetylacetoneethylenediimine (H_2acen) and bisbenzoylacetoneethylenediimine (H_2bzen), we were unable to prepare the corresponding bistrifluoroacetylacetoneethylenediimine (H_2tfen) derivative. In fact, using the chelate-exchange method of Martin[2] the reaction of bis(acetylacetonato)oxovanadium(IV) with H_2tfen surprisingly yielded VO(acen). However, following the modification of Garvey,[3] we have prepared the desired complex (Figure 1) by the chelate-exchange reaction of bis(trifluoroacetylacetonato)oxovanadium(IV) with H_2tfen.[4] In order to determine the substituent effect of the strongly electron-withdrawing trifluoromethyl group on the spectral properties of β-ketimine complexes we have investigated the visible, infrared, and electron spin resonance spectra of VO(tfen).[5]



VO(tfen)

Figure 1.—Structural representation of bistrifluoroacetylacetoneethylenediimineoxovanadium(IV).

The infrared spectrum of VO(tfen) in acetonitrile solution shows the V=O stretching absorption at ~999 cm^{-1}. Under similar conditions VO(acen) shows an absorption at 982 cm^{-1}. The spectrum of the VO(tfen) dissolved in a coordinating solvent, dimethylformamide, ν(V=O), is at ~963 cm^{-1}. This frequency lowering is in marked contrast to the insensitivity of this band to solvent for VO(acen). The infrared spectral behavior of VO(tfen) is consistent with that of most other oxovanadium(IV) complexes.[6] Previous measurements with pyridine N-oxides substantiate our result.[3]

Isotropic esr parameters for VO(tfen) in several solvents are given in Table I. The g_0 values, 1.974, are identical with those of the β-ketimines previously reported.[1] This is not surprising since the g_0 values are not sensitive to solvent and substituents within a particular ligand type. The anisotropic g values for VO(tfen) in tetrahydrofuran and pyridine are $g_{\parallel} = 1.955$ and $g_{\perp} = 1.983$. These values are about the same as those of the other β-ketimine complexes. The nuclear hyperfine coupling constant appears to be solvent and substituent dependent. For example, in tetrahydrofuran A_0 is 104.6 G for VO(tfen) and 102.2 G for VO(acen). A similar increase in A_0 is seen with trifluoromethyl substitution for the β-diketone complexes of oxovanadium(IV).[7] The effect of a coordinating solvent on A_0 is much more pronounced for VO(tfen) than for VO(acen). For example, in pyridine A_0 is 101.0 G for the former and 101.7 G for the latter. The decrease in A_0 is more than four times greater for VO(tfen) than for VO(acen). The anisotropic A values are: $A_{\parallel} = 182$ G, $A_{\perp} = 66$ G in tetrahydrofuran and $A_{\parallel} = 181$ G, $A_{\perp} = 61$ G in pyridine. All the anisotropic A values appear to be slightly higher for VO(tfen) than for VO(acen).

TABLE I

ELECTRONIC ABSORPTION AND ESR SPECTRAL DATA FOR BISTRIFLUOROACETYLACETONEETHYLENEDIIMINE-OXOVANADIUM(IV)

	Absorption max, kK		Esr parameters	
Solvent	ΔE_1	ΔE_2	g_0	A_0, G
Acetonitrile	~16.5 sh	18.4	1.974[a]	103.5[b]
Tetrahydrofuran	~15.5 sh	18.2	1.974	104.6
Pyridine	14.7	18.7	1.974	101.0

[a] Deviation ±0.001. [b] Deviations ±0.5 G.

The visible absorption maxima from the electronic spectra of VO(tfen), in several solvents, are collected in Table I. Typical spectra are shown in Figure 2. For noncoordinating solvents the spectra show one prominent maximum at 18.2–18.4 kK and a red shoulder at 15.5–16.3 kK. The ΔE_1 band is at lower energy and the ΔE_2 band is at higher energy than for VO(acen). The same trend is noted for the trifluoromethyl substitution for the β-diketone complexes.[8] When the complex is dissolved in a good coordinating solvent, pyridine, ΔE_1 undergoes a red shift and ΔE_2 undergoes a slight blue shift. In general, the same behavior is noted for most other oxovanadium(IV) complexes.[9] Finally the magnitude of the shifts in absorption maxima with solvent are much greater for VO(tfen) than for VO(acen); *e.g.*, $\Delta(\Delta E_1) \approx 0.8$ and $\Delta(\Delta E_2) \approx 0.5$ kK for the former complex while $\Delta(\Delta E_1) \approx 0.2$ and $\Delta(\Delta E_2) \approx 0.3$ kK for the latter.

The square-pyramidal five-coordinate complexes of the oxovanadium(IV) ion have the following d-level

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(4) *Anal.* Calcd for $C_{12}H_{12}F_6N_2O_3V$: C, 36.10; H, 3.01; N, 7.02; mol wt, 397. Found: C, 36.49; H, 3.28; N, 6.81; mol wt, 397 (low-voltage mass spectrum); magnetic moment 1.82 BM; mp >300°.

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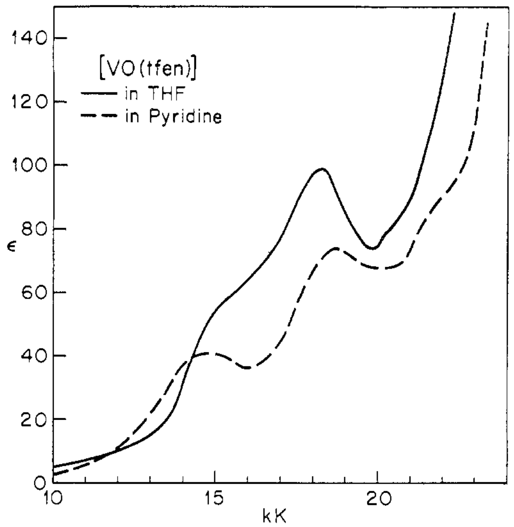

Figure 2. Visible electronic spectra of bistrifluoroacetylacetoneethylenediimineoxovanadium(IV) in tetrahydrofuran and pyridine.

ordering:[10] $d_{xy} < d_\pi(d_{xz}, d_{yz}) < d_{x^2-y^2} < d_{z^2}$. It is reasonable to assign ΔE_1 to the $d_{xy} \rightarrow d_\pi$ and ΔE_2 to the $d_{xy} \rightarrow d_{x^2-y^2}$ transitions of the vanadium. The antibonding d_π orbital is involved in $p_\pi \rightarrow d_\pi$ donation from the axial oxygen atom and the energy for the antibonding $d_{x^2-y^2}$ level should depend on the strength of the in-plane ligand field. In order to minimize charge buildup on the vanadium atom, as the in-plane donor strength of the ligand increases, the π donation from the axial oxygen should decrease. The π donation should be reflected in the frequency of the V=O stretching vibration. The increase in ν(V=O) with trifluoromethyl substitution in the β-diketimine is consistent with the notion of a weaker in-plane ligand field arising because of the presence of the strongly electron-withdrawing $-CF_3$ group.

The magnitude of the esr parameter, A_0, also reflects the strength of the in-plane ligand field. The major contribution to the variation of A_0 for most oxovanadium(IV) complexes appears to be the amount of the 4s contribution to the σ bonding in the complexes.[11] As the bonding MO that contains a 4s metal contribution is stabilized, its contribution to A_0 by a spin-polarization mechanism is lowered. The stability of the MO should be dependent on the strength of the in-plane ligand field, and as the in-plane ligand field weakens, A_0 should increase. Substitution of CH_3 by CF_3 leads to a weaker in-plane ligand field and as expected A_0 increases.

The five-coordinate oxovanadium complexes should readily add a sixth ligand in the vacant coordination position of the square pyramid *trans* to the axial oxygen atom. Charge buildup on the vanadium from the donor molecule should decrease the π donation of the axial oxygen to the metal. The lowering of the V=O stretching frequency in the ir spectra reflects this weakening of the axial oxygen to vanadium bond. In addition to this change, the in-plane ligand to vanadium interaction could increase by a movement of the metal closer to the basal plane of the square pyramid. This proposal explains the decrease in A_0 when oxovanadium(IV) complexes are dissolved in good coordinating solvents.[7]

Visible absorption spectral changes are also consistent with this model for solvent dependence. As expected, ΔE_1 undergoes a red shift with change in solvent (tetrahydrofuran to pyridine) while ΔE_2 shows a slight blue shift. (See Figure 2.) The shifts arise because of the stabilization of the antibonding d_π orbital and the destabilization of the $d_{x^2-y^2}$ orbital with pyridine coordination. While the visible spectra vary in the expected way for the β-ketimine complexes, the change in the bands with CF_3 substitution for CH_3 is difficult to understand. The weaker in-plane ligand field of the VO(tfen) should give ΔE_1 at higher energy and ΔE_2 at lower energy than VO(acen). This is opposite to what is observed. The visible absorption bands are, however, at higher energy for both VO(tfen) and VO(acen) than for the β-diketone complexes. This is consistent with the greater ligand field strength of the β-ketimines.

The spectral properties and their solvent dependence for VO(tfen) are easily rationalized on the basis of a model put forth for β-diketone complexes.[9] This is not the case for the other β-ketimines previously examined, *i.e.*, VO(acen).[1] It has been pointed out that the solvent dependence of the spectral properties cannot be unambiguously interpreted by a complex–solvent coordination. The substantial difference in behavior for the CF_3 and CH_3 derivatives is difficult to explain. The CH_3 complex should have a stronger in-plane ligand field with a resultant weakening of the axial oxygen to vanadium electron donation. The weakening of the V=O bond might be great enough that the *trans*-axial interaction with solvent molecule is only a very small perturbation on the d levels of the complex. A weakening of the in-plane ligand field with CF_3 substitution could strengthen the V=O bond to the point that the electronic structure of the complex becomes sensitive to the donor properties of the solvent. A second explanation which invokes steric hindrance for coordination of a base to the vanadium atom in the β-ketimine can be ruled out. If all of the complexes are square pyramidal, then the CF_3 derivative should be more sterically hindered than the CH_3 derivative. A third explanation involves the detailed molecular structure of the complexes. If VO(tfen) is square pyramidal, then its behavior should be analogous to the square pyramidal β-diketone complexes. This is what is observed. Conversely, if VO(acen) is trigonal bipyramidal, then its spectral properties and their solvent dependence should be much different from the β-diketone case. The infrared V=O stretching frequency should not be sensitive to the geometry of the complex since the vanadium–oxygen π bond should be formed in either case.[12] On the other hand, esr spectroscopy

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should be able to distinguish between the square pyramid and the trigonal bipyramid since the latter would not give an axially symmetric g tensor. Of course, line widths might prevent sorting out of g_x and g_y for small distortion of the molecular structure away from square pyramidal toward trigonal bipyramidal. Since the unpaired electron is still in a nonbonding d_{xy} orbital in both geometries, A_0 values probably should not be sensitive to the structure.[13] Finally, the anomalous position of the visible absorption maxima for VO(acen) and VO(tfen) might be evidence for a difference in geometry. A detailed discussion of this point must await a determination of the molecular structure of the complexes. An X-ray crystallographic study of these complexes is now in progress.[14]

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Electron-Transfer Rate Studies of Metal Complexes of Ethylenediaminetetraacetate and *trans*-1,2-Diaminocyclohexanetetraacetate

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Rate studies of only a relatively small number of redox reactions which are unambiguously outer sphere have been investigated. This is unfortunate since this is an area where the theoretical approach has been most fruitful.[1] Although a large number of metal ions form complexes with the EDTA-type ligand,[2] only the very slow isotopic exchange between Co(EDTA)$^{2-}$ and Co(EDTA)$^-$ ions[3,4] and between Co(PDTA)$^{2-}$ and Co(PDTA)$^-$ ions[4] has been measured. A lower limit of about 10^2 M^{-1} sec^{-1} at 20° can be estimated for the second-order rate constant for the Fe(EDTA)$^{2-}$–Fe(EDTA)$^-$ isotopic exchange.[3,5] We have now investigated the kinetics of a number of redox reactions involving these types of complexes (Table I).

Experimental Section

Materials.—The disodium salt of EDTA (Fischer) and the free acid CyDTA (City Chemical Corp.) were used without further purification. Cr(II) solutions were prepared by dissolving Cr pellets (United Mineral and Chemical Corp.) in deaerated dilute H_2SO_4. H[Cr(EDTA)]·H_2O,[6] K[Mn(EDTA)]·2.5H_2O,[7] K[Mn(CyDTA)]·2.5H_2O,[8] and K[Co(EDTA)]·3H_2O[9] were prepared by known methods. Solutions containing Fe(EDTA)$^-$ and Fe(CyDTA)$^-$ were prepared by aerial oxidation of the corresponding iron(II) complex. The same spectra and results were obtained as using a solution of NH_4[Fe(EDTA)]·H_2O. Other materials used were reagent grade.

Spectra.—The spectra of the air-sensitive species Cr(EDTA)$^{2-}$, Cr(CyDTA)$^{2-}$, Fe(EDTA)$^{2-}$, and Fe(CyDTA)$^{2-}$ have not previously been reported. They were measured by passing deaerated solutions of these ions through a flow-through cell until thoroughly flushed, closing stopcocks at either end of the cell, and fitting into a specially adapted holder which could be placed in the cell compartment of a Cary 14 spectrophotometer. The absence of iron and chromium tervalent metal complex (<5%) was shown by the relatively low absorption at 260 and 400 mμ, respectively.

Kinetic Experiments.—The EDTA or CyDTA complexes of Cr(II), Mn(II), Fe(II), and Co(II) were prepared *in situ* by adding a slight excess of ligand to a buffered solution of the metal ion.[10] Their reactions with solutions containing weighed amounts of the tervalent metal complexes were studied spectrally with a glass–Lucite stopped-flow apparatus or a Cary 14 spectrophotometer. All experiments involving Cr or Fe complexes were carried out in an N_2 atmosphere, but because of the extreme sensitivity of Cr^{II}-EDTA to O_2,[11] it was found more satisfactory to form this complex immediately prior to the redox reaction by mixing Cr_{aq}^{2+} in one syringe with M(III) complex, ligand, and lutidine buffer in the other syringe.

Reaction 1 was followed at 305 mμ where the chromium(III) complexes ($2–5 \times 10^{-3}$ M) have little absorption and the absorption coefficients of Cr(EDTA)$^{2-}$ and Cr(CyDTA)$^{2-}$ (4×10^{-4} M) are 90 and 290, respectively. Similar results were obtained when the small absorbance increase at 540 mμ was followed ($\epsilon_{Cr^{III}(EDTA)}$ - 200,[2,6,12] $\epsilon_{Cr^{III}(CyDTA)}$ - 240[13]).

Reaction 2 was monitored at 490 mμ where the manganese(II) complex ($2 \times 10^{-2}–10^{-1}$ M) has a very small absorption compared with Mn(EDTA)$^-$ and Mn(CyDTA)$^-$ ($2 \times 10^{-4}–10^{-3}$ M) with ϵ_M's of 444[8] and 330,[9] respectively.

An increase of absorbance at 258 mμ accompanies reaction 3 where the absorption coefficients for Fe(EDTA)$^{2-}$, Fe(CyDTA)$^{2-}$, Fe(EDTA)$^-$,[14] and Fe(CyDTA)$^-$ are, respectively, 480, 530, 9.4×10^3, and 8.2×10^3. Reactions were carried out with excess Fe^{II}-EDTA complex ($3.5–7.0 \times 10^{-4}$ M) over Fe^{III}-CyDTA ($4–6 \times 10^{-5}$ M). All studies were at pH 4.5–6.5 using sodium acetate or lutidine buffers. In (1) and (3) the second-order redox reactions were followed by slower, easily separable spectral

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