cipal axes of vibration very nearly in the plane of the circle they define and tangent to that circle.

TABLE VIII

THE HYDROGEN BONDING[a]

From	To	Dist, Å	From	To	Dist, Å
N(1)	O(7), a	3.00	N(6)	O(7), a	3.16
	O(6), d	3.02		O(13), c	3.10
	O(3), c	3.23			
N(2)	O(8), a	3.07	N(7)	O(12), a	3.08
	O(6), d	3.12		O(9), c	2.91
	O(5), c	2.06		O(11), a	3.26
N(3)	O(4), c	3.07	N(8)	O(9), c	2.89
	O(5), d	3.20		O(13), c	3.01
	O(4), d	2.99			
N(4)	O(10), a	3.07	N(9)	O(3), c	3.08
	O(8), a	3.29		O(14), c	3.08
	O(4), c	3.12		[O(8), O(10)], a	3.07
N(5)	O(3), c	2.99	N(10)	O(12), a	2.98
	O(6), d	3.04		O(11), c	3.16
	O(14), d	3.10			
O(11)	O(2), a	2.82	O(13)	O(3), a	2.81
	O(7), a	2.90		O(10), c	2.77
O(12)	O(11), a	2.73	O(14)	O(4), a	2.85
	O(8), c	2.78		O(6), b	2.74

[a] The atom listed in column 1 has coordinates as given in Table III. The symmetry transformation given after the atom listed in column 2 applies to its coordinates. These transformations are: (a) x, y, z; (b) $-x, -y, -z$; (c) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (d) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$, or integral unit-cell translation variants of these.

C. The Over-all Structure.—As is shown in Figure 4, the cation is surrounded by sulfate groups and water molecules, and all of these groups are held together by an intricate network of hydrogen bonds. The hydrogen-bonding scheme is summarized in Table VIII, which lists the short N–O or C–O distances which we have interpreted as hydrogen bonds. The hydrogen atoms themselves were positioned from difference maps and in most cases their positions were unambiguous; where there was any doubt as to the placement of a hydrogen atom, the potential hydrogen bonding was considered. All but three of the ammine protons are involved in the hydrogen bonding, and all of the sulfate oxygen atoms appear to accept at least two and usually three hydrogen bonds. The water molecules each accept two hydrogen bonds from ammine groups (or water) and donate two to sulfate groups (or water). Thus the structure appears to involve a very efficient use of the available donors and acceptors, just as did the structure of the sulfate of the superoxo-bridged cation.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND MELLON INSTITUTE,
CARNEGIE-MELLON UNIVERSITY, PITTSBURGH, PENNSYLVANIA 15213

Spectral Properties of Oxovanadium(IV) Complexes. I. β-Ketimines[1]

BY L. J. BOUCHER, EDMUND C. TYNAN, AND TEH FU YEN

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The spectral properties of oxovanadium(IV) complexes of the β-ketimines bisacetylacetoneethylenediimine, bisbenzoylacetoneethylenediimine, bisacetylacetone-1,2-propylenediimine, and bisbenzoylacetone-1,2-propylenediimine have been studied. The visible electronic spectra, 10–25 kK, were measured with the materials in toluene, tetrahydrofuran, pyridine, chloroform, and ethanol solution. The positions of the prominent ligand field bands at ~16.4 and ~18.0 kK are nearly the same for all the complexes. Only small solvent effects are noted. These do not parallel donor strength of the solvent but appear to be more dependent on hydrogen-bonding and dielectric constant effects. Electron spin resonance spectra have been measured with the complexes in solution and in the frozen solid state. The g values, $g_0 = 1.974$, $g_{\parallel} = 1.954$, and $g_{\perp} = 1.984$, are the same for all complexes in every solvent examined. The vanadium nuclear hyperfine splittings, $A_0 = 103.8$–99.4, $A_{\parallel} = 183$–176, $A_{\perp} = 64$–61 G, vary only slightly with substituent. Solvent effects are small and can be interpreted in the same way as for the visible spectra. The electronic structure of the β-ketimine complexes is discussed by comparison to those of the β-diketone and porphyrin complexes.

Introduction

The occurrence of vanadium in petroleum is widespread.[2] Knowledge about the chemical nature of the metal atom is prerequisite to understanding not only the role that the metal plays in the origin of petroleum, but also to determine how to remove this deleterious element from petroleum products. To a very large extent the vanadium is concentrated in the solid, asphaltic fraction of petroleum[3] as oxovanadium(IV) complexes, which are classified as either porphyrin[4] or nonporphyrin. Nonporphyrin vanadium complexes have never been successfully isolated and the ligand atoms bound to the metal in these compounds are un-

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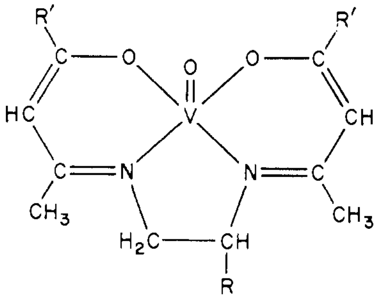
known. It has been suggested that nonporphyrin vanadium is bound to heteroatoms such as nitrogen, oxygen, and sulfur in the polyaromatic portion of asphaltene.[5]

Electron spin resonance spectroscopy represents the best way of observing oxovanadium(IV) in petroleum,[6] and, ultimately, it could be used to learn how nonporphyrin vanadium is bound. Even though the coordination chemistry of the oxovanadium(IV) ion continues to be of interest,[7,8] there are not enough suitable model compound data available to correlate the esr parameters with the ligand atoms bound to the metal. The esr properties of oxovanadium(IV) complexes of β-diketones[9] (four oxygen donors) and porphyrins (four nitrogen donors) have been studied.[10] On the other hand, complexes of similar pseudo-aromatic ligands with mixed donor atoms, *e.g.*, nitrogen–oxygen, oxygen–sulfur, and sulfur–nitrogen, have not been investigated. We propose to synthesize model compounds with these ligand systems bound to oxovanadium(IV) and to study their esr spectra as well as other relevant spectral properties.

Although oxovanadium(IV) complexes with nitrogen–oxygen donors (β-ketimines) have been reported,[11] the electronic properties of these low-symmetry compounds are unknown. We wish to report here some results on the spectral properties of β-ketimine–oxovanadium(IV) complexes. A structural representation of the compounds studied and their abbreviations are given in Figure 1.



	R	R'
VO(acen)	H	CH_3
VO(acpn)	CH_3	CH_3
VO(bzen)	H	C_6H_5
VO(bzpn)	CH_3	C_6H_5

Figure 1.—Structural representation of oxovanadium complexes of β-ketimines.

Experimental Section

Materials.—All chemicals were reagent grade and were used without further purification. Solvents were freshly distilled before use. Chloroform was washed with water several times to remove ethanol and dried. Ligands were prepared by the condensation of acetylacetone or benzoylacetone with ethylenediamine or 1,2-propylenediamine as previously described by Martell.[12] The compounds gave satisfactory melting points and elemental analyses.

Coordination compounds were prepared by following the general procedure of Martin and Ramaiah.[13] Both 0.01 mol (2.7 g) of bisacetylacetonatooxovanadium(IV) and 0.012 mol of the appropriate ligand were intimately mixed together and placed in a 25-ml round-bottom flask. The flask was attached to a cold trap and then to a vacuum pump. The mixture was heated at 250° for 3 hr under vacuum during which time acetylacetone distilled off. The solid product was then removed from the cooled flask and extracted several times with ether. The gray-green powder was then placed in a Soxhlet apparatus and extracted with toluene or chloroform and the undissolved residue was discarded. The impure product was isolated from the solution and then recrystallized from boiling toluene or chloroform. The pure solid was dried at 60° under vacuum for 24 hr.

Spectral Measurements.—Infrared spectra were obtained with a Beckman IR-4 spectrometer. Samples were dispersed in Nujol and placed between rock salt plates or dissolved in dimethylformamide and placed in a sodium chloride cavity cell (0.10 mm). Electronic spectra were obtained at room temperature with a Beckman DK-1 recording spectrophotometer equipped to read directly in wave numbers. Samples were dissolved in the appropriate solvent and the solutions ($1-10 \times 10^{-3}$ *M*) were placed in 10-mm (or longer) quartz cells. Stock solutions were diluted to obtain spectra in the ultraviolet region. Esr spectra were taken with a Varian V4502 X-band spectrometer system with a 12-in. magnet and "Fieldial." A rectangular dual cavity was used with 100-kHz magnetic field modulation at the sample and 400-Hz modulation at the reference. The reference material used was DPPH, 10^{-3} *M* in benzene. The solutions, $\sim 2 \times 10^{-3}$ *M*, were freshly prepared and observed at 20° or they were quick frozen and observed at −150°. In the case of the tetrahydrofuran solution, the samples were prepared and sealed in an esr tube in the absence of atmospheric gases. The spectra were recorded at least twice for each sample and two different samples of the same material were also used. The reproducibility from sample to sample was better than ±0.001 for the g values and better than ±0.5 G for A_0 and ±1 G for $A_{\parallel}$. Mass spectra were obtained at 10 eV and 150° with an AEI MS-9 mass spectrometer equipped with a direct-insertion probe. Magnetic susceptibility measurements were carried out with a Faraday balance using platinum metal as a standard.

Results

The β-ketimine complexes of oxovanadium(IV) were prepared by the ligand-exchange method of Ramaiah and Martin.[13] All but [VO(bzen)] have been previously reported. Analytical data for the materials are listed in Table I.[14] In no case were solvated complexes obtained. Low-voltage mass spectra gave parent peaks at the appropriate molecular weight and indicate that higher molecular weight materials were not present to a significant extent. Ultraviolet and infrared spectral properties agree with those already published.[13] Infrared spectra of the complexes were recorded in the 650–4000-cm^{-1} region. The compounds were dispersed in Nujol as well as dissolved in a coordinating solvent, dimethylformamide. In both cases for all of the complexes the vanadium–oxygen stretching frequency appears at 982 ± 3 cm^{-1}.

Electronic absorption spectra were obtained in the 10.0–25.0-kK region for each complex in a variety of

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[14] Elemental analyses performed by Product Services Division, Gulf Research & Development Co., Harmarville, Pa.

TABLE I

ANALYTICAL DATA FOR COMPLEXES

Compound	Formula	Elemental analyses, % C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	Mol wt	Mp, °C	Magnetic moment,[a] BM
VO(acen)	$C_{12}H_{18}N_2O_3V$	49.8	50.1	6.3	6.3	9.7	9.2	289	236	1.76
VO(acpn)	$C_{13}H_{20}H_2O_3V$	51.5	51.4	6.6	6.4	9.2	9.2	303	199	1.73
VO(bzen)	$C_{22}H_{22}N_2O_3V$	63.6	63.9	5.8	5.2	6.8	6.7	413	>300	1.75
VO(bzpn)	$C_{23}H_{24}N_2O_3V$	64.6	65.4	6.1	5.8	6.6	6.3	427	271	1.84

[a] At 19°.

solvents. The frequencies of the two main visible absorption maxima and their energy difference $D_{\text{II,III}}$ are listed in Table II. Typical electronic spectra are shown in Figure 2. In general, the visible spectra show two closely spaced, broad maxima of nearly equal intensity at 16.1–16.5 and 17.5–18.2 kK ($\epsilon \sim 70$). In addition, a shoulder appears on the red side of band I at 13.0–14.0 kK ($\epsilon \sim 20$) and on the red side of the intense ultraviolet ligand band at 23.0–24.0 kK ($\epsilon \sim 80$). In some cases the two main absorptions, as well as the shoulders, are not resolved and only one broad maximum appears in the spectrum. Band II undergoes a blue shift, and band III undergoes a red shift in going from both the ethylenediamine to the propylenediamine and from the acetylacetone to the benzoylacetone compounds. The result is that the energy separation between the two bands decreases for both substituents. The spectra of the complexes show characteristic shifts in going from poor or noncoordinating solvents to good coordinating or hydrogen-bonding solvents. Band II undergoes a red shift and band III a blue shift; consequently, $D_{\text{II,III}}$ increases in the order ethanol > chloroform > pyridine > tetrahydrofuran > toluene. It is not possible accurately to ascertain substituent or solvent effects on the position of the shoulders at 23–24 and 13–14 kK owing to the band overlap and broadness.

Magnetic susceptibility measurements were made for these solid complexes. Effective magnetic moments are listed in Table I. After the appropriate diamagnetic correction the values lie in the range 1.73–1.84 BM, close to the spin-only value for a d^1 case.[15] Electron spin resonance spectra were determined with the complexes in a variety of solvents. The nuclear g values and vanadium nuclear hyperfine splitting constants, A, are collected in Table III. A typical isotropic spectrum with the complex in solution, at 20°, is given in Figure 3. Also a typical anisotropic spectrum with the complex in the frozen solid state, at −150°, is shown in Figure 4. The g_0 values were determined from the isotropic spectra and second-order corrected.[16] The $g_{\parallel}$ values were determined from the anisotropic spectra by the method of Kuska.[17] The $g_{\perp}$ values were calculated from g_0 and $g_{\parallel}$. The A_0, $A_{\parallel}$, and $A_{\perp}$ values were determined in a way analogous to that used for the g values.

TABLE II

VISIBLE ABSORPTION MAXIMA FOR COMPLEXES IN VARIOUS SOLVENTS[a]

Complex	Solvent	II	III	$D_{\text{II,III}}$
VO(acen)	Toluene	~16.5[b]	17.7	1.2
	Tetrahydrofuran	~16.5	17.7	1.2
	Pyridine	16.3	18.0	1.7
	Chloroform	16.1	18.0	1.9
	Ethanol	16.1	18.2	2.1
VO(acpn)	Toluene	17.2	...	...
	Tetrahydrofuran	17.2	...	...
	Pyridine	16.5	17.9	1.4
	Chloroform	16.3	17.9	1.6
	Ethanol	16.2	18.2	2.0
VO(bzen)	Toluene	...	...	...
	Tetrahydrofuran	~16.4	17.4	1.0
	Pyridine	~16.4	17.5	1.1
	Chloroform	~16.4	17.4	1.0
	Ethanol	...	...	...
VO(bzpn)	Toluene	16.9	...	...
	Tetrahydrofuran	16.8	...	...
	Pyridine	16.7	...	...
	Chloroform	16.8	...	...
	Ethanol	16.1	17.5	1.4

[a] Values in kilokaisers. 1 kK = 1000 cm⁻¹. [b] Shoulder.

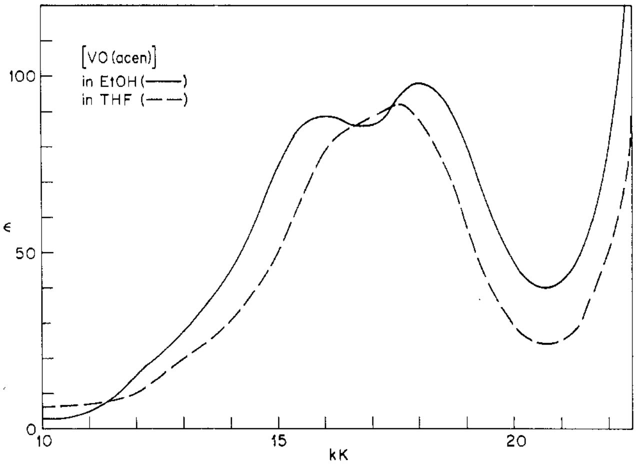

Figure 2.—Visible electronic spectra of bisacetylacetone-ethylenediimineoxovanadium(IV) in ethanol and tetrahydrofuran.

The g values are, within our error limits, independent of the particular complex and solvent. The average values are $g_0 = 1.974$, $g_{\parallel} = 1.954$, and $g_{\perp} = 1.984$. Conversely the A values are dependent on both the complex and the solvent. For example, A_0 decreases from highest to lowest values ($\Delta A \sim 3$ G) in the order toluene > tetrahydrofuran > pyridine > chloroform > ethanol. A_0 increases in going from the ethylenediamine to the propylenediamine derivatives by an average of 0.8 (±0.5) G. The $A_{\parallel}$ values are independent of substituents but do appear to decrease in going from

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TABLE III

ESR PARAMETERS FOR COMPLEXES IN VARIOUS SOLVENTS

Complex	Solvent	$g_0{}^a$	$g_\perp$	$g_{\parallel}$	$A_0{}^b$	$A_{\parallel}{}^c$	$A_\perp$
VO(acen)	Toluene	1.975	...	...	102.5	...	...
	Tetrahydrofuran	1.974	1.984	1.954	102.2	182	62
	Pyridine	1.975	1.986	1.954	101.7	179	63
	Chloroform	1.975	...	...	99.8	...	...
	Ethanol	1.974	1.984	1.953	99.4	176	61
VO(acpn)	Toluene	1.974	1.984	1.953	103.2	182	64
	Tetrahydrofuran	1.974	1.984	1.954	102.6	183	62
	Pyridine	1.975	1.986	1.952	102.2	182	62
	Chloroform	1.975	...	...	101.0	...	...
	Ethanol	1.975	1.984	1.956	100.0	178	61
VO(bzen)	Toluene	...	...	...	...	...	...
	Tetrahydrofuran	1.975	1.986	1.952	102.6	183	62
	Pyridine	1.975	1.984	1.958	101.4	178	63
	Chloroform	1.975	...	...	100.1	...	...
	Ethanol	...	...	...	...	...	...
VO(bzpn)	Toluene	1.974	...	...	103.8	...	...
	Tetrahydrofuran	1.975	1.984	1.957	103.4	182	64
	Pyridine	1.975	1.986	1.954	101.6	181	62
	Chloroform	1.975	...	...	101.8	...	...
	Ethanol	1.974	1.986	1.950	100.1	177	62

[a] ±0.001. [b] ±0.5 G. [c] ±1.0 G.

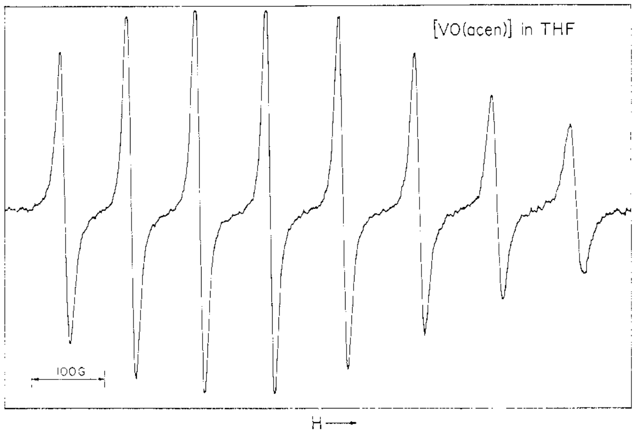

Figure 3.—Electron spin resonance spectrum of bisacetylacetoneethylenediimineoxovanadium(IV) in tetrahydrofuran at 25°.

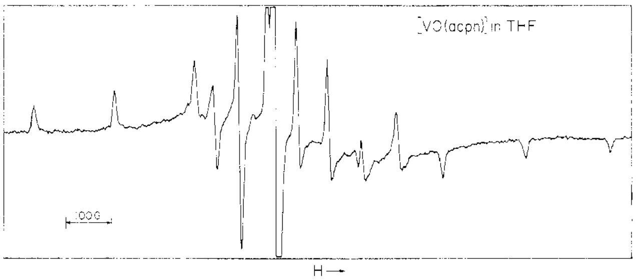

Figure 4.—Electron spin resonance spectrum of bisacetylacetone-1,2-propylenediimineoxovanadium(IV) in tetrahydrofuran at −150°.

noncoordinating to coordinating solvent. In no case was x,y splitting noted on the perpendicular features of the anisotropic spectra. Further, ligand nitrogen superhyperfine splitting was not observed on the vanadium lines even in the absence of oxygen.

Discussion

The electronic structure of oxovanadium(IV) d^1 complexes is the subject of keen interest today, and much discussion of the assignment of electronic transitions has appeared in the literature.[18,19] Recent molecular orbital calculations on β-diketone[20] and porphyrin[21] complexes indicate the detailed ordering of the metal d energy levels. In both cases the single unpaired electron is in an essentially pure metal d_{xy} orbital and the lowest energy transition is $d_{xy} \rightarrow d_{xz}, d_{yz}$ (I). For β-diketone complexes, the remaining transitions with increasing energy are $d_{xy} \rightarrow d_{x^2-y^2}$ (II) and $d_{xy} \rightarrow d_{z^2}$ (III). This order is inverted for the porphyrins, *i.e.*, transition III is at lower energy than transition II. The $d_{x^2-y^2}$ level is very sensitive to the ligand field strength of the in-plane donor atoms and increases in energy as their donor strength increases. The β-ketimines are expected to have a ligand field strength intermediate to that of the β-diketones and porphyrins.[22] Therefore, the energy level ordering should be intermediate between the two extremes and the d_{z^2} and $d_{x^2-y^2}$ levels should lie close to each other in energy.

The visible spectra of the β-ketimine complexes show three low-intensity absorption bands, in the 10–20-kK region, at 13–14 (sh), 16.1–16.5, and 17.4–18.2 kK. The absorption spectra are qualitatively similar to those of the β-diketone complexes.[18] All three bands are, however, at higher energy, in agreement with the expected increased ligand field of the β-ketimines. Also the splitting $D_{\mathrm{II,III}}$ is less than that for the β-diketones. It is reasonable to assign the bands in the 10–20-kK region to ligand field transitions. A possible assignment scheme is as follows: the shoulder at 13–14 kK can be assigned to transition I while the bands at 16.1–16.5 and 17.4–18.2 kK can be assigned to transitions II and III. Analogous assignments have been made for the absorption spectra of the oxovanadium(IV) complexes of salicylaldimines.[23] A fourth band in the visible region at 23–24 kK (sh) is not thought to be a ligand field absorption but rather is attributed to a spin-forbidden transition more or less internal to the ligand.[24]

Spectral variations with substituent can be qualitatively understood using ligand field considerations. For example, phenyl substitution decreases the ligand field strength of the β-ketimine and the absorption maxima shift to lower energy. In going from ethylenediamine to the propylenediamine derivative band II appears to shift to slightly higher energy. This is surprising since the ligand field strength of the two materials should be very nearly the same. The propylenediamine derivative exists as a mixture of four stereoisomers.[25] The methyl group can be on either carbon atom of the ethylene bridge and either in the axial or equatorial position, depending on the conformation of the chelate ring. Molecular models suggest

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that the methyl substituent sterically interacts with the β-ketimine methyl groups for all of the isomers. A slight distortion of the donor atom geometry around the metal could relieve these interactions and also change the ligand field.

If the β-ketimine oxovanadium(IV) compounds are square pyramidal like the β-diketones, they should readily add a ligand to the metal in the vacant sixth (axial) coordination position. Marked shifts of the visible maxima have been observed to result from the β-diketone complex–donor molecule interaction.[9] The β-ketimine complexes show only slight solvent-dependent spectral shifts in going from non- (or poorly) coordinating solvents, such as toluene and tetrahydrofuran, to a good donor solvent, such as pyridine. The over-all effect of pyridine is small and, in fact, may be related to the increase in dielectric constant of the solvent, not to its donor strength.[26] The largest solvent shift is observed with ethanol. Thermodynamic studies on β-diketone complexes show that alcohols are the weakest donors toward the vanadium atom.[27] This suggests that the major part of the large spectral shift noted there is due to the hydrogen-bonding ability of the solvent. Hydrogen bonds could be formed between the solvent and either the axial oxygen atom or the in-plane oxygen atoms. The significant shift noted here with a noncoordinating but hydrogen-bonding solvent, chloroform, supports this explanation.

Electron spin resonance spectral properties of the β-ketimine oxovanadium(IV) complexes are consistent with the supposition that the single unpaired electron is the nonbonding metal d_{xy} orbital.[8] The isotropic g values, $g_0 = 1.974$, lie between the values for β-diketones, 1.969, and those for porphyrins, 1.979. This corresponds to the position expected from ligand field considerations. The anisotropy of g, $|g_\perp - g_\parallel|$, is smaller for the β-ketimines than for the β-diketones, reflecting the increased donor strength of the in-plane ligands. Substituent and solvent effects on g values are as small for the β-ketimine complexes as for those of β-diketones.[28] Ligand field effects should not produce as great a change in g values as is noted for different donor atoms. Kivelson and Lee[29] have calculated orbital coefficients from visible and esr spectral data and have concluded that electron delocalization increases in going from β-diketones to porphyrins. Since the β-ketimine g values fall intermediate to those of both ligands, the orbital coefficients and electron delocalization might fall in the same order.

Vanadium nuclear hyperfine splittings for the β-ketimines fall between those of the β-diketones and porphyrins. For example, the isotropic values, A_0, in toluene solution are ~108, ~102, and ~95 G for the three ligand types. A configuration interaction mechanism has been suggested by Kivelson to be operative in A_0 variation for oxovanadium complexes.[29] A decrease in A_0 then can be related to an increase in ligand field about the metal atom. As expected, the dipolar term $|A_\perp - A_\parallel|$ remains essentially constant for the three ligand types. Small but real solvent effects are noted for A_0 values. The highest value of A_0 occurs for the complexes in noncoordinating solvents, *e.g.*, toluene. In pyridine solution the A_0 is lowered by about 1 G. The decrease is consistent with an increased ligand field about the metal resulting from the addition of a donor molecule to the free sixth coordination position of the metal. The magnitude of the decrease is, however, smaller here than for the β-diketones.[28] In fact, it is small enough to be accounted for by a dielectric constant solvent effect.[28] The largest solvent effect on A_0 is a decrease of about 3 G for ethanol solutions. This may be attributed to a hydrogen-bonding ability of this solvent. It is interesting to note that chloroform solutions show a shift of about 2 G. This is about twice as large as that for pyridine solutions. The dipolar term appears to decrease slightly in the order tetrahydrofuran < pyridine < ethanol. The rather small solvent dependence on the dipolar term is in contrast to the large variation observed for the β-diketones.[28]

In general, the spectral properties of the β-ketimine complexes of oxovanadium(IV) can be qualitatively rationalized using a ligand field approach which places these ligands between the β-diketones and the porphyrins. The variation of electronic absorption and esr spectral properties for the three ligand types might be evidence for closely similar molecular structures. X-Ray structures of several of the β-diketone complexes have been carried out.[30] The compounds are square pyramidal in geometry with the metal atom above the plane of the four oxygen atoms of the β-diketones. The porphyrins are more or less restricted to square-pyramidal geometry by the very nature of the ligand. The placement of the metal with respect to the four nitrogen donors is unknown. There is some evidence for thinking that the metal is out of plane in the most stable situation.[21] It seems unlikely that the β-ketimine complexes have a geometry grossly different from square pyramidal, *e.g.*, trigonal bipyramidal. Of course, small distortions may exist. Normal magnetic moments rule out the possibility of six-coordinate vanadium–oxygen–vanadium structures.[17]

A marked difference between the β-ketimine and β-diketone complexes of oxovanadium(IV) is the very slight solvent dependence of the visible and esr spectra for the former. In fact, the solvent effects for the β-ketimine complexes cannot be unambiguously assigned to a specific vanadium–donor molecule interaction. Rather, a general but little understood dielectric constant and/or hydrogen-bonding effect seems to dominate. Infrared spectral studies of the β-ketimine complexes of oxovanadium(IV)[31] show that the axial vanadium–oxygen stretching absorption is not shifted at all when the materials are dissolved in good donor

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solvents or are in the presence of good donor molecules. Conversely, β-diketone complexes show marked infrared shifts under similar conditions.[32] Steric interaction of the base molecule with the ethylene bridge might, of course, prevent close approach of the donor atom to the vanadium atom in the β-ketimine complexes. It must be pointed out that lack of spectral variation with solvent cannot be construed as evidence for nonexistent or even weak interaction of the donor atoms with the vanadium. Thermodynamic measurements are needed to settle this point.

In the β-diketone oxovanadium(IV) complexes, the axial oxygen atom dominates the ligand field about the metal. Implicit in this is the substantial $p\pi \rightarrow d\pi$ bonding between the axial oxygen and vanadium atoms. It is reasonable to expect that addition of a donor molecule to the vanadium atom opposite to the axial oxygen would effect the $p\pi \rightarrow d\pi$ interaction. This should lead to a change in the d-orbital energy levels, and, consequently, the spectral properties would change with solvent. An important consideration here is the extent of ligand–metal $p\pi \rightarrow d\pi$ interaction with the in-plane donor atoms. To the extent that this is important, axial π interaction should be lessened. If this occurs, one would expect that axial coordination to the vanadium atom of a donor molecule might not effect the energy of the d levels to a large extent. As a result the spectral properties would not be markedly dependent on the donor properties of the solvent. It has been suggested[21,29] that with porphyrin ligands there is a greatly increased π bonding of the metal with the in-plane donor atoms (nitrogen) over that for the β-diketones. The esr parameters reported here can be interpreted from the point of view that π bonding of the in-plane ligands is greater for the β-ketimines than for the β-diketones (but less than for the porphyrins). The decreased solvent dependence of the spectra noted here for the β-ketimines might then be a consequence of this. The fact that the vanadium axial oxygen stretching frequency for the β-ketimine complexes is $\sim$20 cm^{-1} lower than that for the β-diketone compounds might also be evidence for a weakened vanadium–axial oxygen bond.

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Contribution from the Michael Faraday Laboratories,
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Fluoro-Containing Complexes of Chromium(III). III. The Synthesis and Characterization of Some Fluoroacidobis(ethylenediamine)chromium(III) Complexes[1]

By Joe W. Vaughn, Otto J. Stvan, Jr.,[2] and Virgil E. Magnuson[3]

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A series of five new monofluoro complexes of chromium(III) of the type $[Cr(en)_2FX]^{n+}$ (en is ethylenediamine) has been prepared and characterized. The complexes which contain Cl^-, Br^-, I^-, or NCS^- as the X^- group all appear to involve a *cis* arrangement of the FX ligands. However, those complexes which contain ONO^- or F^- as the X^- groups appear to have the FX ligands *trans* to each other. Structures were established *via* ultraviolet–visible spectral studies, by ion-exchange techniques, and in one case by the resolution of a complex into its optical antipodes. In addition, new synthetic methods are presented for some known complexes of chromium(III).

Introduction

Complexes of the general type $[Cr(en)_2FX]^{n+}$ have not been investigated to any great extent for those cases where X is a uninegative monodentate ligand. In 1957 Dahme[4] reported the syntheses of fluorohydroxobis(ethylenediamine)chromium(III) chloride, fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate, and difluorobis(ethylenediamine)chromium(III) chloride. This work was followed by the synthesis of *cis*-difluorobis(ethylenediamine)chromium(III) iodide by Fehrmann and Garner[5] in 1960. In addition, these workers presented evidence for the *cis*-fluoroaquobis(ethylenediamine)chromium(III) ion in solution.

The present investigation was initiated to develop suitable synthetic methods for the preparation of unknown fluoro complexes of the type $[Cr(en)_2FX]^{n+}$ and if possible to determine the spatial relationship of the F and X ligands.

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[1] For the previous publication in this series see J. W. Vaughn, L. N. Coward, and B. K. Winter, *Inorg. Chem.*, **5**, 2061 (1966).

[2] Taken in part from a thesis submitted by O. J. S. to the Graduate School of Northern Illinois University in partial fulfillment for the M.S. degree.

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