TABLE III

LOSS IN WEIGHT OF THE $K_2Cr_2O_7$–$NaNO_2$ SYSTEM WHEN HEATED TO 300°

Expt no.	mmol of $K_2Cr_2O_7$	Wt loss, mg	Ratio[a]
1[b]	1.73	112	5.46
2[b]	1.69	109	6.68
3[c]	1.73	124	1.91
4[c]	1.82	136	1.20
5[c]	1.70	126	1.29
6[c]	1.75	132	1.11

[a] Ratio of millimoles of NO to millimoles of NO_2. [b] Experiment done under atmospheric pressure. [c] Experiment done under dynamic vacuum.

Discussion

The manometric studies support the stoichiometry of eq 1 in that 2 mol of gaseous products is produced per mole of dichromate which reacts with the nitrite, a reaction which proceeds to completion within the limits of the experimental observations. Although dichromate is generally considered to be a strong oxidizing agent, there was no indication of oxidation of nitrite by dichromate since no visually observable chromium(III) species were detected.

The variation in the relative proportion of NO to NO_2 in the gaseous products indicated by the gas absorption and weight loss experiments can best be explained by considering the oxidation of NO_2^- by NO_2 gas according to the reaction

$$NO_2(g) + NO_2^- \longrightarrow NO(g) + NO_3^- \qquad (2)$$

This reaction has been suggested by other workers.[2] Verification was obtained by placing NO_2 gas in a closed tube with molten sodium nitrite at 300°. The brown color of NO_2 disappeared in about 0.5 hr with no change in pressure. When oxygen gas was added to the system, the brown color reappeared. This indicated that NO_2 had been reduced to NO which was subsequently reoxidized by oxygen.

Apparently in both the gas absorption and weight loss experiments, some of the NO_2 produced reacted with the molten nitrite and as a result the ratio of NO to NO_2 increased. Furthermore, the departure from an equimolar ratio of NO to NO_2 was least when the weight loss and gas absorption experiments were performed under vacuum. This suggests that the less contact the gaseous products have with the melt, the less the conversion of NO_2 to NO occurs.

The results of the manometric experiments are insensitive to the relative amounts of NO and NO_2 produced. Since 1 mol of NO is produced for every mole of NO_2 which reacts with the sodium nitrite, the number of moles of gaseous products remains constant and consequently the pressure measurement will not indicate to what extent this secondary reaction takes place.

Topol, Osteryoung, and Christie[2] reported that in reactions between nitrite and different acids in an alkali metal nitrate melt, the relative amounts of NO and NO_2 formed varied with the acid. $K_2Cr_2O_7$ gave a mixture of about 90% NO and 10% NO_2 whereas $K_2S_2O_7$ gave a mixture of about 50% NO and 50% NO_2. In view of the strong-base behavior of nitrite as compared to nitrate, it would seem reasonable that the primary reaction in the case of dichromate is directly with nitrite according to reaction 1, followed by the reaction of NO_2 gas with nitrite to form NO as in reaction 2. The reaction of dichromate with the nitrate melt would be negligible. In the case of pyrosulfate, however, the increase in the relative amount of NO_2 produced is most likely the result of several factors. Because of the strong acidic nature of pyrosulfate as compared to dichromate, the reactions of pyrosulfate directly with nitrite and with nitrate are probably both important, *i.e.*

$$S_2O_7^{2-} + 2NO_2^- \longrightarrow 2SO_4^{2-} + NO + NO_2 \qquad (3)$$

$$S_2O_7^{2-} + 2NO_3^- \longrightarrow 2SO_4^{2-} + 2NO_2 + 0.5O_2 \qquad (4)$$

Also, the oxygen produced in (4) would react with the NO produced in (3) to produce more NO_2. The decrease in NO_2 due to reaction 2 would be offset to some degree by this reaction.

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Spectral Properties of Oxovanadium(IV) Complexes. III. Salicylaldimines

BY L. J. BOUCHER AND TEH FU YEN

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Previous papers have dealt with the β-ketimine complexes of the oxovanadium(IV) ion.[1,2] To add data for our model compound studies of naturally occurring vanadium complexes, we report here some new work on the electronic absorption and esr spectra of some oxovanadium(IV) salicylaldimine complexes (Figure 1). Ligands[3,4] and coordination compounds were prepared as previously described.[5] Elemental analyses, mass spectral molecular weight, and effective magnetic moments agree with the formulation given. Spectroscopic methods used have been completely described elsewhere.[1]

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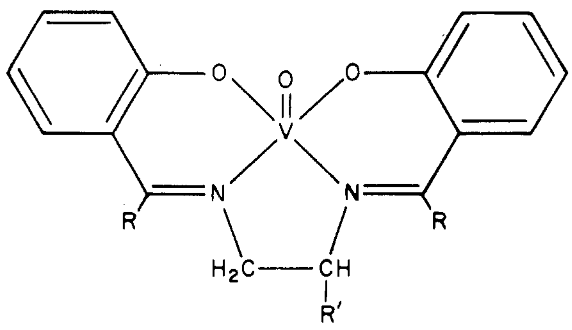

Compound	R	R′
[VO(Salen)]	H	H
[VO(Salpn)]	H	CH_3
[VO(Aceten)]	CH_3	H
[VO(Acetpn)]	CH_3	CH_3

Figure 1.—Structural representation of oxovanadium(IV) salicylaldimines.

Results

Electronic absorption spectra were obtained in the 10.0–25.0-kK region for each complex in pyridine and for VO(Salpn) in a variety of solvents. The frequency of the one prominent visible absorption maximum is given in Table I and typical electronic spectra are shown in Figure 2. In general, the visible spectra show only one maximum at 16.8–17.4 kK, with ϵ ~180 for VO(Salen) and VO(Salpn) and ϵ ~100 for VO(Aceten) and VO(Acetpn). In addition, several prominent shoulders appear in the spectra at ~13.0, 15.0–16.0, and ~21.0 kK. Solvent effects on the frequency of the absorption maxima are quite small. For example, the positions are nearly identical in toluene, tetrahydrofuran, and pyridine. Chloroform gives rise to a slight blue shift while ethanol gives a somewhat greater blue shift (~0.4 kK). Substituent effects on the spectra are somewhat larger. When R = CH_3, the maximum is blue shifted by ~0.5 kK from the case where R = H. In addition there is a slight red shift in going from R′ = H to R′ = CH_3.

TABLE I

VISIBLE ABSORPTION MAXIMUM AND ESR PARAMETERS FOR COMPLEXES IN VARIOUS SOLVENTS

Complex	Solvent	ν_{max}, kK	g_0[a]	A_0,[b] G
VO(Salen)	Pyridine	16.9	1.973	100.0
	Tetrahydrofuran	16.8	1.973	101.7
	Chloroform	16.9	1.974	99.0
VO(Aceten)	Pyridine	17.4	1.974	99.0
	Tetrahydrofuran	17.3	1.973	100.5
VO(Acetpn)	Pyridine	17.3	1.974	99.8
	Tetrahydrofuran	17.2	1.973	100.0
VO(Salpn)	Toluene	16.8		
	Tetrahydrofuran	16.8	1.973	101.8
	Pyridine	16.8	1.973	100.8
	Chloroform	16.9	1.973	100.6
	Ethanol	17.2		

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

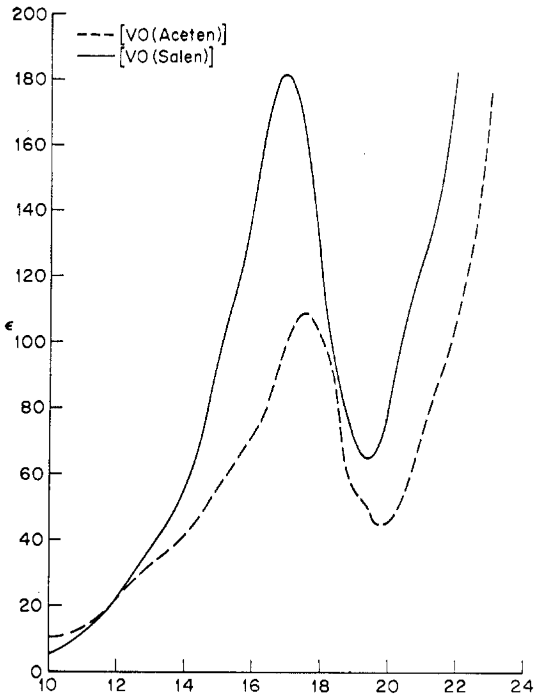

Figure 2.—Visible electronic spectra of bis(salicylaldehyde)-ethylenediimineoxovanadium(IV) and bis(*o*-hydroxyacetophenone)ethylenediimineoxovanadium(IV) in pyridine.

Electron spin resonance spectra were determined with the complexes in several solvents. The g_0 values and vanadium nuclear hyperfine splitting constant, A_0, are collected in Table I. The g_0 and A_0 values were determined from spectra taken at 20°.[1] Anisotropic esr parameters were taken from spectra with VO(Salen) and VO(Salpn) in frozen tetrahydrofuran at −150°.[1] The g_0 values (average, 1.973) are independent of the particular complex and solvent. Anisotropic g values are the same for the two complexes studied, $g_{\parallel}$ = 1.949 and $g_{\perp}$ = 1.985. Conversely, the A_0 values are dependent on both complex and solvent. While the change of R′ = H to R′ = CH_3 does not observably affect the A_0 values, the change of R = H to R = CH_3 lowers the A_0, 1.0–1.8 G. The change of solvent from tetrahydrofuran to pyridine gives a small decrease in A_0, 0.2–1.7. The decrease in A_0 in going from tetrahydrofuran to chloroform is even greater, 1.2–2.7 G. Finally, $A_{\parallel}$ = 179 and $A_{\perp}$ = 63 G for VO(Salen) and $A_{\parallel}$ = 181 and $A_{\perp}$ = 62 G for VO(Salpn). In no case was x,y splitting noted on the perpendicular features of the anisotropic spectra. Further, ligand nitrogen or hydrogen superhyperfine splittings were not observed on the vanadium lines even in the absence of oxygen. Although splittings of this sort are common for copper(II) complexes, only a very few examples are known for oxovanadium(IV) complexes.[6]

Discussion

A startling solvent dependence of their spectroscopy (ir, visible, esr) is a characteristic of the β-diketone

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complexes of the oxovanadium(IV) ion.[7] The substantial solvent complex interaction resulting from the coordination of a donor molecule to the vacant axial position of the square pyramid gives rise to a change in the electronic structure of the oxovanadium(IV) ion.[8] The spectroscopy of the salicylaldimine complexes is not solvent dependent. For example, the vanadium–oxygen stretching frequency in the infrared is the same in a good donor solvent as in noncoordinating media.[4] Also, the visible spectra do not show any shifts in the absorption maxima in going from toluene to pyridine. The blue shift noted for chloroform or ethanol solution is thought to arise from the hydrogen-bonding properties of the solvent.[9] Finally, the changes in the esr, A_0 value, with solvent can be interpreted by invoking dielectric constant or hydrogen-bonding effects.[10] Why is there such a difference in behavior between the β-diketone and salicylaldimine complexes of the oxovanadium(IV) ion? Steric hindrance to the complex–base interaction is a reasonable possibility. While the five-coordinate square-pyramidal geometry of the β-diketone oxovanadium complexes allows an unhindered complex–base interaction, another common five-coordinate geometry, trigonal bipyramidal, does not. A recent report gives the molecular structure of dichlorobis(trimethylamine)oxovanadium(IV) as trigonal bipyramidal with the vanadium–oxygen double bond in the trigonal plane.[11] An X-ray crystallographic study of bis(acetylacetone)ethylenediamineoxovanadium(IV) indicates that the coordination polyhedron is not significantly distorted away from square-pyramidal geometry.[12] Transformation of the square pyramid to the trigonal bipyramid requires an expansion of one of the V–O in-plane ligand angles and a compression of the other angle. For the β-ketimine complex the angle is decreased from ~164° for the water complex[13] to ~142°. This distortion is not sufficient to prevent strong complex–base interactions. While it is unlikely that the salicylaldimine complexes are actually trigonal bipyramidal, it is plausible that some distortion away from square-pyramidal geometry could exist which is at least as great as for the β-ketimines. The distortion of the salicylaldimine complexes could result from intraligand hydrogen–hydrogen steric repulsions in the ethylenediamine chelate ring, which arise from the steric restrictions placed on the ligand when it behaves as a tetradentate donor.

Although a distortion should give rise to a rhombic g tensor, in each case an axial g tensor is observed. This shows that the ligand field about the vanadium is strongly dominated by the metal–oxygen multiple bond. The position and donor strength of the other four ligand donor atoms only give rise to a perturbation on this interaction. While the g_0 values of the salicylaldimine complexes are higher than those of the β-diketones, they are consistently lower than those of the β-ketimines. Since the $g_\perp$ values are about equal for the salicylaldimines and for the β-ketimines, the decrease in g_0 is due to the substantial change in $g_\parallel$ (~0.005). The decrease in g when going from the β-ketimines to the salicylaldimines is a consequence of both the decrease in ligand field and in covalency. The vanadium hyperfine splitting constants are slightly larger for the β-ketimine than for the salicylaldimines. This is not consistent with the general observation that A_0 increases with a decrease in ligand field strength of the ligand for oxovanadium(IV) complexes.[14] If the symmetry of the oxovanadium complex is lowered sufficiently, the direct mixing of the 4s orbital into the ground-state d_{xy} orbital can occur with a resulting lowering of A_0. The value of A_0 might be diagnostic of the extent of distortion for similar ligands. The increase in A_0 in going from the *o*-hydroxyacetophenone to the salicylaldehyde derivative does conform to the ligand field generalization, however. The dipolar term $(A_\perp - A_\parallel)$ remains approximately the same for all of the complexes. This is consistent with the nonbonding nature of the electron-containing d_{xy} level.[6]

In a square-pyramidal ligand field, C_{4v}, three electronic transitions are expected for the d^1 oxovanadium(IV) ion: (I) $d_{xz} \rightarrow d_{xz}, d_{yz}$; (II) $d_{xy} \rightarrow d_{x^2y^2}$; (III) $d_{xy} \rightarrow d_{z^2}$.[13] In a trigonal-bipyramidal ligand field, C_{2v}, with the oxygen atom in the trigonal plane and all other donor atoms equivalent to each other, transition I is split into two components.[11] For the distorted salicylaldimine complexes the two components of transition I could occur near ~13 and 15–16 kK. The frequency of these transitions should be dependent on the vanadium–oxygen multiple bond. Although it is difficult to determine its position accurately, it appears that it is the same for the salicylaldimines as for the β-ketimines. This and the equivalence of the $g_\perp$ values indicate that the vanadium–oxygen interaction is equivalent in the two series of complexes. The maximum at 16.8–17.4 kK for the salicylaldimines can be assigned to transition II. The energy of this band should depend on the strength of the nonaxial ligand field. Accordingly, it is at higher energy for both the salicylaldimine and β-ketimine complexes than for the β-diketones. In fact, the frequency order is: β-ketimines > salicylaldimines > β-diketones. Further, when going from R = H to R = CH_3 for the salicylaldimine complexes, the absorption maximum is blue shifted. Finally, going from the ethylenedimine to the propylenediamine derivatives, the maximum is red shifted. Similar ligand field strengths are found for all of the corresponding Cu(II) complexes.[15] Transition III is of high energy for the majority of cases (>20 kK)

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and is generally obscured by ligand bands.[16] The shoulder at 21 kK in the salicylaldimine spectra may be such a ligand absorption. The assignment of the electronic spectra given here can only be tentative. Circular dichroism measurements on similar optically active complexes will be valuable in making firmer assignments.

Acknowledgment.—The authors thank Mr. Edmund C. Tynan and Mr. Timothy R. Drury, Research Services, Mellon Institute, for their assistance in the experimental work. This work was sponsored by Gulf Research and Development Co. as part of the research program of the Multiple Fellowship on Petroleum.

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The Electronic Structure of the Thiotrithiazyl Cation[1]

BY PAUL FRIEDMAN

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The thiotrithiazyl cation has been found to possess a planar structure, with very short, approximately equal sulfur–nitrogen bonds.[2] It is unusually stable for a sulfur-nitrogen heterocycle and has well-defined absorptions in the ultraviolet region indicative of $\pi \rightarrow \pi^*$ transitions.[3] These facts imply a well-defined π-electron system and a considerable amount of aromatic character.

Some recent efforts[3] have been made to gain understanding of the physical and chemical properties of this compound by attempting correlations with values determined by calculations using molecular orbital theory. These correlations were of limited utility because the methods which were used, the HMO and free-electron procedures, are too approximate to yield anything but qualitative agreement.

This situation led us to apply the semiempirical SCF–MO procedure developed by Pople,[4] which we had used successfully[5] with thiaaromatic compounds such as thiophene, thiazole, and thiazole derivatives, with the hope of obtaining more useful results for correlation. The known geometry of thiotrithiazyl cation[2] was simplified by assuming equal S–N bond lengths of 1.55 Å. The S–S bond length of 2.06 Å was used (Figure 1). Each sulfur was assumed to donate two electrons to the π system resulting in a ten-π-electron system in the cation. This geometry was used (Figure 1) to calculate the two-center, two-electron repulsion integrals (ii/jj) by the Mataga method.[6] The complete set of semiempirical parameters is given in Table I.

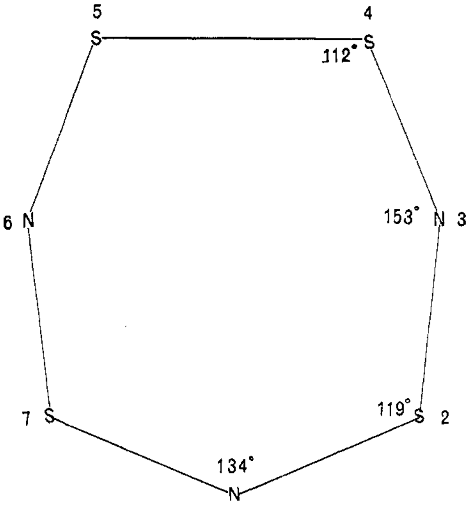

Figure 1.—Modified geometry of $S_4N_3^+$. The N–S bonds are all 1.55 Å; the S–S bond is 2.06 Å.

TABLE I

VALUES OF INTEGRALS USED (IN eV)

11/11	12.27	33/55	3.24
11/22	6.14	33/66	3.09
11/33	3.64	44/55	4.66
11/44	2.59	β_{12}	−2.0
22/22	11.90	β_{45}	−1.2
22/44	3.18	W_S	−23.0
22/55	2.51	W_N	−14.5
22/66	2.89		
22/77	3.42		

No special adjustments, such as calibration against observed spectral values, were made in these parameters in terms of the particular molecule being investigated. Rather, these parameters were carried over from our previous calculations of thiaaromatic compounds, except for β_{NS} and β_{SS}, which, not having been encountered previously, were given reasonable values based on bond lengths. The results of these calculations listed in Table II were correlated with the only available experimental data—ultraviolet[3] and ^{15}N nmr spectra.[7]

Discussion of Results

Uv Spectra.—A strong case has been made for considering both observed uv absorption bonds to be $\pi \rightarrow \pi^*$ in origin.[3] This enhances the significance of our calculations which give only the values of singlet and triplet $\pi \rightarrow \pi^*$ transitions for thiotrithiazyl cation. Our assumption of C_{2v} symmetry for thiotrithiazyl

[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; see Abstract M44.

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