Contribution from Overman Chemistry Laboratory
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Oxovanadium(IV) Complexes Containing Bidentate Nitrogen-Sulfur and Oxygen-Sulfur Ligands[1]

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A number of oxovanadium(IV) complexes containing nitrogen-sulfur and oxygen-sulfur bidentate ligands have been synthesized. The ligands employed include 2-aminoethanethiol, N-n-decyl-2-aminoethanethiol o-aminobenzenethiol, and 2-mercaptopyridine N-oxide. All the resulting oxovanadium(IV) complexes have the formula VOL_2, where L is the bidentate ligand. At tempst to prepare the N,N,-dialkyl-2-aminoethanethiol complexes of oxovanadium(IV) resulted in failure. Pyridine adducts of bis(2-mercaptopyridine N-oxide) oxovanadium(IV) ($VO(PTO)_2Py$) and the pyridine adduct of bis(o-aminobenethiolo)oxovanadium(IV) ($VO(ABT)_2Py$) have also been prepared. The stereochemistry of these complexese has been interpreted using chemical analyses and infrared and visible spectral data and all of these complexes appear to have square pyramidal geometries except bis(2-mercaptopyridine N-oxide)oxovanadium(IV). An attempt was made to correlate the specific Lewis base acceptor and infrared spectra. It was found that the reaction of $VO(ABT)_2Py$ with a variety of 4-substituted pyridine N-oxides (pyno) resulted in a systematic change in the visible spectra, and these changes were correlated to the Hammett σpyno values.

Introduction

Jorgensen[2] observed that the specific Lewis acid acceptor ability of the central metal ion is influenced by the degree of « hardness » or « softness » of the atoms bonded to that metal ion. The long range objective of this research is to study systematically how various combinations of « hard » and « soft » donor atoms bonded to a central metal ion can affect the capability of a central metal ion to act as a specific Lewis acid. This information would be extremely valuable in understanding how metal complexes produce stereospecific products in organic and biochemical systems.

Complexes of the oxovanadium(IV) ion should make a convenient system for such a study. The most important advantages of using oxovanadium(IV) complexes include: 1) These complexes are relatively stable.[3,4] 2) These complexes are commonly arranged in square pyramidal structures.[3-5] The coordination number of such complexes can be expanded from five to six by reacting with a Lewis base.[3,4,6] Therefore, there is a simple one-to-one interaction between metal complex and donor because only one site is available for attack. 3) Often the stability of the resulting adducts permits a direct measurement of their properties.[3,4,7] 4) These complexes have an internal probe, the vanadium-oxigen bond, which is sensitive to the nature of the Lewis base coordinated *trans* to oxy-oxigen. The extent of the interaction between a Lewis base and the reference oxovanadium(IV) complex is paralleled in the systematic changes in the visible and infrared spectra.[6,8-11]

Most of the studies of complexes of oxovanadium(IV) have utilized only nitrogen and oxygen ligands.[3,4] Only very recently have studies been conducted using oxovanadium(IV) complexes containing only sulfur donors.[6,12-16] Even more limited has been the research on oxovanadium(IV) complexes containing mixed sulfur ligands. Larkworthy, Murphy and Phillips[17] prepared *o*-aminobenzenethiol complexes of most of the first row transition metal ions including oxovanadium(IV). Only the magnetic moment of $VO(ABT)_2$ and its mull spectrum were briefly dicussed. Also, oxovanadium(IV) has been coordinated to the bidentate sulfur-oxygen ligands, monothio-β-diketones,[18,19,20] as well as to a variety of nitrogen-sulfur tridentate ligands derived from 2-aminothiophenol and salicylaldehyde or 2-hydroxynaphthaldehyde.[21]

In order to make a systematic study of the specific Lewis acid acceptor strength of various oxovanadium-

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(IV) complexes coordinated to ligands containing both hard and soft donor atoms, it is first necessary to understand the chemical and physical properties of these complexes. Our research has been concerned with the preparation and characterization of neutral oxovanadium(IV) complexes containing bidentate sulfur-oxygen and sulfur-nitrogen ligands. The ligands included in this study are *o*-aminobenzenethiol (ABT); 2-aminoethanethiol (AET); N-n-decylaminoethanethiol (DAET); N,N-dimethyl-2-mercaptoethylamine (DMAET); N,N-diethyl-2-mercaptoethylamine (DEAET); and 2-pyridinethiol l-oxide (PTO).

Experimental Section

Materials. All solvents used for synthesis were reagent grade and were used without further purification. Vanadyl sulfate-pentahydrate was obtained from A.D. MacKay, Ind., 2-Aminoethanethiol hydrochloride, N,N-diethylaminoethanethiol hydrochloride, and N,N-dimethylaminoethanethiol hydrochloride were commercial grade obtained from Matheson, Colemen and Bell while the N-n-decylaminoethanethiol and sodium 2-mercaptopyridine N-oxide were obtained from the Aldrich Chemical Co., Inc. All these ligands were used without further purification. Pyridine and 4-methylpyridine were purified by vacum distillation. Pyridine N-oxide, 4-methylpyridine N-oxide, and 4- methoxypyridine N-oxide were purified by sublimation to give white crystals.

Synthesis of bis(2-mercaptoethylamine)oxovanadium (IV). To a 500 ml round bottom flask was added 200 ml absolute ethanol, 1.04 g sodium metal (0.045 mol), and a solution of 5.16 g 2-aminoethanethiol hydrochloride (0.045 mol) in 140 mol absolute ethanol. The white NaCl precipitate was filtred off and then another 1.04 sodium (0.045 mol) was added, causing a white precipitate to form. The mixture was stirred and flushed with dry nitrogen for 25 minutes as a solution of 3.80 g $VOSO_4{\cdot}5H_2O$ (0.015 mol) in 5 ml water/65 ml absolute ethanol was added. Nitrogen pressure was used to transfer the oxovanadium solution to the ligand solution. A green precipitate formed which turned brown-green by the end of the addition. The mixture was stirred for five minutes and then filtered under a nitrogen atmosphere. The dark blue residue was washed with three 15 ml portions of oxygen-free ether and dried under vacuum over P_2O_5.

A sample of the dry blue residue was extracted with oxygen-free absolute methanol in a Soxhlet extractor under nitrogen for 36 hours. The blue methanol extract was condensed by rotary vacuum evaporation to near dryness and blue crystals precipitated out of solution. *Anal.* Calcd for $VO(C_2H_6NS)_2$: C, 22.0; H, 5.5; N, 12.8; V, 23.4. Found: C, 21.6; H, 5.55; N, 12.75; V, 23.6.

Synthesis of bis(N-n-decylaminoethanethiol)oxovanadium(IV). To a 500 ml round bottom flask was added 200 ml of absolute ethanol and 0.53 g sodium (0.023 mol). When the sodium had dissolved, 5.00 g of N-n-decylaminoethanethiol (0.023 mol) in 60 ml absolute ethanol was added. The solution was then flushed with dry nitrogen for 25 minutes to remove the oxygen. A solution of 2.28 g $VOSO_4{\cdot}5H_2O$ (0.009 mol) in 2 ml water/50 ml absolute ethanol was quickly added under a stream of nitrogen. Upon addition the solution first turned green-brown, and later a fine, dark blue-grey precipitate formed. This precipitate turned to green-brown again when the mixture was digested on a hot plate at 65° for 40 minutes. The mixture was then filtered under nitrogen in an inert atmosphere filter. The blue filtrate was concentrated on a rotary evaporator until a blue precipitate formed. This precipitate was filtered and dried under a vacuum over P_2O_5. *Anal.*[22] Calcd for $VO(C_{12}H_{25}NS)_2$: C, 59,6; H, 10.75; N, 5.8; V, 10.5. Found: C, 55.1; H, 10.1; N, 5.4; V, 10.65.

Synthesis of bis(2-mercaptopyridine N-oxide)oxovanadium(IV). To a 500 ml round bottom flask was added 225 ml absolute ethanol and 3.74 g of sodium salt of 2-pyridinethiol 1-oxide (0.025 mol). The mixture was then flushed with dry nitrogen for 20 minutes, followed by the addition of a solution of 2.78 g $VOSO_4 \cdot 5H_2O$ (0.011 mol) in about 3 ml water/30 ml ethanol. A light purple precipitate formed immediately and was filtered under a stream of dry nitrogen, washed with three 25 ml portions of water and two 10 ml portions of 95 percent ethanol, and then dried under a vacuum over P_2O_5 for 12 hours. *Anal.* Calcd for $VO(C_5H_4NOS)_2$: C, 37.7; H, 2.51; N, 8.8; V, 16.0. Found: C, 37.75; H, 2.49; N, 8.6; V, 16.0.

Synthesis of bis(2-mercaptopyridine N-oxide) oxovanadium(IV) pyridine adduct. To a 100 ml round bottom flask was added 20 ml methylenechloride and 25 ml pyridine. After flushing with dry nitrogen for 25 minutes, 0.64 g $VO(PTO)_2$ (0.020 mol) was added. The flask was stoppered and partially evacuated. The solution turned green as the $VO(PTO)_2$ dissolved. The flask was then shaken for 48 hours. A small amount of light green precipitate formed after 36 hours. This precipitate was filtered off in a glove bag under nitrogen and the remaining filtrate was concentrated to about 1 ml volume by rotary vacuum evaporation. The green precipitate was filtered under nitrogen and dried under a vacuum over P_2O_5. *Anal.* Calcd for $VO(C_5H_4NOS)_2 \cdot C_5H_5N$: C, 45.2; H, 3.27; V, 12.8. Found: C, 44.12; H, 2.93; V, 12.8.

Synthesis of bis(2-aminobenethiolo)oxovanadium (IV). The *o*-aminobenzenethiol was purified by distilling it at 5 mm of pressure at 97-98°C. Immediately after distilling, 11.8 g (.1 mole) of *o*-aminobenzenethiol was dissolved in a nitrogen-purged solution of 75 ml absolute ethanol and 25 ml of water. This solution was added to 10.0 g (.5 mole) of vandyl sulfate which had been dissolved in 100 ml of nitrogen-purged water. The solutions were mixed under a nitrogen atmosphere and a precipitate formed immediately. After ten minutes solid sodium bicarbonate was added, to adjust the pH to 7. The green precipitate was then filtered, washed with absolute meth-

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[22] Since $VO(C_{12}H_{26}NS)_2$, is an unstable compound, the nitrogen and vanadium analyses were done on fresh samples. However the carbon and hydrogen analyses were carried out by a service laboratory; and apparently some decomposition did occur in the interval between their preparation and analyses.

anol and dried in a vacuum dessicator over anhydrous P_2O_5. This method is a modification of the procedure employed by Larkworthy, Murphy, and Phillips.[17] *Anal.* Calcd for $VO(NH_2C_6H_4S)_2$: C, 45.71; H, 3.83; N, 8.88. Found: C, 45.82; H, 4.06; N, 8.82.

Synthesis of bis(2-aminobenzenethiolo)oxovanadium (IV) pyridine adduct. A nitrogen-purged solution of 15 ml (.15 mole) pyridine and 10 ml carbon tetrachloride was added to 5 g (0.15 mole) $VO(ABT)_2$ and stirred in a dry nitrogen atmosphere for 1 hour. Then 50 ml of nitrogen-purged carbon tetrachloride was added and the solution was stirred an additional hour. The solution was filtered in a dry atmosphere, and the brown precipitate which formed was discarded. The filtrate was stored in a refrigerator for twenty-four hours; during this time blue-green (aqua) crystals formed on the sides of the flask while a small amount of brown product appeared on the surface. The aqua crystals were mechanically removed and recrystallized from an anhydrous mixture of 30 percent pyridine 70 percent carbon tetrachloride. The resulting aqua crystals were then stored in the recrystallizing solution. *Anal.* Calcd for $VO(NH_2C_6H_4S)_2(C_5H_5N)$: C, 51.78; H, 4.31; N, 10.66. Found: C, 50.91; H, 4.62; N, 10.95.

Physical Measurements. Molecular weight determinations were made using an A. H. Thomas vapor pressure osmometer which was standardized using benzil and stilbene (Baker grade, J. T. Baker Co.) in the concentration range of 7.8×10^{-3} to 3.7×10^{-2} molal. Methylenechloride was chosen as the solvent because it was the same solvent used for solution spectra studies. Bath operating temperature was $31.95°\pm.05°C$. Magnetic susceptibilities were determined by the Guoy method. Samples were prepared in air and compared with $Hg[Co(CNS)_4]$ as the standard. Diamagnetic corrections were obtained using Pascal's law and employing tabulated constants.[23] Infrared spectra were taken on a Perkin Elmer 337 using KBr windows. Samples for solid spectra were prepared as Nujol mulls. Electronic spectra were taken using a Beckman DK-2 Ratio Recording Spectrophotometer. The spectra of the solids were measured in Nujol mull using diffuse transmittance techniques.[24] All solutions were prepared and studied under a nitrogen atmosphere and the infrared and electronic spectra were taken immediately after the solutions were prepared. (Decreases in the extinction coefficients of all peaks were noted an average of two hours after the solutions were prepared.) Nitrogen analysis was conducted on a Coleman Nitrogen Analyzer II and the vanadium analysis was done by combustion of the sample in air at 565°C for 12-24 hours.

Results and Discussion

Complexes. The green $VO(ABT)_2$ was originally prepared by Larkworthy, Murphy, and Phillips,[17] but its chemical and physical properties were not extensively studied. This complex is relatively stable for an indefinite period if stored in a vacuum over P_2O_5, but its stability in most solvents is limited to a few hours. Unfortunately, $VO(ABT)_2$ is only slightly soluble in polar solvents such as pyridine, N,N-dimethylformamide and ethanol; and therefore, only limited solution studies were possible.

The purple $VO(PTO)_2$ appears to be the most stable of the complexes investigated in this study. It was stable in dry air for several weeks but reacted with moist air forming a red-purple solid. The chemical analysis of this red-purple solid suggested that it was a mixture. Although $VO(PTO)_2$ is soluble in a large variety of solvents (chloroform, methylenechloride, methanol, dimethylsulfoxide, and nitromethane), these solutions are often different colors. For example, $VO(PTO)_2$ si green in pyridine and dark blue in CH_2Cl_2 or $(CH_3)_2SO$. In methylenechloride the $VO(PTO)_2$ is a monomer: (Molecular weight expected 319, found 307).

The $VO(AET)_2$ and $VO(DAET)_2$ are both blue crystalline solids that are only slightly soluble in methanol and dimethylsulfoxide. Unfortunately, both of these complexes decompose quickly in solution. The $VO(AET)_2$ can be stored for months in dry air but the $VO(DAET)_2$ will decompose in a dry box filled with dry nitrogen within two hours if moistened with ethanol. The dry $VO(DAET)_2$ decomposes in air within an hour and must be stored under a vacuum. The instability of $VO(DAET)_2$ made analysis extremely difficult. All attempts to prepare oxovanadium(IV) complexes of N,N-dimethyl-2-aminoethanethiol and N,N-diethyl-2-aminoethanethiol resulted in failure.

The difference in the stabilities of $VO(AET)_2$ and $VO(DAET)_2$ might be due to the greater steric hindrance imposed by the decyl groups either on the axial vanadyl-oxygen or on the donor atom *cis* to the coordinated nitrogen. Our inability to prepare the oxovanadium(IV) complexes of N,N-dimethyl-2-aminoethanethiol and N,N-diethyl-2-aminoethanethiol may also be related to steric factors.

Pyridine adducts of $VO(ABT)_2$ and $VO(PTO)_2$ were isolated. The $VO(ABT)_2Py$ is aqua-colored and was obtained from a CCl_4-pyridine mixture. This adduct is extremely unstable in air. Even in a vacuum the molecule decomposes to a mixture of white, brown, and green powders. The characterization of $VO(ABT)_2Py$ was hampered by its ease of decomposition. We were not able to separate the pyridine from the $VO(ABT)_2Py$ without completely destroying the complex. The $VO(ABT)_2Py$ is soluble in a large variety of polar solvents but the color of the solution varies with the solvent. This variation in color as a function of solvent suggests that the coordinated pyridine may be totally or partially displaced by the solvent molecule. Spectral evidence for such a conclusion is discussed in the section on electronic spectra.

A green pyridine adduct of $VO(PTO)_2$ could be isolated from a pyridine-methylenechloride solution of $VO(PTO)_2$. The $VO(PTO)_2Py$ appears to be more stable than $VO(ABT)_2Py$. Unlike the $VO(ABT)_2Py$, the $VO(PTO)_2Py$ can be stored under a vacuum. Nevertheless, the $VO(PTO)_2Py$ is considerably less stable

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Table I. Infrared Spectral Data (cm^{-1})

	ν_{VO} region	ν_{NH} region	ν_{NO}
$VO(ABT)_2$	997, 989	3050, 3180	
$VO(ABT)_2Py$	962		
$VO(PTO)_2$	966		1240
$VO(PTO)_2Py$	990 w, 974, 966, 940, 930		
$VO(AET)_2$	965, 985	3206, 3110, 1575	
$VO(DAET)_2$	944, 997	3197	

than the pyridine adduct of bis(acetylacetonato)oxovanadium(IV)[25] ($VO(acac)_2$). The $VO(acac)_2Py$ is stable in a variety of inert solvents but the $VO(PTO)_2Py$ will revert to $VO(PTO)_2$ if it is washed in any of a variety of solvents such as $(CH_3)_2SO$, CH_2Cl_2 or $(C_2H_5)_2O$. Other pyridine adducts of sulfur-containing oxovanadium(IV) complexes are also unstable. For example, the pyridine adduct of the dithiocarbamate complex of oxovanadium(IV) can be easily decomposed forming parent complex and pyridine if the adduct is merely washed in a non-coordinating solvent such as diethylether.[7]

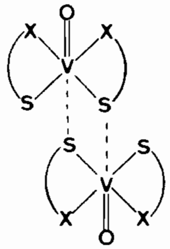
Magnetic Moments. The $VO(ABT)_2$ and $VO(PTO)_2$ have magnetic moments close to the spin-only value for a d^1 system, 1.76 BM and 1.72 BM, respectively. The magnetic moment for $VO(AET)_2$ has a subnormal magnetic moment of 1.54 BM. Subnormal magnetic moments have been observed for a number of oxovanadium(IV) complexes and have been attributed to either direct vanadium-vanadium metal interaction or antiferromagnetic exchange.[21,26]

Infrared Spectra. There were no indications of either lattice water or coordinated water in any of the infrared spectra of the complexes prepared in this study. The absence of bands in the S–H stretching region suggests that the mercaptide group has coordinated to the vanadium(IV), and the N–H stretching frequencies (Table I) of $VO(AET)_2$, $VO(ABT)_2$, and $VO(DAET)_2$ fall within the range expected for coordinated amines.[27] Although the N–H stretching frequency for $VO(DAET)_2$ at 3147 cm^{-1} (Table I) is considerably lower than the frequency expected for an uncoordinated amine[27] ($\sim$3300 cm^{-1}), it is higher than the N–H stretching frequency found for $Ni(DAET)_2$, 3090 cm^{-1}.[28] The higher N–H stretching frequency for $VO(DAET)_2$ suggests that the nitrogen-vanadium(IV) bond is weaker than the nitrogen-nickel (II) bond because the stronger the nitrogen-metal bond, the lower the electron density between the nitrogen and hydrogen.

A decrease in the frequency for the N–O stretching vibration in PTO would also be expected if the oxygen were coordinated to the vanadium.[29] The $VO(PTO)_2$ complex contains two bands in the 1200-1300 cm^{-1} region. The most intense band is at 1240 cm^{-1}, and is probably the N–O stretching frequancy which shfited from 1260 cm^{-1} in NaPTO. This shift suggests that the oxygen is coordinated; however, the small difference in the ν_{NO} between NaPTO and $VO(PTO)_2$ indicates tehat the oxygen is not very strongly bonded to the vanadium(IV).[30] Unfortunately, there are too many peaks in the N–O region to make an assignment for $VO(PTO)_2Py$.

The vanadyl-oxygen bands are normally found between 1050 cm^{-1} and 930 cm^{-1}. The V–O stretching frequency of $VO(ABT)_2$ falls in approximately the same range as other oxovanadium(IV) complexes. (Table I). The acetylacetonate,[25] the monothio-β-diketones[19,20] and dithiocarbamates[15] complexes of oxovanadium(IV) also have V–O stretching frequencies in the 995 cm^{-1} region.

In constrast, the V–O stretching frequencies of $VO(PTO)_2$, $VO(AET)_2$ and $VO(DAET)_2$ are considerably lower than most oxovanadium(IV) complexes (966-944 cm^{-1}) (Table I). These low stretching frequencies found in the solid state may be due to the coordinated mercapto groups acting as a bridge (I and II). Such an association should exert a degree of *trans* influence on the V–O bond resulting in a decrease in the pπ→dπ interaction between the vanadyl-oxygen and vanadium ion; and hence, lower the V–O stretching frequency. There are many examples of mercaptides coordinated to transition metals that associate in such a manner.[31] It is also possible that intermolecular association could occur *via* the vanadyl-oxygen. Although there are some examples of the V=O–V type associations, the vanadyl-oxygen is a weaker nucleophile than the coordinated mercaptide; therefore, such an association appears less likely. Also, the V–O stretching frequency for V=O–V association is found in the 900 cm^{-1} region.[32] No band



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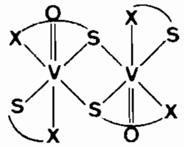

II

X = nitrogen or oxygen

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was found in this region. Another explanation may be that the in-plane ligands have such a strong electron-donating capacity to the vanadium ion that the charge built up on the vanadium ion reduces its capacity to accept the p_π electrons from the oxygen. This reduction in the π-bonding between the vanadium and oxygen is manifested in the lower V–O stretching frequency. Boucher and Yen observed lower V–O stretching frequencies for the stronger in-plane ligands than for weaker in-plane ligands.[33]

The ν_{V-O} is lower for solid $VO(ABT)_2Py$ than for solid $VO(ABT)_2$ (Table I). Also the ν_{V-O} stretching frequency decreases for $VO(ABT)_2$ in all polar solvents (Table II). Such data suggest that either the pyridine or the polar solvent is coordinating to the vacant sixth apical position in $VO(ABT)_2$; thereby, decreasing the vanadium-vanadyl-oxygen double bond character.[34]

Table II. Infrared Spectral Data for $VO(ABT)_2$ in Various Solvents.

Solvent	ν_{VO}
Nujol	997, 989
Ethanol	960
Pyridine	960
N,N-dimethylformamide	980

The V–O stretching frequency region for solid $VO(PTO)_2Py$ is more complicated than for $VO(ABT)_2Py$. Peaks were found at 990 cm^{-1}, 947 cm^{-1}, 966 cm^{-1}, 940 cm^{-1}, and 930 cm^{-1}. The strongest bands are found at 940 cm^{-1} and 930 cm^{-1}. Although the presence of all these bands cannot be fully explained, it is possible that $VO(PTO)_2Py$ is a mixture of geometric isomers. For example, the coordinated pyridine may be *cis* or *trans* from the oxo-oxygen. DaSilva and Wootton have postulated the existence of *cis* and *trans* $VO(acac)_2Py$ in equilibrium with each other in solution.[35] *Cis* and *trans* isomers may also exist in the solid state for $VO(PTO)_2Py$. Such a mixture of isomers may explain why the N-O stretching frequency range is far more complicated for $VO(PTO)_2Py$ than for $VO(PTO)_2$.

The V–O stretch for $VO(PTO)_2$ in the nonpolar solvent, chloroform, and the polar solvent, N,N-dimethylformamide, are about the same, 983 cm^{-1} (Table III). However, in strongly coordinating solvents such as pyridine and 4-methylpyridine the V–O stretch is lowered. But in a 25 to 1 ratio of pyridine or 4 substituted pyridine N-oxide to $VO(PTO)_2$ in CH_2Cl_2 (Table IV), the V–O stretching frequency of $VO(PTO)_2$ is identical to that in pure CH_2Cl_2. These data in Table IV indicate that the V–O stretching frequency for $VO(PTO)_2$ is less sensitive to polar solvents than are the stretching frequencies for $VO(ABT)_2$, $VO(acac)_2$[9] or the monothio-β-diketones oxovanadium(IV) complexes.[19]

Table III. Infrared Spectral Data for $VO(PTO)_2$ in Various Solvents

Solvent	$\nu_{VO}cm^{-1}$*
Nujol	978 w, 965
Methylenechloride	983
Chloroform	984
N,N-dimethylformamide	983
Pyridine	978, 948
4-methylpyridine	984, 948

* Most intense peak underlined

Table IV. Infrared Spectral Data for $VO(PTO)_2$ in CH_2Cl_2 with Various Bases.

Base (B)	Ratio B: $VO(PTO)_2$	$\nu_{VO}(cm^{-1})$
Pyridine N-oxide	25: 1	983
Pyridine N-oxide	35: 1	984
4-methylpyridine N-oxide	20: 1	984, 939 sh.
4-methylpyridine N-oxide	30: 1	983, 940 sh.
4-cyanopyridine N-oxide	sat.	983
Pyridine	25: 1	989, 984, sh.

The V–O stretch for $VO(PTO)_2$ is lower in the solid state (966 cm^{-1}) than in inert solvents (984 cm^{-1}). This difference may be due to either crystal packing forces or because $VO(PTO)_2$ is a polynuclear complex in the solid state (I or II) and a monomeric in CH_2Cl_2.

The nature of monomeric $VO(PTO)_2$ in nonpolar solvents is not known. That the V–O stretch is invarient upon the addition of potential Lewis bases (Table IV) to a CH_2Cl_2 solution of $VO(PTO)_2$ may be due to one or more factors: a) $VO(PTO)_2$ is a trigonal bipyramidal structure. b) $VO(PTO)_2$ is a square pyramid but the sixth site *trans* to the apical oxygen is sterically hindered. However, models give no indication of steric hindrance of the acceptor site. c) $VO(PTO)_2$ is a square pyramid but the V–O stretching frequency is insensitive to the nature of the base coordinating *trans* to oxy-oxygen because effective in-plane bonding reduced the acceptor ability of the vanadium(IV) ion. Boucher and co-workers[36] observed small solvent effects on square pyramidal oxovanadium(IV) complexes which they attributed to strong in-plane bonding. However, there is no reason to believe that PTO is a stronger sigma donor than other bidentate sulfur-containing ligands. Therefore, it appers likely that $VO(PTO)_2$ has a trigonal bipyramidal structure in nonpolar solvents.

Visible Spectra. The mull spectrum of $VO(ABT)_2$ contains three bands, 16 kK, 19 kK, and 22.3 kK (Table V). Larkworthy, Murphy, and Phillips[17] used the Ballhausen and Gray[37] Molecule Orbital Scheme for $VO(H_2O)_5^{2+}$ to assign transitions to these bands

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in order of increasing energy: $b_2 \rightarrow e_\pi^*$ (I); $b_2 \rightarrow b_1$ (II); and $b_2 \rightarrow a_1^*$ (III). Although the electronic structure of oxovanadium(IV) has been the focus of much discussion,[3,4,37,38] there is no general agreement on the relative ordering of the b_1^* and e_π^* levels; and therefore, it is difficult to make a definite assignment. The same reasonable assignments used for $VO(ABT)_2$ can be given to the three bands found in the complex $VO(DAET)_2$ (Table V).

Table V. Electronic Spectral Data in Nujol (in kK).

	I	II	III
$VO(ATB)_2$	16.4	19.0	22.3
$VO(ABT)_2Py$	12.7	156	21.6
$VO(PTO)_2$	—	17.4	19.2
$VO(PTO)_2Py$	12.9	17.5	20.6
$VO(AET)_2$	17.4	19.1	—
$VO(DAET)_2$	13.8	17.3	19.1

Assigning the electronic transitions for $VO(AET)_2$ and $VO(PTO)_2$ is difficult because only two bands were observed for both compounds. Nevertheless, the electronic spectrum of pyridine adducts of $VO(PTO)_2$ can aid in assigning electronic transitions. Coordination of a polar molecule such as pyridine *trans* to the apical oxygen atom stabilizes the e_π^* level because it reduces the commitment of the d_{zx} and d_{zy} orbitals to the vanadium-oxygen bond. Therefore, a red shift for Band I ($b_2 \rightarrow e_\pi^*$) is observed in most oxovanadium(IV) complexes.[3,4] However, the b_1^* level is sensitive to the strength of the in-plane donors, and consequently the $b_2 \rightarrow b_1^*$ transition either is not affected by a base coordinating to the vacant axial position or only a small increase in energy may occur. The increase in energy of the $b_2 \rightarrow b_1^*$ transition has been attributed to the base positioned *trans* to the apical vanadyl-oxygen which forces the vanadium atom closer to the basal plane. When pyridine is coordinated to the $VO(PTO)_2$, the band at 17.4 kK does not significantly change strongly indicating that the 17.4 kK band for $VO(PTO_2$ and the 17.5 kK band for the $VO(PTO)_2Py$ is caused by the $b_2 \rightarrow a_1^*$ transition. Therefore, the 19.2 kK band for $VO(PTO)_2$ and the 20.6 kK band for $VO(PTO)_2Py$ can be assigned either the $b_2 \rightarrow a_1^*$ transition or a charge transfer band. Since the $VO(AET)_2$ and the $VO(ABT)_2$ appear to have similar stabilities, it is believed that the 19.1 kK band for $VO(AET)_2$ and the 19.0 kK band for $VO(ABT)_2$ are produced by the $b_2 \rightarrow b_1^*$ transition and the lower energy bands, 17.4 kK and 16.4 kK for $VO(AET)_2$ and $VO(ABT)_2$ recpectively, are produced by the $b_2 \rightarrow e_\pi^*$ transition.

The mull spectra of $VO(ABT)_2$ and $VO(ABT)_2Py$ are considerably different from $VO(PTO)_2$ and $VO(PTO)_2Py$. Upon coordination of pyridine to $VO(ABT)_2$, both Band I and Band II decrease in energy (Table V). The shift of Band II from 19 kK to 15.6 kK upon coordinating pyridine to the sixth vacant site of $VO(ABT)_2$ indicates that the pyridine has weakened the in-plane donor strength of *o*-aminobenzenethiol. This reduction in donor strength explains why heating the $VO(ABT)_2Py$ in a vacuum results in a decomposition of the entire molecule. Steric hindrance imposed by the pyridine on the in-plane *o*-aminobenzenethiol might be causing this weakening of the in-plane ligand. However, unlike $VO(ABT)_2$, coordinating pyridine to $VO(PTO)_2$ had little effect on the in-plane donor strenght. Also, unlike $VO(ABT)_2Py$, the coordinated pyridine can be removed from the $VO(PTO)_2$ without decomposing the parent molecule. These properties of $VO(PTO)_2$ are quite similar to those of bis(N,N-dimethyldithiocarbamato)oxovanadium(IV) and its pyridine adducts. The band in the electronic spectrum assigned the transition $b_2 \rightarrow b_1^*$ has similar energy in both the parent molecule and its adduct. Also, like the $VO(PTO)_2Py$ the pyridine is weakly coordinated to bis(N,N-dimethyldithiocarbamato)-oxovanadium(IV) and can be easily removed.[7]

In polar solvents such as pyridine and ethanol, the electronic spectrum of $VO(ABT)_2$ does not resemble its spectrum in Nujol mull (Table VI). This difference again indicates that the polar solvent is coordinating *trans* to the vanadyl oxygen and provides additional evidence that $VO(ABT)_2$ has a square pyramidal configuration in the solid state.[11,39] Also, it is significant to note that when the $VO(ABT)_2$ is dissolved in pyridine, the spectrum exhibits peaks at 12.7 kK and 15.6 kK as does the mull spectrum of $VO(ABT)_2Py$; thus, strongly reaffirming our hypothesis that the oxovanadium(IV) species in pyridine solution is the same species as the solid $VO(ABT)_2Py$. Finally, in polar solvents both Band I and Band II of $VO(ABT)_2$ decrease in energy (Table VI) suggesting that the in-plane ligands have been weakened upon coordination of the polar solvent.

Table VI. Electronic Spectral Data of $VO(ABT)_2$ in Various Polar Solvents (in kK).

Solvent	I	II	III
Nujol	16.4	19.0	22.3
Ethanol	11.8	17.4	—
Pyridine	12.7	15.6	—
N,N-Dimethylformamide	13.3	—	—

The spectra of $VO(ABT)_2Py$ in a variety of solvents are tabulated on Table VII. Since the spectra are a function of the solvent, the data suggest that coordinated pyridine can be partially or totally replaced by a solvent molecule. If pyridine is added to an ethanol solution of $VO(ABT)_2Py$, the spectrum reverts to a spectrum similar to that of $VO(ABT)_2Py$ in pure pyridine.

The electronic spectrum of $VO(PTO)_2$ in CH_2Cl_2 (Table VIII) is considerably different from that found in Nujol mull. A band was observed at 19.8 kK, a poorly defined shoulder at 15.2 kK, and a very broad weak band at 10.1 kK. The differences between the

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Table VII. Electronic Spectra of $VO(ABT)_2Py$ in Various Polar Solvents (in kK).

Solvent	I	II	III
methanol	12.30	17.40	hidden under
ethanol	12.40	16.00	charge transfer
N,N-dimethylformamide	12.20*	14.50	23.80
Dimethylsulfoxide	12.20*	14.50	29.40
4-methylpyridine	12.70	15.60	21.50
3-methylpyridine	12.70	15.60	21.50

* these bands were broad.

Table VIII. Electronic Spectra of $VO(PTO)_2$ in Solution (in kK).

Solvent	Base (B)	Ratio B: $VO(PTO)_2$	I	II	III
CH_2Cl_2	—	—	10.1(3.9)	15.2(57)	19.8(76)
CH_2Cl_2	Pyridine	25.1	12.5	16.3	19.3
CH_2Cl_2	Pyridine N-oxide	25.1	13.6	—	19.6
Pyridine	—	—	12.7(41)	13.8(48)	—
$(CH_3)_2SO$	—	—	—	—	19.8(105)
Aniline	—	—	—	17.6(116)	19.1(120)

solid spectrum and the nonpolar solvent CH_2Cl_2 again provide evidence that different structures exist in the solid state and in solution. Although the poorly defined peak at 15.2 kK was not observed in $(CH_3)_2SO$ (Table VIII) and limited solubility prevented observation of the weak peak at 10.2 kK, the spectra of $VO(PTO)_2$ in $(CH_3)_2SO$ resembled the spectra in CH_2Cl_2. In addition, both solutions had similar colors. The similarity of the spectra taken in $(CH_3)_2SO$ and in CH_2Cl_2 indicates that both solvents are not reacting with $VO(PTO)_2$. Spectra taken in pyridine and aniline are quite different from spectra taken in $(CH_3)_2SO$ and CH_2Cl_2 indicating that some type of interaction with these solvents had occurred. Neither the electronic spectrum of $VO(PTO)_2$ in pure pyridine or the electronic spectrum of $VO(PTO)_2$ plus pyridine in a 1 to 25 ratio in methylenechloride resembles the solid spectrum of the adduct $VO(PTO)_2Py$. Since the chemical changes occurring in the presence of pyridine can only be speculated upon, it is fruitless to overinterpret the data on Table VIII.

Relative Base Strengths and Steric Effects. Selbin and coworkers[6] have attempted to rank base strength relative to $VO(acac)_2$ by measuring variations in the V–O stretching frequencies as various Lewis bases in equal molar quantities are added to a $CHCl_3$ solution of $VO(acac)_2$. We have also found the V–O stretching frequency is insensitive to potential bases (Tables II and III). For example, the V–O stretching frequencies for $VO(TPO)_2$ in pyridine and 4-methylpyridine are shifted the same number of cm^{-1} units compared to $VO(PTO)_2$ in CH_2Cl_2 (Table III).

Selbin and Ortolano[11] found a more sensitive parameter for ranking Lewis bases relative to the Lewis acid $VO(acac)_2$. They related the relative base strengths to the difference between the first two lowest energy bands, $D_{I,II}$. Using the $D_{I,II}$ parameter Selbin and Ortolano[11] were able to rank base strengths relative to the Lewis acid $VO(acac)_2$. Although $D_{I,II}$ appeared to be more sensitive to base strength than the ν_{VO}, the ordering of base strengths as measured by either parameter did not parallel the spectrochemical series or any other known series of base strengths. We also found no logical ordering of base strength could be correlated with the $D_{I,II}$ obtained upon dissolving $VO(ABT)_2Py$ in various solvents. The order obtained is: $CH_3OH > C_2H_5OH >$ 4-methyl-pyridine > N,N-dimethylformamide. A similar order was obtainned by Selbin and Ortolano for $VO(acac)_2$.[11]

Popp, Nelson, and Ragsdale[40] proved the ordering of base strength relative to $VO(acac)_2$ was dependent on steric factors, and it was for this reason that no logical ordering of base strengths was observed by Selbin and co-workers. Popp, Nelson, and Ragsdale employed para-substituted pyridine N-oxides in order to hold the steric factor of the base constant and obtained a linear correlation between σ_{pyno} versus the heat of reaction of $VO(acac)_2$ with these bases. To test the applicability of the Selbin and Ortolano new parameter, $D_{I,II}$, we measured the $D_{I,II}$ for a mixture of $VO(acac)_2$ with 4-substituted-pyridine N-oxides in CH_2Cl_2 in a constant 10 to 1 base to $VO(acac)_2$ ratio.

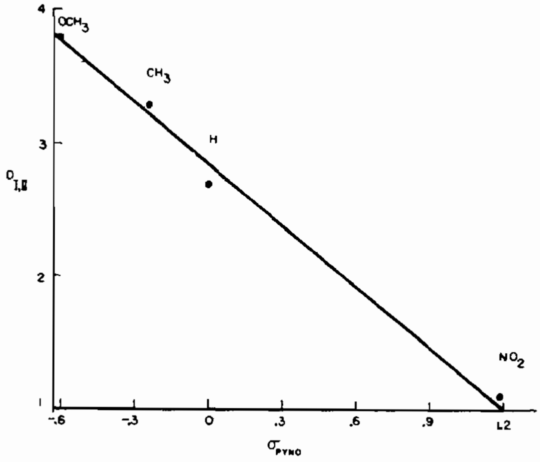

Figure 1. $D_{I,II}$ vs. σ_{pyno} for 4-substituted Pyridine N-oxides and $VO(ABT)_2Py$ in C_2H_5OH.

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[40] C. J. Popp, J. H. Nelson, and R. O. Ragsdale, *J. Amer. Chem. Soc.*, *91*, 610 (1969).

Table IX. Electronic Spectra of VO(ABT)$_2$Py and Various Bases in Ethanol (in kK)

Reacting group	transition (in kK) I	II	III	difference II-I
p-CH$_3$O-pyridine N-oxide	12.70	16.50	—	3.80
p-CH$_3$-pyridine N-oxide	12.70	16.00	—	3.30
pyridine N-oxide	12.70	15.40	—	2.70
p-NO$_2$-pyridine N-oxide	12.70	13.80	20.00	1.10

An excellent linear relation was obtained upon plotting $D_{I,II}$ versus σ_{pyno}, suggesting that the $D_{I,II}$ parameter has some general applicability for ranking base strengths.[41] A similar experiment was attempted with VO(ABT)$_2$Py using 4-substituted pyridine N-oxides in CH$_2$Cl$_2$. (The greater solubility of VO(ABT)$_2$Py as compared to VO(ABT)$_2$ was the reason for its use.) The $D_{I,II}$ parameter measured the extent of displacement of pyridine by 4-substituted pyridine N-oxide (Table IX). Again a linear relationship was obtained between $D_{I,II}$ and σ_{pyno} (Figure 1). It can therefore be concluded that the vanadium(IV) ion is not in the basal plane of the in-plane ligands for the complex VO(ABT)$_2$Py; and hence, steric factors are significant in determining relative base strengths. Because of these steric factors, a systematic study of the specific Lewis acid character of various oxovanadium(IV) complexes as a function of the «hardness» or «softness» of the in-plane donor atoms should be extremely difficult.

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[41] To be published.