

EPR Study of Vanadium Complexes

Objective

To prepare two vanadium complexes and observe what effect different chemical environments has on the electron paramagnetic resonance (EPR) spectrum of each compound.

Introduction

Element 23, first claimed to have been discovered by A. M. del Rio in 1801, then rediscovered by N. G. Sefström in 1830, was named vanadium after Vanadis, the Scandinavian goddess of beauty, because of the richness and variety of colors in its compounds. While vanadium is widely spread with a natural abundance of ~0.014% (making it the nineteenth most abundant element and fifth most abundant transition metal), there are few concentrated deposits and pure vanadium is rare due to its reactivity toward oxygen. The primary commercial uses are in alloy steels and cast iron to which it adds ductility and shock resistance. Consequently, most commercial production of vanadium is as an iron alloy, ferrovanadium. Although vanadium can possess formal oxidation states from +5 to -1, the most stable under normal conditions is +4, with +3 and +2 states also having many well-characterized compounds. The chemistry of V^{IV} is dominated by the formation of the oxo species, and a wide range of compounds with VO^{2+} (vanadyl) groups are known. Some of the wide variety of vanadium complexes is shown below.

Oxidation State	Coordination Number	Geometry	Complex
-1	6	Octahedral	$[V(CO)_6]^-$
0	6	Octahedral	$V(CO)_6$
1	6	Octahedral	$[V(bipy)_3]^+$
2	6	Octahedral	$[V(CN)_6]^{4-}$
	6	Trigonal prismatic	VS
3	3	Planar	$V(N(SiMe_3)_2)_3$
	4	Tetrahedral	$[VCl_4]^-$
	5	Trigonal bipyramidal	$VCl_3(NMe_3)_2$
	6	Octahedral	$[V(C_2O_4)_3]^{3-}$
4	4	Tetrahedral	VCl_4
	5	Trigonal bipyramidal	$VOCl_2(NMe_3)_2$
	5	Square pyramidal	$VO(acac)_2$
	6	Octahedral	$VCl_4(bipy)$
	8	Dodecahedral	$VCl_4(diars)_2$
5	4	Tetrahedral	$VOCl_3$
	5	Trigonal bipyramidal	VCl_5
	5	Square pyramidal	$[VOF_4]^-$
	6	Octahedral	$[VF_6]^-$
	7	Pentagonal bipyramidal	$VO(S_2CNEt_2)_3$
	8	Dodecahedral	$[V(O_2)_4]^{3-}$

The extremely stable VO^{2+} complexes are the most widely studied of the vanadium(IV) complexes and are often a result of hydrolysis of other vanadium(IV) complexes. Many of compounds containing the VO^{2+} unit are blue to green, form stable complexes with *F*, *Cl*, *O*, and *N* donor ligands, and can be cationic, neutral, or anionic. Most often, these compounds are 5 coordinate and are almost always square pyramidal. Frequently, these vanadium(IV) complexes are studied by EPR spectroscopy as they have one unpaired electron and possess very characteristic spectra.

As you remember, Electron spin resonance (ESR) spectroscopy, also referred to as electron paramagnetic resonance (EPR) spectroscopy, is a versatile, nondestructive analytical technique which can be used for a variety of applications including: oxidation and reduction processes, biradicals and triplet state molecules, reaction kinetics, as well as numerous additional applications in biology, medicine and physics. However, this technique can only be applied to samples having one or more unpaired electrons. When an electron is placed within an applied magnetic field, B_o , the two possible spin states of the electron have different energies. This energy difference is a result of the Zeeman effect. The lower energy state occurs when the magnetic moment of the electron is aligned with the magnetic field and a higher energy state where m is aligned against the magnetic field. In EPR spectrometers a phase-sensitive detector is used. This results in the absorption signal being presented as the first derivative. So the absorption maximum corresponds to the point where the spectrum passes through zero. In the EPR spectrum, there are two important pieces of information to obtain, the proportionality factor and hyperfine interactions (if present).

As spectra can be obtained at a variety of frequencies, the field for resonance (the strength of the magnetic field where absorption occurs) does not provide unique identification of compounds. The proportionality factor, however, can yield more useful information. This can be thought of as being analogous to a chemical shift in NMR. The proportionality factor, g , is calculated from the strength of the magnetic field at the center of the EPR signal and the frequency the spectrum was obtained at:

$$g = \frac{h\nu}{\mu_B B_o} = \frac{714.48\nu(\text{GHz})}{B(\text{G})}$$

For a free electron, the proportionality factor is 2.00232. For organic radicals, the value is typically quite close to that of a free electron with values ranging from 1.99-2.01. For transition metal compounds, large variations can occur due to spin-orbit coupling and zero-field splitting and results in values ranging from 1.4-3.0.

In addition to the applied magnetic field, unpaired electrons are also sensitive to their local environments. Frequently the nuclei of the atoms in a molecule or complex have a magnetic moment, which produces a local magnetic field at the electron. The resulting interaction between the electron and the nuclei is called the hyperfine interaction which is observed as a 'splitting' of the EPR signal. Hyperfine interactions can be used to provide a great deal of information about the sample including providing information about the number and identity of nuclei in a complex as well as their distance from the unpaired electron.

The coupling patterns that are observed in EPR spectra are determined by the same rules that apply to NMR spectra. However, in EPR spectra it is more common to see coupling to nuclei

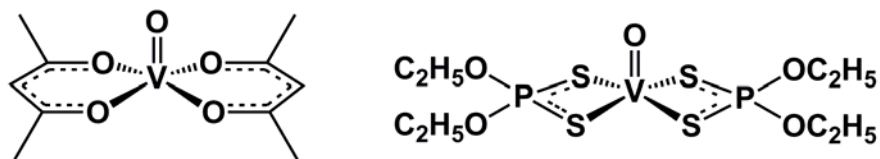
with spins greater than $\frac{1}{2}$. The number of lines which result from the coupling can be determined by the formula:

$$2NI + 1$$

where N is the number of equivalent nuclei and I is the spin. It is important to note that this formula only determines the number of lines in the spectrum, not their relative intensities. The relative intensities of the lines are determined by the number of interacting nuclei. Coupling to a single nucleus gives lines of equal intensity. When multiple nuclei of spin $\frac{1}{2}$ are interacting, the relative intensities of the lines follow the binomial distribution shown below.

# of equivalent nuclei	Relative Intensities
0	1
1	1:1
2	1:2:1
3	1:3:3:1
4	1:4:6:4:1
5	1:5:10:10:5:1
6	1:6:15:20:15:6:1

Similar distributions can be derived for n equivalent nuclei with spins greater than $\frac{1}{2}$.



In this experiment we will prepare and characterize two complexes, vanadium (IV) bis(acetylacetonato)oxide and bis(O,O'-diethyldithiophosphato)oxovanadium (IV). Characterization of these two complexes by IR and EPR spectroscopy allows for study of the same unpaired d^1 electron system while observing how changing the chemical environment affects the spectra.

Safety

WEAR SAFETY GOGGLES AT ALL TIMES WHEN IN THE LABORATORY.

Toluene is a flammable, toxic solvent; keep away from open flame or other sources of ignition.

Materials

Vanadium (IV) sulfate oxide hydrate, acetylacetone, sodium bicarbonate, ammonium O,O'-diethyldithiophosphate and toluene.

Procedures

Be sure to record all scientific observations during each step of the procedure.

Synthesis of bis(O,O'-diethyldithiophosphato)oxovanadium (IV)

1. In a small beaker or flask (25 mL) dissolve 1 g vanadyl sulfate in 2 mL deionized water.
2. Once completely dissolved, add 2.5 g ammonium O,O'-diethyldithiophosphate.
3. Stir the reaction mixture with a glass stir rod until the ligand is fully dissolved, then transfer the reaction flask to an ice bath. Leave the flask on ice until all of the purple crystals have formed. (Continue with synthesis of VO(acac)₂ while waiting)
4. Add a small amount of toluene (5-10 mL) to the flask to dissolve the purple crystals.
5. Carefully pipet the toluene phase into a small vial and bubble nitrogen through the solution for 5 minutes. Quickly cap the vial, keeping the vial filled with nitrogen. The complex is more stable in solution than as a solid, but prolonged exposure to air will cause the complex to decompose.
6. Use a small amount of the toluene solution to collect an IR spectrum of the complex.

Synthesis of vanadyl acetylacetonate

1. In a small beaker or flask (50 mL) with a magnetic stir bar, dissolve 1 g vanadyl sulfate in 10 mL deionized water.
2. Add 1.5 mL acetylacetone and stir for 15 minutes.
3. Slowly add very small portions of solid sodium bicarbonate to the reaction mixture with vigorous stirring. Continue adding until the evolution of CO₂ ceases.
4. Stir the reaction for an additional 15 minutes.
5. Collect the solid by vacuum filtration. Wash the solid with (2) 5 mL portions of cold DI water and (2) 5 mL portions of cold acetone.
6. Collect an IR spectrum of the complex.

Collection of EPR spectra

1. Dissolve a small amount (20-30 mg) of vanadyl acetylacetonate in 20 mL of toluene.
2. Fill a 4 mm quartz EPR tube approximately 2-3 inches full with the sample. The solution in the tube should be just faintly colored—too concentrated and you will be unable to collect a spectrum.
3. In a separate vial, dilute one drop of the bis(O,O'-diethyldithiophosphato)oxovanadium (IV) toluene solution with an additional 10 mL of **dry** toluene.
4. Fill a separate 4 mm quartz EPR tube approximately 2-3 inches full with the sample. Again the solution should be just faintly colored.

Pre-lab Questions

1. Predict the EPR spectrum for each vanadium complex. Would you expect to see every predicted line? What might be one reason to see a different number of lines than predicted?
2. Vanadyl complexes also have characteristic IR spectroscopic features. Where would you expect to observe the V=O stretch in these complexes?

Additional Information

For additional reading about the chemistry of vanadium see:

Greenwood, N. N.; Ernschaw, A., Chapter 22: Vanadium, Niobium and Tantalum. In *Chemistry of the Elements*, Second ed.; Elsevier Science Ltd.: Oxford, 1997; pp 976-1001.

Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M., Chapter 17B: The Elements of the First Transition Series: Vanadium. In *Advanced Inorganic Chemistry*, Sixth ed.; John Wiley & Sons, Inc.: New York, 1999; pp 714-735.

For additional reading about EPR spectroscopy see:

Atkins, P., Chapter 18: Spectroscopy 3: Magnetic Resonance. In *Physical Chemistry*, Sixth ed.; W. H. Freeman and Company: New York, 1998; pp 527-566.

Ebsworth, E. V. A.; Rankin, D. W. H.; Craddock, S., Chapter 3: Electron Spin and Nuclear Quadrupole Resonance Spectroscopy. In *Structural Methods in Inorganic Chemistry*, Second ed.; CRC Press: Boca Raton, 1991; pp 115-141.

For a more in-depth review:

Weil, J.; Bolton, J. R., *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*. Second ed.; John Wiley & Sons, Inc.: Hoboken, 2007; p 664.

Atherton, N. M., *Principles of Electron Spin Resonance*. Ellis Horwood PTR Prentice Hall: New York, 1993; p 585.