

VANADIUM TARTRATE COMPLEXES

Objective of this experiment: to study paramagnetism and colours in transition metals; optical isomerism; co-operative research.

A feature of the transition elements is that they possess valence electrons that sit in the d-orbitals. As is usual, up to two electrons of opposite spin can be paired to sit in each orbital. There are five such d-orbitals, which when in a coordination complex, are not of equal energy. Thus, there is now a choice of whether the lowest energy orbital is to be occupied first, or have other factors influenced the preference for a higher energy orbital to be used? This can be a complex issue which we do not need to fully contemplate in this course.

Colours

Of more immediate interest is the fact that since we can have filled, half-filled and empty orbitals in close proximity to one another on the energy scale, we can easily move d electrons from one orbital to another. The energy given by visible light will do this, so that some of the daylight is absorbed, removing that wavelength from the spectrum and reflecting back the remaining wavelengths. This causes many transition complexes to appear coloured. Visible spectroscopy allows us to put a number to the wavelengths involved, but of course, our eyes have already defined the colour. This colour is influenced by the size of the gap between the d-orbitals and thus characterises the compound's structure to some degree.

Visible spectroscopy

Although our eyes are good at detecting light in the visible range, it is a subjective process to measure the intensity. Instruments that can do this are visible spectrometers (sometimes called spectrophotometers). A beam of light is passed through a solution causing some of it to be absorbed and re-emitted in all directions. The beam leaving the sample passes through a wavelength filtering device (like a prism) and then to a detector. The result is compared to that obtained by passing the same beam through a control solution, or blank. In some cases, the incident beam may be only one wavelength, or it may be multiple wavelengths, in which case, the scan that is produced is the spectrum characteristic of the sample.

Magnetism

Another feature that is commonly seen in, but is not unique to, transition elements is the existence of unpaired electrons. By knowing how many unpaired electrons exist per molecule (and thus the number of half-filled d-orbitals), we have an understanding of the

The Johnson Matthey Magnetic Susceptibility Balance.

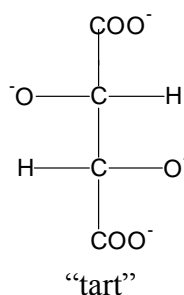
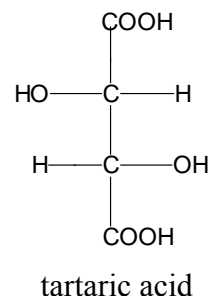
To measure paramagnetism, one must measure the attractive force of a known mass of the pure substance when it is put into a magnetic field. The "old" way of doing this was to weigh a tube of the substance inside and outside of the magnetic field - usually done by switching on and off an electromagnet.

The balance that we will use is more compact, robust and easier to use. It does effectively the same operation but actually measures the force exerted by the sample on a suspended magnet. It does this by measuring the amount of current needed to pass through a coil to create a force to prevent that magnet from moving.

bonding and structure of the complex, and possibly an idea of the oxidation state of the central metal atom. Unpaired electrons can be measured by observing their paramagnetism - which is a property of a substance that is drawn into a magnetic field.

Example

Elemental vanadium has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. V^{3+} has a d^2 configuration, having lost two of the valence electrons from the $4s^2$ orbital first, and then one from the $3d$ set. The electrons could be paired and sit in the same orbital, in which case the magnetic susceptibility will give a value of $n=0$, where n is the number of unpaired electrons. Alternatively, the electrons could have parallel spins and occupy two different orbitals (d orbitals have five possible orientations). Thus, n should have a value of 2.



In the complex to be prepared in this experiment, one of the ligands is derived from tartaric acid. This has the basic structure as given in the drawing, but some subtleties are possible. You will notice that there are two carboxylic acid groups, COOH . Each has a proton that can be removed to allow the oxygen to bond to a metal. This would allow the tartrate dianion (a 2- ion) to be a bidentate ligand. That is, a ligand that has two points of attachment to the metal. Under some circumstances, the two alcohol groups, OH , can also be persuaded to release their

hydrogens and these oxygens will also bond to the metal. Thus the 4- ion is believed to become tetradentate i.e. the tartrate wraps itself around the vanadium so that each of the negative sites forms a bond between the metal and the oxygen.

For the purposes of this experiment, we will define the abbreviation “tart” to represent that 4- ion. Be warned though, that it is more common to find the tartrate as a dianion, and the expression “tart” will often be used to represent it.

In tartaric acid, one can rearrange the atoms to get isomers. Some types of isomers are related to each other by being non-superimposable mirror images of one another. These are known as optical isomers. Tartaric acid has two chiral carbon centres and thus exhibits optical activity.

This property is the ability to rotate the plane of polarised light. Typically, a polarimeter will operate using one source of light, the sodium D line at 589 nm. At any particular wavelength, one enantiomer will rotate the plane of light by an amount proportional to the size of the cell used, and the concentration of solution. The other enantiomer, under similar conditions of concentration, will, of course, rotate the light by exactly the same amount, in the opposite direction.

Measuring Optical Activity

To standardize the units for expressing rotations, the following equation is used:

$$[\alpha_D] = \frac{\alpha}{c.l}$$

where $[\alpha_D]$ = specific rotation for the sodium D line ($\lambda = 589 \text{ nm}$)

α = rotation measured in degrees

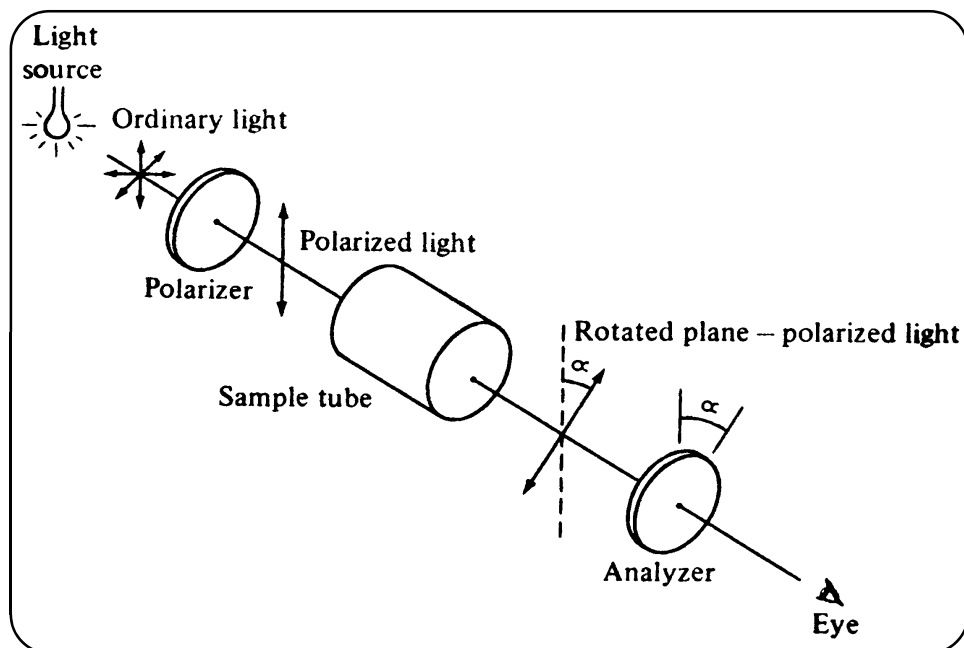
c = concentration in grams of solute per mL solution

l = path length of cell in decimetres

(the standard size is 1 dm = 10 cm)

$$\% \text{ optical purity} = \frac{\alpha_D (\text{measured})}{\alpha_D (\text{theoretical})} \times 100$$

Schematic representation of a polarimeter



Historical note

In 1847, Louis Pasteur had just finished the equivalent of his undergraduate studies at the age of 25. His first research project was to look at some earlier work on the crystals of tartaric acid salts. These were present in the fermentation sludge of the wine industry (mainly potassium hydrogen tartrate or cream of tartar) and had earlier (1831) been shown by Berzelius to have two isomers - one optically active, the other not.

Upon crystallising several salts (using different cations) of tartaric acid, Pasteur noticed that the crystals had a form similar to that of known optically active quartz crystals. More importantly, those crystals all looked identical rather than a mixture of crystals with opposite images. Turning to the other isomer found by Berzelius (dubbed racemic acid), Pasteur expected to not find such a pattern in the crystal form because it was known to be optically inactive. To his surprise, he did find the distinctive pattern. On closer examination, he found that the pattern was present in half the crystals and present in the opposite sense for the remaining half of the crystals. He was able to sort the crystals with a pair of tweezers and ultimately showed that one set rotated the plane of polarised light in one direction whilst the other set rotated in an *equal and opposite* direction.

Although the understanding of molecular structure was not developed at this time, Pasteur reasoned that the external shape of the crystals was indeed related to the internal arrangement of the molecules. Thus, the chirality of the crystal orientation was also the chirality of the molecule.

The synthesis

The half equations for the two reagents involved in the first part of the synthesis are given in the appendix of half-reactions. Once the VO^{2+} has formed, it can react with the tartaric acid in its 4-state to generate the $[\text{VO}(\text{tart})]^{2-}$ ion.

The features of this experiment are:

- a. To observe the colour changes created by reduction of a metal centre during the synthesis of a vanadium(IV) tartrate complex.
- b. To relate the theoretical number of valence electrons with the measurement of the number of unpaired electrons.
- c. To investigate the nature of the complex at different pH, and the reversibility of any changes.
- d. To compare the optical activity of the starting tartaric acid ligand, with the activity of the vanadium tartrate complex.

These properties may be inter-related. The change of colour may be the result of the changes in occupancy of the d orbitals as electrons are added during reduction. Similarly, this may affect the magnetism. (Note: Colour changes can also be the result of rearranging the ligands around the metal as this will also influence the relative positions of the d orbitals.) Changing the pH may change the ability of parts of the tartaric acid molecule to link with the metal. Whether or not optical activity is retained during synthesis can give important information about the mechanism of synthesis.

Procedure:

Pre-lab Assignment:

1. Calculate the molecular weights for the following compounds (a) tartaric acid, (b) cream of tartar, (c) hydrazine monohydrate, (d) ammonium metavanadate, (e) $(\text{NH}_4)_2[\text{VO}(\text{tart})]\text{H}_2\text{O}$.
2. Using the two half-equations for the hydrazine and the vanadate ion given in the appendix of half-reactions, give the balanced equation for this part of the synthesis. Is this an oxidation or reduction of the vanadium?
3. Give a balanced equation for the complete synthesis of $(\text{NH}_4)_2[\text{VO}(\text{tart})]\text{H}_2\text{O}$.
4. Calculate the theoretical yield of $(\text{NH}_4)_2[\text{VO}(\text{tart})]\text{H}_2\text{O}$ based on the quantities in the procedure.
5. What is the oxidation state, and how many valence electrons are there on the vanadium in the following compounds:
 - (a) elemental vanadium, V
 - (b) NH_4VO_3
 - (c) $(\text{NH}_4)_2[\text{VO}(\text{tart})]\text{H}_2\text{O}$

6. Complete the following table using the formulae in the appendix attached to this experiment.

Sample	$(\text{NH}_4)_2[\text{VO}\{-\text{tart}\}]\text{H}_2\text{O}$
m_o (g)	0.8333
m (g)	0.9942
R_o	-30
R	134
length (cm)	3.4
temperature ($^{\circ}\text{C}$)	21
$\chi_g = \{C_{\text{Bal}} \cdot l \cdot (R - R_o)\} / \{(m - m_o) \times 10^9\}$ where $C_{\text{Bal}} = 1.083$	
MW $(\text{NH}_4)_2[\text{VO}\{-\text{tart}\}]\text{H}_2\text{O}$	
$\chi_m = \chi_g \times \text{mol. wt.}$	
diamagnetic corrections (total)	
$\chi_A = \chi_m + \text{diamagnetic corrections}$	
temp (K)	
$\mu_{\text{eff}} = 2.828\sqrt{\chi_A T}$ where T = temp in Kelvin	
$n = \# \text{ unpaired electrons}$	(nearest integer)

- In the synthesis for student C, the masses of the two isomers of tartaric acid are recommended to be the same. Why?
- What does the expression “retention of configuration” mean? Explain it using an example.
- Which is the most toxic reagent that you will use? What precautions will you take?
- Draw a flowchart of the procedure. Construct the data tables that you will need to complete in the lab.

Procedure

Everyone must make the target vanadium compound, with each member of the group using a different optical isomer of tartaric acid during the procedure. There are four parts to the analytical portion - each student is responsible for one part. If your group has only three members, leave out the synthesis using the cream of tartar.

Synthesis of $(\text{NH}_4)_2[\text{VO}(\text{tart})]\text{H}_2\text{O}$:

Precautions:

Hydrazine hydrate is a CANCER SUSPECT AGENT and is highly toxic.

Ammonium metavanadate is toxic and an irritant.

Acetic acid is corrosive.

Ammonia is corrosive and a lachrymator.

In a 50 mL beaker, add water (3.2 mL), glacial acetic acid (1.8 mL) and 3 drops hydrazine monohydrate (0.1 mL, 2 mmol). Heat to 65° with stirring. Add ammonium metavanadate (0.59 g, 5.0 mmol) and 5 mL water and heat until dark blue in color, about 10-15 min. Cool to room temperature and add:

Student A L-tartaric acid (0.76 g, 5.1 mmol)

Student B D-tartaric acid (0.76 g, 5.1 mmol)

Student C L-tartaric acid (0.38 g, 2.5 mmol) and D-tartaric acid (0.38 g, 2.5 mmol) (*note: it is important that the masses of L- and D- tartaric acid be EQUAL*)

Student D cream of tartar (potassium hydrogen tartrate, 0.96 g, 5.1 mmol) followed by ammonium hydroxide (2.5 mL). Stir until the solution is dark purple in color, and cool the mixture in an ice bath. Remove the beaker from the ice-bath and with rapid stirring, add 30 mL acetone slowly to the mixture. Stir 10 min. Vacuum filter, wash with 2 x 5 mL acetone and air-dry. Record the yield. Calculate the percent yield. Hand in a labeled sample.

Analysis of the complex:

Student A: Magnetic susceptibility of $(\text{NH}_4)_2[\text{VO}\{(+)\text{tart}\}]\cdot\text{H}_2\text{O}$ and NH_4VO_3

Refer to the appendix attached to this experiment for the procedure. Record the magnetic susceptibility of your $(\text{NH}_4)_2[\text{VO}\{(+)\text{tart}\}]\cdot\text{H}_2\text{O}$ product as well as the ammonium metavanadate starting material. Calculate μ_{eff} and n for each sample, if the diamagnetic contributions are:

vanadium, V	13×10^{-6}	oxygen, O^{2-}	6×10^{-6}
ammonium, NH_4^+	13×10^{-6}	tartrate, $\text{C}_4\text{H}_2\text{O}_6^{4-}$	55×10^{-6}
water, H_2O	13×10^{-6}		

How do the number of unpaired electrons, n, compare to the oxidation state of the vanadium center and the theoretical number of d electrons?

Student B: Visible spectra of $(\text{NH}_4)_2[\text{VO}\{(-)\text{tart}\}]\cdot\text{H}_2\text{O}$

Dissolve 0.25 g of your $(\text{NH}_4)_2[\text{VO}\{(-)\text{tart}\}]\cdot\text{H}_2\text{O}$ product in 20 mL of distilled water, and divide in half. Record the spectrum (350 - 900 nm) and note the colour.

To the first portion, A, sequentially add:

- 10 drops ammonium hydroxide. Record the spectrum and note the colour. Return the sample to the bulk solution, A.
- 20 drops hydrochloric acid. Record the spectrum and note the colour. Return the sample to the bulk solution, A.
- 60 drops ammonium hydroxide. Record the spectrum and note the colour.

To the second portion, B, add:

- 10 drops hydrochloric acid. Record the spectrum and note the colour.

In a table, report λ_{max} and absorbance values for each peak in each sample. Is the same species present in both acidic and basic solution? Is the conversion from acidic to basic species reversible? Is the conversion from basic to acidic species reversible? Can you suggest what these species might be?

Student C: Optical activity of starting materials

Weigh each of the following accurately and dissolve in exactly 25.00 mL of distilled water in a volumetric flask.

- a) 0.5 g L-tartaric acid
- b) 0.5 g D-tartaric acid
- c) 0.25 g L-tartaric acid and 0.25 g D-tartaric acid (*note: it is important that the masses of L- and D- tartaric acid be EQUAL*)
- d) 0.05 g cream of tartar (potassium hydrogen tartrate)

Transfer the contents of each to a polarimetry cell and record the rotation at 589 nm. Calculate $[\alpha_D]$ for each reagent. How do the $[\alpha_D]$ values of the starting materials compare with each other. How do they compare with the value given on the bottle (or in the Aldrich catalogue)? Express your answer as a % purity.

Student D: Optical activity of products

Weigh accurately ~0.1 g of each product prepared by your team and dissolve each in exactly 100.00 mL of distilled water in a volumetric flask. Transfer the contents of each to a polarimetry cell and record the rotation at 589 nm. Calculate $[\alpha_D]$ for each product. How do the $[\alpha_D]$ values of the starting materials compare to those of the products? Which is more important, the sign or the magnitude of the number? Was this a retention of configuration from the starting materials?

Waste:

All analytical solutions are very dilute and can be flushed down the drain. All solids should be handed in.

Report:

Read the Course Notes to determine the exact requirements for this report, which will be dependent on when you completed the experiment. The core component should include tables of all the data and calculations collected by your group.

Appendix for the magnetic susceptibility measurements using the Johnson-Matthey MSB-1 balance.

The instrument should be turned on about 10 minutes before use. Turn on the scale to x1 and zero before use. Check the position of the rubber collar on the sample tube. It tends to swell if it absorbs solvent and will slide along the tube. For correct use, the bottom of the collar should be 5 cm from the bottom of the tube.

Weigh a clean empty sample tube (m_o) on an analytical balance and then record the reading (R_o) on the magnetic balance. Pack the tube with the sample to a height of 2.5 - 3.5 cm. Tap the tube carefully to pack the sample tightly. Record the weight (m) and the new reading on the magnetic balance (R). Measure the length of the sample (l) in cm.

The mass susceptibility, χ_g , is calculated from the equation :

$$\chi_g = \{C_{Bal} \cdot l \cdot (R - R_o)\} / \{(m - m_o) \times 10^9\}$$

where l = sample length (cm); $m - m_o$ = sample mass (g); R = reading for tube + sample; R_o = reading for empty tube; C_{Bal} = the balance calibration constant written on the back of the instrument ($C_{bal} = 1.083$). This incorporates the area cross-section of the sample tube.

Now χ_g is the magnetic susceptibility per gram and must be a positive number. If $R \approx R_o$ then diamagnetism is indicated. To convert this to the molar susceptibility, χ_m , multiply $\chi_g \times$ molecular weight. Because ligands will contribute a negative effect as a result of their diamagnetism, the magnetic susceptibility for the metal can be found by adding the diamagnetic contributions of the ligands and the metal to χ_m . This gives χ_A .

The effective magnetic moment, μ_{eff} is given by

$$\mu_{eff} = \sqrt{[3 \cdot k \cdot T \cdot \chi_A] / [N \cdot B^2]}$$

where N = Avogadro's number; B = the Bohr magneton; k = Boltzmann's constant; T = absolute temperature in Kelvin.

Combining the constants reduces the formula to $\mu_{eff} = 2.828\sqrt{\chi_A T}$. The same result can be calculated using a simplified formula of $\mu_{eff} = \sqrt{[n(n + 2)]}$ (n = # unpaired electrons) which works fairly well for first row transition elements when the orbital contribution is not significant. So, by measuring μ_{eff} , one can estimate the value of n , which is the number of unpaired electrons around the metal.

Hence, if

$\mu_{eff} =$	0,	$n =$	0
	1.73,		1;
	2.83		2
	3.87		3
	4.90		4
	5.92		5
	6.93		6

Round to the nearest integral value of n and deduce what this means in terms of numbers of unpaired electrons in your compound.