Imperial College of Science Technology & Medicine

Department of Chemistry

2nd Year Synthesis Course

Projects and Further Techniques

Spring Term 2003

Student Laboratory Manual

Laboratory Supervisors:

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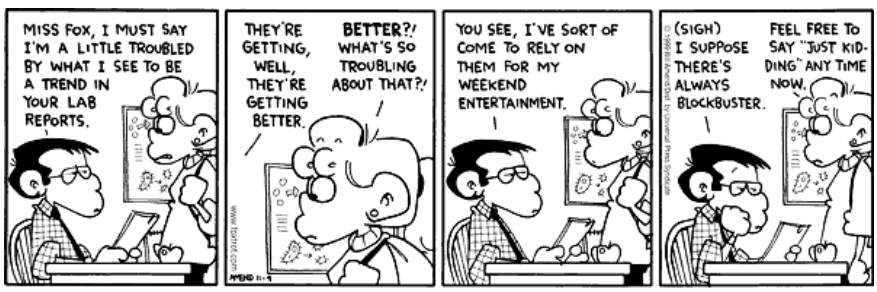


1 General:

A. Safety.

i) **YOU MUST WEAR A LAB COAT AND SAFETY GLASSES OR GOGGLES AT ALL TIMES IN THE LABORATORY**. Failure to do so means that you will be asked to leave the laboratory.

ii) Eating and drinking and the carrying of either are forbidden in the lab.

iii) Use of mobile phones is not allowed; please turn them off before entering the lab; failure to do so will result in their confiscation.

iv) Make sure that you read and understand the safety regulations given on page 6 of this booklet, and that you have read the safety documents you were given for the Foundation Course. If you have any questions about safety rules or about the safety aspects of any experiments in this course, ask a demonstrator. Please avoid wearing open toed shoes or sandals in the laboratory.

B. Course Dates.

Spring Term

Group A: 13th January - 14th February 2003
Group B: 17th February - 21st March 2003

C. Laboratory Hours.

The labs are open during the course from 11-5 Monday, Tuesday, Thursday and Friday.

2 Running of the laboratory

A. Allocation, Handing in and Marking of Experiments.

The synthesis project (Exp 1) is worth 300 marks, the ferrocene experiment (Exp 2) 200 marks and all the rest are worth 100 marks each. If you have time and carry out an extra experiment your worst mark will be eliminated (across both SPRING and AUTUMN courses; inorganic experiments 5-10 only).

You should attempt to complete and write up each experiment in turn. However, since many experiments involve one or more long processes efficient use of lab time can be achieved by starting another experiment whilst the first is still in progress.

Experimental Reports **MUST** be handed in accordance with the following schedule:

Group A

13th Jan				20th Jan				27th Jan				3rd Feb				10th Feb			
M	T	T	F	M	T	T	F	M	T	T	F	M	T	T	F	M	T	T	F
				Proposal@12				1@12				1@12							Rest in@12

The Synthesis Proposal must be in before 12 on the first Monday and discussed with a staff demonstrator that afternoon

Group B

17th Feb				24th Feb				3rd March				10th March				17th March			
M	T	T	F	M	T	T	F	M	T	T	F	M	T	T	F	M	T	T	F
				Proposal@12				1@12				1@12							Rest in@12

The Synthesis Proposal must be in before 12 on the second Monday and discussed with a staff demonstrator that afternoon
Each lab report must be logged in the book on the demonstrators' bench by a demonstrator and yourself with a date and time.

Late hand-ins are liable to incur a penalty of 10% for Monday between 12-5 and then 20% each day thereafter. The final two reports must be handed in before 12(noon) on the final Friday of the course BUT will not be accepted unless your bench and fumehood have been cleaned and inspected by a demonstrator

One or two specific demonstrators mark each experiment. This ensures uniformity of marking and also easily allows the staff to identify instances where collaboration/copying has taken place.

THE SYNTHESIS PROJECT REPORT SHOULD BE HANDED IN TO THE DEMONSTRATOR (AND SIGN IT IN!) AND THE SAMPLES PLACED IN THE DRAWERS PROVIDED.

EXPERIMENT 2-10 REPORTS SHOULD BE SUBMITTED FOR MARKING BY ENCLOSING YOUR WRITE-UP AND LABELLED SAMPLES IN ONE OF THE PLASTIC ENVELOPES PROVIDED AND HANDING IT IN TO A DEMONSTATOR (SIGN IT IN!).

ALL samples must be clearly labelled with the date, your name, what it is and the experiment number.

3 Laboratory Records and Reports.

It is vital (and mandatory) to keep an accurate Laboratory Record while you work. (In industry and in some academic institutions, these records are the property of your employer or institute; you may be allowed to keep a copy, but this is not always the case). You should record all essential experimental details, on which your Report is based, including amounts of materials, relevant equations, summaries of procedures, observations, measurements (including balance readings for magnetic determinations and weight loss studies, *etc*.) and product yields. From these, you will compile a report.

The Report should ideally be TYPE WRITTEN on A4 paper. **Put your name, the experiment number and the date on the front page.** The Laboratory Record for any experiment must be available and may be checked and assessed at any time.

Guidelines for report writing can be found at the end of each experiment. Please be aware that due to the differing and varied nature of the experiments in this course, these guidelines do vary slightly from experiment to experiment.

If you make a statement based on the literature you should quote the reference. Literature references should be given as superscript numbers in the text: *e.g*. "the (M-X) band at 697 cm^{-1} corresponds well with the literature[1] value of 698 cm^{-1}", and the quoted references should be listed at the end. *e.g.*

1 M.J. Mays and J.D. Robb, *J. Chem. Soc. A*, **1968**, 329.
2 H.L. Conder and W.R. Robinson, *Inorg. Chem.*, **1972**, 11, 1527.

Textbooks and Literature. Some of the practical textbooks (referred to in the lab manual by the abbreviations given below) are available in the laboratory. To ensure general availability and to prevent damage or loss they must not be taken to the workbenches or for photocopying. They are also available in the Departmental library, but on restricted loan.

Abbreviations: IS = Inorganic Syntheses; Palmer = Experimental Inorganic Chemistry; M and R = Marr and Rockett, Practical Inorganic Chemistry.
Collected photocopies of many of the literature references quoted in the lab manual are available, and should be used in preference to the original journals. Folders are kept in the PERKIN lab for overnight loan against your signature. **Failure to return these folders will result in loss of marks.** If you come across additional material that might well be included in these collections, please discuss it with Drs. Davies and Braddock.

4 Apparatus, chemicals and instruments.

Equipment not in the bench sets may be obtained from the service room; it must be returned immediately in clean state when it is no longer required. Hoarding of items will lead to a general shortage for everyone. Do not leave unwanted apparatus in or on the benches or in the fume cupboards overnight. This will be taken into account in the 'tidiness' assessment.

Most Starting Chemicals required for each experiment are obtainable from the technicians; some may be in the freezer or on the benches; if in doubt ask a demonstrator. Other chemicals are also issued from the Service Room. Chemicals, even the common ones, are expensive nowadays so please don't waste them - take only as much as you need. Take care not to contaminate the stock bottles and always re-seal any container from which you have taken chemicals. Never leave the caps off solvent bottles or reagent containers. Unless otherwise stated, we don't recover organic solvents after use, but please remember that they MUST NOT BE PUT DOWN THE SINKS, instead put them in the special containers provided. Please try not to remove standard reagents, solvents and stock solutions from their correct places on the shelves.

Instruments: If you find that a spectrometer or other instrument does not work properly, report the fact immediately to the lab staff so that we can have it repaired promptly. As the spectrometers are heavily used we may have to use a booking sheet system. Please take care of IR salt-plates/cell windows and be economical with chart paper.

5 Miscellaneous Random Bits of Advice.

- Prepare **before** you come to lab. Plan your day and the sequence of steps that you wish to take. Make sure you have all the equipment ready for the next time you'll come to lab.
- If you don't know why you're doing something then you shouldn't be doing it!
- Keep a good notebook. Do not write information on scrap paper -- it is a waste of time. If you keep a really good lab notebook you can write your lab reports in a fraction of the time it would take otherwise.
- Learning is not a one-way street. If we have not made a point clear it is your responsibility to let us know. Ask questions. Ask why. There are no stupid questions except for the ones you didn't ask because you were afraid of looking stupid.
- If you have any concerns regarding the course, content *etc.* then please make them known to us as early as possible. Feedback (both positive and negative) is welcome. No, it will not affect your grade.

SAFETY REGULATIONS

YOU MUST ATTEND THE SAFETY TALK BEFORE YOU CAN COMMENCE WORK IN THE LABORATORY

1. The laboratories are open at the times shown in the Timetable and on the notice boards; practical work must not be done at any other times when no staff demonstrator is present.
2. Wear a lab coat and safety spectacles or goggles **at all times** (these will be provided). Do not wear contact lenses if you have any alternative. However, if you do have to wear contact lenses, please take particular care to wear goggles and tell the senior technician that you wear contact lenses. If you get corrosive liquids in your eye, it is essential to remove the contact lenses immediately; the necessary equipment is available in the service room.
3. Do not eat, drink or smoke, whilst in the laboratory. No mobile phones allowed in lab either.
4. Note the positions of the fire extinguishers, fire blankets, emergency sprays and first aid kits.
5. Any accident involving personal injury, however trivial, must be reported to the member of staff in charge of the laboratory and to the chief technician.
6. Before using any chemical, you should check its properties (flammability, toxicity, etc) by reference to the Wall Charts and books on Hazardous Chemicals and the list in this manual; if it is not mentioned there, consult a Demonstrator.
7. Experiments using dangerous or noxious chemicals (HCl, Br_2, HNO_3, etc) must be carried out in a fume cupboard. After use clear the fume cupboard immediately.
8. Bunsen burners should be used in fume cupboards unless specific permission is given for their use elsewhere in the lab. Pay particular attention that there are no flammable chemicals in the fume cupboard you are using. Do not carry flammable solvents about the lab in open vessels such as beakers.
9. Note carefully, before starting an experiment, any safety points pertinent to that experiment, *e.g.*, do not put sodium residues or organic liquids down the drains, take care when pushing glass tubing or thermometers through holes in rubber bungs or corks, *etc*.
10. Waste organic liquids and solvents should be put into the special containers provided. They must NOT be put down the drains.
11. DO NOT PIPETTE ANY SOLUTIONS BY MOUTH; use only the pipette fillers available from the Service Room.
12. Use vacuum desiccators only for the purpose recommended, and only in conjunction with adequate screening (ask first how to use them).
13. Don't put chemicals in bottles other than those for which they are intended.
14. Don't relabel bottles.
15. Clear up all the spillages immediately, (except mercury spillage, which must be reported to the Service Room immediately).
16. Get a demonstrator to inspect any experiment which is to be left running overnight, and get him to leave a signed notice for the night security men, who will otherwise turn it off. Rubber tubing carrying water must be wired on to the nozzles of taps and condensers.
17. Obtain the assistance of the laboratory technician; demonstrator or member of staff to separate jammed Quickfit apparatus.
18. Don't leave clothing on the benches; use your locker / drawer.
19. Don't leave retort stands, bags, stirrers *etc*. in the aisles. Take care not to block the aisles with stools.
20. Do not sit on the laboratory benches. Also, it is unwise to sit in front of an experiment involving a glass vessel containing a hot or corrosive liquid in case of breakage and subsequent splashing.
21. Samples placed in the refrigerator must be well stoppered and clearly labelled with the sample identity and your name.
22. Fume cupboards. The proper way to use these is with the windows as far down as possible. As soon as you have finished any manipulation in a fume cupboard shut the windows. Make sure there is nothing to impede the closing of the windows. As soon as you have finished with a fume cupboard leave it ready for the next user.

EXPERIMENT 1

Synthesis Project

Introduction

At the start of the project you be given a compound for synthesis from the demonstrator's list. No two students will have the same final product. One (or more) leading reference(s) will be supplied. No schedule will be provided for the synthesis, you will be required to design your own three-stage process using reactions described in the literature, and devise your own experimental procedure. The objectives of the exercise are thus to increase your familiarity with the literature, to give you first hand experience of synthesis design, albeit using known reactions, and to give you experience of the technical design of an experiment.

Design of The Synthesis

Using reactions described in the literature, specifically for the compounds concerned (not homologues or analogues) produce the best three step synthesis of the chosen compound you can, the merit being judged by overall yield, technical ease of reaction and cost. Consider carefully that:

(i) The synthesis is subject to the constraints of availability of materials and apparatus. Exceptionally hazardous materials such as inorganic cyanides, or techniques such as catalytic hydrogenation cannot be used.
(ii) The synthesis should be designed backwards from the final product and unless the first route worked out is particularly efficient, alternatives should always be considered.
(iii) The cost of the chosen route can be of overriding importance.

Design of Experiments

When the best route is fixed, consider in detail the reactions involved with the following points in mind.

(i) Special apparatus that may be required to carry out the various operations of the reaction.
(ii) Conditions of reaction, e.g: should the solvent be specially dry or should the reaction be carried out under nitrogen because of the sensitivity of reactants/intermediate/product to oxidation.
(iii) How is the reaction to be followed (an essential part of any well conceived experiment)
(iv) How will the product(s) be purified?
(v) What physical data needs to be checked on the product? Always m.p. (b.p.), IR and NMR spectra, TLC purity check, and, when appropriate, UV spectrum, rotation, refractive index (liquids)
(vi) Is the process safe? What precautions are necessary? Always check this with a staff demonstrator.

When all this is decided, ***submit a detailed proposal*** (see below) including the starting quantity, the technique to be used, and the necessary safety precautions, ***to a staff demonstrator for checking and marking*** **BEFORE** ***commencing the project including your completed COSHH forms for each step.*** Signed approval is required for you to draw your starting materials.

General Points

(i) Aim to start work on a 0.1 molar scale or to make *ca* 1-2g of the final product as appropriate. Allow for a drop of 10% on the literature yields at each stage.
(ii) If the compound chosen can be prepared in two stages from available material then a further appropriate transformation of the product must be proposed.

(iii) If a stage or operation is particularly hazardous, ensure that a demonstrator is on hand while the process is carried out, and ensure that all the recommended precautions are adhered to.
(iv) If an early stage in the series fails, even after a repeat effort, then alternative reactions to the later stages can be obtained from a staff demonstrator.

The Proposal and Final Report

This will be completed in two parts that will be marked separately.

(a) *The proposal:*
The chosen route should be presented for assessment by a staff demonstrator and should cover all the design points raised above. The sequence should be:
1. The target molecule
2. Equations to express the three stages
3. One alternative synthesis (if available) from the literature
4. The proposed experimental procedure. In most cases, this is most conveniently presented as a photocopy of the literature procedure. Remember to make appropriate modifications to quantities of chemicals and solvents.
5. A cost estimate of the three stages. Cost reagents at a 0.1 molar scale using the Aldrich catalogues available in the laboratory. Allow £3 for the general usage of solvents and a further £1 if column chromatography is involved.
6. Answers to design points (i) - (vi) above.
7. References

The proposal should be as brief as possible consistent with the above information, typically about 3-4 sheets of A4 paper.

(b) *The experimental account:*
This should be written up on completion of the project in the style (**5 marks overall**) of *J. Chem. Soc. Perkin Trans.1.* It should take the following format.
TITLE
SUMMARY: A short (1 sentence) statement of the project including balanced equations for each step (**5 marks**);
INTRODUCTION: Objectives, background, choice of reactions, comparisons with other methods, general usefulness of products and/or methods (**5 marks**);
EXPERIMENTAL: A detailed account of each step in the past passive voice including masses molar ratios and volumes etc. (**3 marks per procedure**) Past passive voice. A clear statement of %yield and description of sample and comparison with literature (**12 marks per sample**);
DISCUSSION: A general account of your reactions and results, including mechanisms (**3 marks per step**), comprehensive analysis of your spectra to prove the identity for your two intermediates (**11 marks**) and analysis of final product (**20 marks**) to prove both purity (*e.g.,* mp, bp, refractive index) and identity (*e.g.,* ^{1}H NMR, IR). A comparison with the literature data is required for full marks.
REFERENCES: Include literature references.

Total 100 marks x 3 = 300 marks.

Hand in with Your Report:

Small purified samples of each stage and final poduct.
The spectra of these samples (IR, NMR, and UV [if relevant]).

General References

Organic Syntheses - series
Original Journals as necessary - reached *via* Chemical Abstracts and/or Beilstein on-line.

EXPERIMENT 2

Ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, and its acetylation.

Introduction

The discovery in 1951 of *bis*(pentahaptocyclopentadienyl)iron, commonly known as ferrocene, with its unusual "sandwich" type structure and remarkable thermal inertness, resulted in a vast amount of research into the synthesis and reactions of related organometallic compounds. A variety of organic reactions can be carried out on the cyclopentadiene rings, which have aromatic character. In this experiment ferrocene is prepared and acetylated and then studied by ^{1}H NMR spectroscopy.

Safety Information

Dicyclopentadiene, cyclopentadiene and dimethylsulphoxide are poisonous. Avoid breathing vapour and skin contact. The KOH/ether mixture prepared in this experiment is very corrosive. Acetic anhydride is an irritant and should be used in a fume cupboard.

Experimental

a) Preparation of ferrocene.

Cyclopentadiene dimerises readily at room temperature to dicyclopentadiene by a Diels-Alder reaction. Accordingly, the commercial sample must be 'cracked' first thing on the day you plan to use it. The apparatus for doing this is set up in a fume-cupboard and it may be convenient for you to carry out the cracking process in collaboration with other people doing this experiment. Check that the flask contains at least 60 cm^3 of dicyclopentadiene (100 cm^3 if more than one sample of cyclopentadiene is needed). Collect the distillate that condenses in the range 42-44 ˚C, and keep it cooled - ice-bath around receiving flask. (You will need 8.5 cm^3). Take care not to overheat the still flask as this causes frothing and wastes time.

While you are cracking the dicyclopentadiene, fit a three-necked 500 cm^3 flask with a stirrer in the central neck, a 100 cm^3 dropping funnel fitted to one side neck by means of a side arm adaptor (connecting the side arm to a nitrogen supply), and a Liebig condenser in the other side neck, with the exit end of the condenser connected to a bubbler to prevent air entry and to monitor the nitrogen flow rate. Charge the flask with diethyl ether (100 cm^3) and flake potassium hydroxide (40 g), stir well and flush with nitrogen. (If this preparation is not carried out in a fume-cupboard a safety screen should be used). Meanwhile, dissolve finely powdered iron(II)chloride tetrahydrate (10 g) in dimethylsulphoxide degassed beforehand by bubbling nitrogen through it (40 cm^3) avoid skin contact; vigorous stirring for about an hour is usually required). Keep the iron(II)chloride solution in a sealed container to prevent oxidation.

With vigorous stirring and under a slow stream of nitrogen add cyclopentadiene (8.5 cm^3) to the KOH/ether mixture. After *ca*. 15 min., discontinue the nitrogen flow and add the iron(II)chloride solution dropwise. The reaction is exothermic and the ether may boil. When this subsides, restore a slow nitrogen flow. Replace any ether lost by evaporation. Continue stirring for a further 30 min. (CARE: The KOH/solvent mixture is extremely corrosive). Decant the ethereal layer and wash the dark residue in the flask with 50 cm^3 of ether. Combine the ether potions and wash the solution with 2 M HCl (2 x 40 cm^3) to neutralize any hydroxide and then with water (2 x 40 cm^3). Carefully evaporate off the ether to deposit orange crystals of ferrocene. Purify a small sample by sublimation using a Petri dish and lid on a warm hotplate in a fume cupboard. (Careful: too rapid heating or cooling of the dish may crack it). Remove the

golden crystals of ferrocene periodically from the Petri dish lid. Record the m.p., IR and NMR spectrum ($CDCl_3$), and write equations for the reactions involved in the preparation.

Examine the solubility of ferrocene in (a) water, (b) dichloromethane, (c) toluene and account for your observations in terms of the structure and bonding of the molecule. Add ferrocene (0.1 g) to water (5 cm^3) followed by concentrated nitric acid (5 cm^3) - extreme caution. Shake the tube gently for 2 min. and record your observations.

b) Acetylation.

Add crude ferrocene (3 g) to acetic anhydride (10 cm^3) in a 50 cm^3 round-bottomed flask provided with a calcium chloride or silica gel guard tube. Carefully add orthophosphoric acid (2 cm^3) dropwise with shaking. Heat the mixture on a steam bath for 20 min. then pour the hot mixture onto crushed ice (80 g) with stirring. Wash your flask out with some additional ice and combine the aqueous materials. When all the ice has melted neutralize the solution with solid sodium bicarbonate, cool the mixture in ice for 20 min. and then filter off the brownish-yellow solid. Dry it in a vacuum desiccator.

Recrystallise your product from cyclohexane and check its purity by TLC (repeat the recrystallisation and TLC examination if necessary, and draw a representation TLC development in your report, including R_f values). Record the m.p., IR, and NMR spectrum ($CDCl_3$).

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write equations for each stage of the reaction, giving yields and m.p. for each stage. What are the point groups of ferrocene if the rings are staggered and eclipsed?
4. Report your solubility tests and the reaction of ferrocene with nitric acid. Account for your observations.
5. Show your TLC study of the acetylation stage.
6. The reduction of acetylferrocene by $NaBH_4$ gives a product having the ^1H NMR spectrum shown on the sheet available from a demonstrator. Tabulate your NMR data and data from the copies of the ^1H NMR spectra of acetylferrocene and its reduction product, interpret them and identify the reduction product paying attention to the following points.
   i) For each peak, calculate the chemical shift in ppm relative to $SiMe_4$. Some peaks show fine structure. The centre of the pattern is the chemical shift for that hydrogen. For example, the lowest field multiplet in the spectrum of the reduced product is a doublet of quartets whose overall centre represents the shift.
   ii) From the integration traces calculate relative numbers of hydrogen's in each environment.
   iii) Assign the various peaks to the several groups of non-equivalent hydrogen's in each molecule, giving simple explanations in terms of the molecular formulae.
   iv) Note fine structure where it occurs. Give a detailed interpretation only of the non-Cp ring protons in the reduced product.
7. Tabulate your IR spectra and assign the major peaks.

Hand in with the report: Samples of ferrocene and acetylferrocene.
Infrared Spectra of both samples.
Assigned NMR of both samples and reduced product

Allocation of marks (Total = 200):	Experimental write-up/presentation	20
	Samples (quality/yields)	60
	Tests	25
	NMR spectra (discussion/interpretation)	20
	IR spectra (quality/assignment)	20
	Point groups	10
	Conclusion / Results and Discussion	45

References

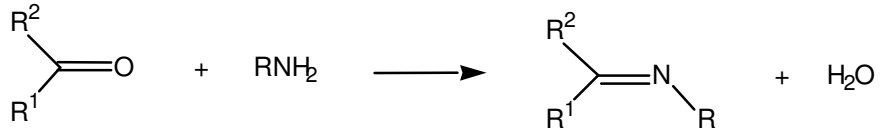
1. M. Rosenblum, J. O. Santer, W. Howells, *J. Am. Chem. Soc*., **1963**, 85, 1450.
2. Maddox, Stafford and Kaesz; *Advances in Organometallic Chemistry,* Vol. 3, (1965), p. 1 (use Tables III and XVII)

EXPERIMENT 3

Nickel(II) Complexes of some Schiff Base Ligands

Introduction

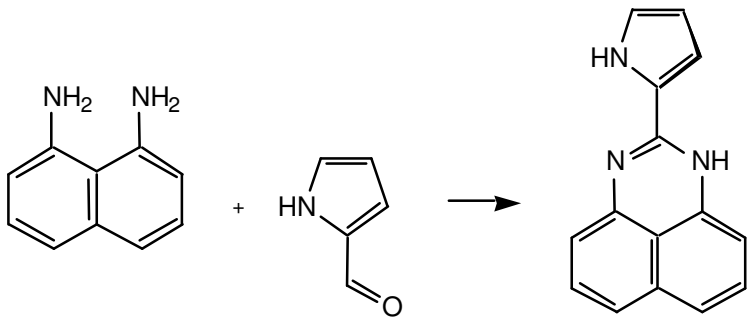
The condensation of an aldehyde or ketone with a primary amine leads to the formation of an azomethine (imine) linkage with the liberation of one molecule of water as follows where, R, R^1 and R^2 are hydrocarbyl substituents:



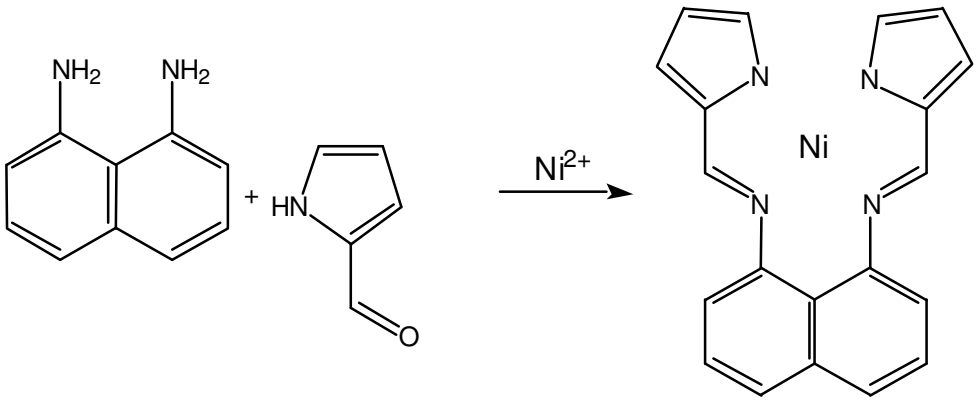
The nitrogen atom in the product carries a lone pair of electrons and can function as a Lewis base, forming complexes with transition metal ions. The first recorded example of such a complex was reported as early as 1840 by Ettling, who isolated a copper complex of the product formed in the reaction between salicylaldehyde and ammonia. However, it was Schiff who, in 1869, established the 1:2 metal:ligand stoichiometry of this complex and lent his name to the compounds containing the azomethine fragment.

Since these early discoveries a wide range of complexes derived from Schiff base ligands have been isolated.[1-3] These compounds have played a major role in the development of modern coordination chemistry providing examples of macrocyclic ligand systems and the effects of steric interactions on coordination geometries. Schiff base complexes have also been used to model biological systems, such as haem and Vitamin B_{12} coenzyme, which contain transition metals.

Two general methods may be used to prepare Schiff base complexes. The first entails the prior formation and isolation of the ligand system, followed by its reaction with the metal to form a complex. The second method does not entail prior isolation of the ligand: instead the condensation and complexation reactions are performed together during a single synthetic process. In fact, there are some ligands that will only form in the presence of a metal ion in a so-called 'template' reaction. In some reactions of this type it is thought that the metal ion complexes one or both of the ligand precursors before the condensation reaction occurs in what has been called a kinetic template effect. Thus the metal ion can act as a template orienting the reaction species and controlling the product formed. One example of such a system is provided by the reaction between 1,8-diaminonapthalene and pyrrole-2-aldehyde in air to give a heterocycle:



However, with pryyole-2-aldehyde in the presence of nickel (II) ions a different product can be obtained as its nickel complex:



In the following experiments nickel complexes of two isomeric ligands derived from diaminopropane and pyrrole-2-aldehyde are prepared using different methods.[4] ^{1}H NMR, MS and IR spectral measurements can be used to investigate the structures of these compounds.

Safety Information

Action to be taken in the event of an accident. If any chemicals in this experiment should come in contact with your skin wash them off immediately with copious amounts of water then consult a demonstrator. In the event of spillage in the fume hood consult a demonstrator and flush all the spilled materials down the hood drain with copious amounts of water. In the event that a diamine is spilled outside a fume hood keep others away from the area of the spill and consult a demonstrator. Absorb the spillage on an inert absorbent (*e.g.* vermiculite) and remove it to a fume hood to be packaged for disposal. Consult a demonstrator about spillage of any other chemicals involved. Skin contamination by, or inhalation of, these materials must be avoided.

Nickel (II) ethanoate $Ni(O_2CCH_3)_2.6H_2O$	Toxic
1,2-Diaminopropane	Corrosive
1,3-Diaminopropane	Toxic, Corrosive
Pyrrole-2-aldehyde	Irritant, Flammable
Ethanol	Harmful, Flammable
Dichloromethane	Harmful
Sodium carbonate	Irritant
Petroleum ether 40/60	Irritant, Flammable
Sodium hydroxide	Corrosive

Disposal of Wastes

Waste solvents must be disposed of into the containers provided. For further information consult May & Baker Data sheet numbers 416 (nickel(II)ethanoate), 395 (dichloromethane).

Experimental

Part 1

(a) Preparation of a Schiff base ligand from 1,3-diaminopropane and pyrrole-2-aldehyde.

Procedure - This reaction is to be carried out in a fume cupboard. Dissolve pyrrole-2-aldehyde (0.95 g) in ethanol (5 cm^3) in a round-bottomed Quickfit flask (100 cm^3). Using a graduated pipette add 1,3-

diaminopropane (0.40 cm^3) to the solution and mix the liquids. Fit a reflux condenser and warm the flask and contents on a steam (or boiling water bath) to boiling for 3-4 min. and then stand it in an ice bath for about 2 hours. The mixture may solidify to a crystalline mass or remain liquid. If a solid has deposited on cooling collect this by filtration and wash it with a few $cm^3$of diethyl ether. The combined filtrate and washings may deposit more product, as crystalline needles, on standing. If the mixture remains liquid evaporate the ethanol on a rotavap until solid starts to appear and then stand in ice to complete the crystallisation. Proceed to collect the product as described above. Allow the product to air dry and record your yield. Record the IR and ^1H NMR spectra of your product.

(b) Preparation of a Ni(II) complex from the Schiff base ligand

Procedure - Dissolve a portion (0.5 g) of the ligand prepared in PART 1(a) in warm ethanol (10 cm^3). Slowly add a solution of nickel ethanoate (nickel acetate, $Ni(OCOCH_3)_2.4H_2O$, 0.5 g) in water (10 cm^3) to produce a turbid brick red mixture. Next add a solution of sodium carbonate (0.2 g) in water (5 cm^3) and stir the mixture for 20 minutes. After this, collect the crude product by filtration and wash it with a little ethanol-water mixture (1:1, a few cm^3). Redissolve the red product in dichloromethane (*ca*. 40 cm^3) and dry the solution over a little magnesium sulphate. Remove the magnesium sulphate by filtration and wash it with a little dichloromethane. Combine washings and the filtrate and then add light-petroleum (80-100°, 40 cm^3) then remove the dichloromethane using a rotary evaporator (use a room temperature water-bath, do not heat the flask). The red product will precipitate from the light-petroleum as the dichloromethane is removed. The product may be collected by filtration and air-dried. Record the yield and the IR spectrum of your product. The ^1H NMR and mass spectra of your product are provided.

Part 2.

Preparation of a nickel(II) complex with 1,2-diaminopropane and pyrrole-2-aldehyde

Procedure - In a fume cupboard set up a round-bottomed Quickfit flask (100 cm^3) equipped with twin-necked adaptor, reflux condenser and dropping funnel. Place ethanol-water mixture (1:1 v/v, 50 cm^3) in the flask along with pyrrole-2-aldehyde (0.95 g), nickel ethanoate (nickel acetate, $Ni(OCOCH_3)_2.4H_2O$, 1.25g) and 3 or 4 antibumping granules. Heat the flask to dissolve the nickel ethanoate (a turbid rather than clear solution will form) and then add an aqueous solution of NaOH (10% w/v, 4 cm^3). Dissolve 1,2-diaminopropane (0.4 cm^3) in water (20 cm^3) in the dropping funnel. Add this diamine solution dropwise, over a period of about 20 minutes to the refluxing suspension of nickel hydroxide and aldehyde. Next add water (10 cm^3) and allow the mixture to cool. Collect the crude orange product by filtration and wash it with a little ethanol-water (1:1). Redissolve the product in dichloromethane (*ca*. 40 cm^3) while it is still in the filter funnel, and allow the orange dichloromethane solution to filter into a clean conical flask (100 cm^3). Dry this solution with a little magnesium sulphate, remove the magnesium sulphate by filtration, and wash it with a little dichloromethane. Add light-petroleum (80-100) to the combined filtrate and washings and remove the dichloromethane using a rotary evaporator. (Use a room temperature water bath and do not heat the flask). The orange product will precipitate from the light-petroleum as the dichloromethane is removed and may then be collected by filtration and allowed to dry in air. Record your yield and the IR spectrum of your product. ^1H NMR and mass spectra are provided.

<u>Report</u>

Consult the IR spectra obtained. Given that >N-H bonds give rise to IR bands (ν NH) in the region 3000 to 3400 cm^{-1} and that >C=N- bonds give rise to bands (ν C=N) in the region 1550 to 1600 cm^{-1}; what evidence do the spectra provide for the formation of a nickel complex from the ligand in PART 1. What are the point groups of the Ni complexes that you have prepared?

Consult the mass spectra and comment on the appearance of the molecular ion peaks in the nickel complexes and explain why prominent ions are observed at m/z 284 and 286 in each case? How do the spectra of the two isomers differ?

Draw the structures of the complexes prepared in PARTS 1(b) and 2. Consult the ^{1}H NMR spectra recorded and those provided and list the shifts and, where appropriate, coupling constants of the signals. Show how these spectra are consistent with the structures of the compounds prepared and how the spectra of the two isomeric nickel complexes differ. Explain the appearance of the signals in the region δ, TMS 3 to 4 ppm in the NMR spectrum of the compound derived from 1,2-diaminopropane. If you wish, you can check your interpretation of the NMR spectra by simulating them using the geNMR program that is on the departmental Macintosh computers.

Hand in with the report:	Samples of Parts 1a, 1b and 2. Infrared Spectra of all samples. Assigned NMR of 1a, 1b and 2 Assigned Mass Spec. of 1b and 2

Allocation of marks (Total = 100):	Experimental write-up/presentation	10
	Samples (quality/yields)	20
	Point groups (+ workings)	10
	IR spectra (quality/interpretation)	10
	Mass spectra (interpretation/discussion)	15
	NMR spectra (interpretation/discussion)	25
	Discussion/conclusions/equations etc.	10

References

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EXPERIMENT 4

Identification of Stereochemical (Geometrical) Isomers of $[Mo(CO)_4(L)_2]$ by Infrared Spectroscopy

Introduction

Physical techniques are widely used to obtain structural information at a molecular level in both organic and inorganic chemistry.[1,2] A quick and convenient laboratory bench-top spectroscopic analysis of a sample will often allow chemists insights into a structural problem without recourse to single crystal X-ray diffraction study. Vibrational spectroscopy is one such spectroscopic technique. Functional groups within a molecule vibrate at characteristic frequencies (group frequencies) and in doing so absorb radiation in the infrared (IR) region of the electromagnetic spectrum, 4,000-200cm^{-1}. Mononuclear metal carbonyl complexes are well suited to study by IR spectroscopy since intense absorptions due to the CO oscillations usually occur in the range 2,100-1,750cm^{-1}. Furthermore, this region is also generally free from interference from absorptions due to other functional groups.[3]

Separable geometrical isomers of complexes are common in ligand substituted mononuclear metal carbonyl chemistry. Group theory can be used to predict the number of IR active CO absorption bands to be expected for any particular isomer[4], so that if the structural formula of a metal carbonyl complex is known it is often possible correctly to identify which particular isomer is present by examining the CO stretching region of its IR spectrum. Thus, four carbonyl absorption bands are to be expected from a *cis*-$[M(CO)_4(L)_2]$ complex whereas only one band is expected from the *trans*-isomer.[5]

In this experiment you will prepare, according to convenient literature methods,[6] one isomer of the molybdenum carbonyl complex $[Mo(CO)_4(pip)_2]$ and both possible isomers of $[Mo(CO)_4(PPh_3)_2]$. Examining the CO stretching region of their IR spectra will identify these isomers.

Safety Information

Molybdenum hexacarbonyl and its derivatives are highly toxic, volatile materials. Chlorinated hydrocarbons, including CH_2Cl_2 are toxic and may be carcinogenic. Piperidine is a highly toxic, flammable liquid. Toluene, methanol and 60-80 °C petroleum ether are toxic and flammable. Triphenylphosphine is an irritant. The reactions given in the experimental are on a small scale and should present no special hazards provided reactions and manipulations (*e.g.* weighing, making up nujol mulls, etc) are carried out under a fume hood.

Experimental

(1) Preparation of an isomer of $[Mo(CO)_4(pip)_2]$ (1) (pip = piperidine, HNC_5H_{10})

$[Mo(CO)_6]$ (1.0 g) is suspended in dry toluene (40 cm^3) under N_2 and piperidine (10 cm^3) is added. The mixture is heated at reflux for 2 hours and the $[Mo(CO)_6]$ should fully dissolve to give a yellow/orange solution. This solution should slowly become opaque as a yellow precipitate of the product (**1**) is produced. The reaction mixture is filtered hot using a Buchner flask/pump set up and the bright yellow solid is washed with cold 60-80 °C petroleum ether (2 x 10 cm^3 portions, previously cooled in an ice bath for 15 min.). The product is conveniently dried at the pump. Record the weight of the product and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum as Nujol mull.

(2) Preparation of an isomer of $[Mo(CO)_4(PPh_3)_2]$ (2)

$[Mo(CO)_4(pip)_2]$ (**1**) (0.5g, 1.32 mmol) is partially dissolved in dry CH_2Cl_2 (20 cm^3) under N_2 and PPh_3 (0.75g, 2.86 mmol) is added as a solid. The reaction mixture is heated to reflux (whereupon **1** should fully dissolve) and reflux is maintained for 15 min. The reaction solution is allowed to cool to room

temperature and the orange solution is filtered. The solvent is reduced in volume to *ca*. 8 cm^3 (rotary evaporator or vacuum pump) and methanol (15 cm^3) is added. The solution is cooled in a freezer (< 0°C) for 15 min. and the pale yellow product should crystallize out. The product is collected by filtration using a Buchner flask/pump set up and dried at the pump. Record the weight of the product and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum as a nujol mull.

(3) Thermal isomerisation of (2) to give (3)

$[Mo(CO)_4(PPh_3)_2]$ (**2**) (0.5g, 0.68 mmol) is dissolved in dry toluene (10 cm^3) under N_2 to give a pale yellow solution. This solution is heated at reflux for 30 min. and then is allowed to cool to room temperature. The solution may darken up upon heating. The toluene is removed on a rotary evaporator (or vacuum pump) to yield the product as a brownish off-white residue (**3**). The off white crystalline product can be obtained by recrystallisation of the residue from $CHCl_3$/MeOH at 0 °C. Record the weight of the residue and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum as a nujol mull.

Report

1. Decide, by inspection of the CO stretching region of your IR spectra, the stereochemistry (*cis*- or *trans*-geometrical isomers) of your products. What is the point group symmetry at molybdenum for each isomer?
2. Draw a reaction scheme that clearly shows the stereochemistry of **1, 2** and **3** and conditions for conversions.
3. Compare the melting points of your complexes with those quoted in the literature.[7-9]
4. Do the metal carbonyl substitution reactions go *via* a dissociative or an associative mechanism?
5. Explain why the mechanisms for the isomerisation of $[Mo(CO)_4(L)_2]$ with L = P^nBu_3 and L = PPh_3 are different.[10]
6. Is the *cis*- or the *trans*- isomer of $[Mo(CO)_4(PR_3)_2]$ thermodynamically more stable?

Hand in with the report: Samples of **(1)**, **(2)** and **(3)**.
Infrared Spectra of all samples.

Allocation of marks (Total = 100):

Experimental write-up/presentation	10
Samples (quality/yields)	15
Questions 1a. Stereochemistry and IR	10
1b. Point groups	5
2. Reaction scheme	10
3. Melting Points	10
4. Mechanism	5
5. Mechanistic explanation	10
6. Stability	5
IR spectra quality	10
Conclusion / Results and Discussion	10

References and Notes

1. 'Spectrometric Identification of Organic Compounds', R.M. Silverstein, C. G. Bassler, T. C. Morril, John Wiley and Sons, 5th edition, **1990**.
2. 'Structural Methods in Inorganic Chemistry', E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, Blackwell Scientific, 2nd edition, **1991**.

3. The N-N and N-O stretches in M-N_2 and M-NO complexes and M-H stretches also occur in this region. The method used for the preparation of the compounds should give some indication as to whether such functional groups might be present.
4. "Infrared and Raman Spectra of Inorganic and Coordination Compounds', K. Nakamoto, John Wiley and Sons, New York, 3rd edition, **1978**.
5. M. Y. Darensbourg and D. J. Darensbourg, *J. Chem. Ed*., **1970**, 47, 33.
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8. W. Hieber and J. Peterhans, *Z. Naturforsch*, **1959**, 14B, 462.
9. A. D. Allen and P. F. Barrett, *Can. J. Chem*., **1968**, 46, 1649.
10. D. J. Darensbourg, *Inorg. Chem*., **1979**, 18, 14.

EXPERIMENT 5

Preparation of *bis*(triphenylphosphine)copper(I) tetrahydroborate and study of its thermal decomposition products.

Introduction

There is appreciable interest in the use of transition metal hydrides and tetrahydroborates as selective reducing agents. The copper(I) tetrahydroborate complex you prepare in this experiment is also of interest because: (a) two of the hydrogen atoms of the BH_4^- ion bridge the copper and boron atoms in the solid compound and (b) the catalytic nature of the thermal decomposition of the complex has found use in various imaging processes.

Safety Information

Chloroform is poisonous and a possible carcinogen, handle in a fume cupboard.

Experimental

Add finely powdered (using mortar and pestle) hydrated copper sulfate (1.5 g) to a solution of ground triphenylphosphine (7.5 g) in ethanol (100 cm^3). Stir the mixture and warm it on a hotplate until the blue solid has dissolved (the yellowish solution may be decanted from any small amount of blue residue). Cool the solution to 50 °C. Carefully add powdered sodium tetrahydroborate (1.5 g) with stirring, until precipitation is complete and the vigorous effervescence has subsided. Filter off the crude solid and stir it with 75 cm^3 of chloroform. Filter the solution. Warm the $CHCl_3$ filtrate on a hotplate to about 50 °C and then add ethanol slowly with constant stirring (keeping the solution hot) until the faint cloudiness produced changes to fine, white crystals. It may be necessary to add ethanol in a quantity of up to 150% of the vol. of $CHCl_3$ that you start with. Allow the mixture to cool, filter off the product, wash it with diethyl ether and dry it in air. Record the yield, m.p. and an infrared spectrum of your product. (A further crop of the compound can sometimes be obtained by concentration of the mother liquor - but do not mix the two samples - record the amounts and melting points separately.)

Thermal Decomposition.
Examine the products of the thermal decomposition of the *bis*(triphenylphosphine)copper(I) tetrahydroborate and record your observations during the decomposition:

Take about 1.5 g of the dried complex and heat it gently in a test tube (yellow Bunsen flame with about 1 min. of gentle spasmodic heating). Allow the residue to cool and then wash it with 3 x 5 cm^3 toluene. Filter the combined toluene washings and evaporate off the toluene on a rotary evaporator to leave a crude solid. Wash this crude solid with 3 x 5 cm^3 ethanol and retain both the combined ethanol washings (**A**) and the residue (**B**).

Ethanol solution (**A**): Heat the solution gently to boiling and then add water dropwise, maintaining boiling, until the solution is permanently cloudy. Allow the mixture to cool and then filter off and air-dry the white crystals of triphenylphosphine. Record the m.p. and an infrared spectrum of your product.

Residue (**B**): Extract residue B into about 15 cm^3 toluene and filter. Concentrate the solution by evaporating off most of the toluene on a rotary evaporator. Allow the solution to cool when crystals of Ph_3PBH_3 should form. Filter these off and air-dry them. Record the m.p. and an infrared spectrum of your product. Write an equation to account for your observations.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write an equation for the formation of $[Cu(PPh_3)_2(BH_4)]$ and give the yield.
4. Record your observations for the decomposition of $[Cu(PPh_3)_2(BH_4)]$. Give the yields of the products and write an equation for the thermal decomposition.
5. With respect to the IR spectra of $[Cu(PPh_3)_2(BH_4)]$ and Ph_3PBH_3; assign the ν(B-H) vibrations and comment on any differences between the two compounds. What are the point groups for both compounds and for BH_3 and BH_4^- ?
6. Give a brief account of the structure of $[Cu(PPh_3)_2(BH_4)]$ and of the bonding between the metal and the BH_4^- ions.[2]
7. Write a short conclusion.

Hand in with the report: Samples of $[Cu(PPh_3)_2(BH_4)]$, Ph_3PBH_3 and PPh_3.
Infrared Spectra of all samples

Allocation of marks (Total = 100):

Experimental write-up/presentation		10
Samples (quality/yields)		20
Questions	1. Equations	10
	2. Point groups	10
	3. IR assignment	10
	4. Bonding explanation	10
Melting points		10
IR spectra quality		10
Conclusion / Results and Discussion		10

References

1. Lippard and Ucko, *Inorg. Chem.*, **1968**, 7, 1051.
2. Lippard and Melmed, *Inorg. Chem.,* **1967**, 6, 2223.

EXPERIMENT 6

Nitrosyl Complexes of Iron and Nickel

Introduction

The nitric oxide (NO) molecule is closely akin to the carbon monoxide (CO) molecule except that it contains one more electron, which resides in a π^* orbital. There is some similarity between the NO molecule and carbon monoxide and nitric oxide does form a series of binary nitrosyls analogous to the binary carbonyls of the first row transition metals. However, unlike carbon monoxide, nitric oxide is not stable in air as it is rapidly oxidised to NO_2. This experiment illustrates two methods of forming nitrosyl complexes without the use of free NO.

Safety Information

Chloroform is extremely harmful and very easily ingested. Work in a fume cupboard.
Most of the reagents and the product are toxic to some degree. Wear gloves.

Experimental

Preparation of $Fe(NO)(S_2CNEt_2)_2$

Dissolve ferrous sulphate (approx. 5.6 g) in dilute sulfuric acid (25 cm^3) (in a fume cupboard). Mix together solid sodium nitrite (1.5 g) and solid sodium diethyldithiocarbamate (10 g) and then add this mixture to the ferrous sulphate solution and stir vigorously for 5 min. Place the reaction mixture in a 100 cm^3 separatory funnel and extract successively with 1 x 50 $cm^3$and 2 x 25 cm^3 chloroform. (Chloroform is denser than water so less than the volume added can be run out of the funnel even if the interface is difficult to see). Dry the combined chlorocarbon extracts over $MgSO_4$, filter, and remove the solvent on a rotary evaporator. The crude compound is purified and recrystallised simultaneously by Soxhlet extraction with 150 cm^3 of 80-100 ^oC petroleum ether - it is helpful to fill the Soxhlet with solvent when you set up the apparatus - (3-4 hours should be sufficient; longer periods, especially if solid starts to separate in the flask, may lead to loss of product and the formation of impurities). You may wish to consider replacing the round bottom flask with a second flask containing a fresh solution of pet. ether after 2-3 h. and thus collect two crops. Dark green crystals should separate from the extract on cooling (if they do not - concentrate slightly on the rotary evaporator). If you concentrate the solution too much, then crystals of $Fe(S_2CNEt_2)_3$ will also come down. Record the infrared spectrum of the compound. Calculate your yield based on the amount of ferrous sulphate used.

Preparation of $NiBr(NO)(PPh_3)_2$

This preparation requires the use of $NiBr_2(PPh_3)_2$. Synthesize this by adding the stoichiometric amount of nickel bromide in ethanol (*ca*. 30 cm^3) to a refluxing solution (0.5h; if there appears to be a large quantity of unreacted $NiBr_2$ (brownish) in your mixture - dissolve the material in THF and filter to remove it) of triphenylphosphine in propan-2-ol (*ca*. 80 cm^3) (NOTE: Please try and figure this out yourselves before coming and asking a demonstrator). Place finely powdered, dry sodium nitrite (8 g) in a flask with $NiBr_2(PPh_3)_2$ (5 g), triphenylphosphine (1.8 g) and tetrahydrofuran (50 cm^3). Stir under reflux for about 35 minutes. Cool and filter the solution and reduce the volume to about 25 cm^3 by evaporation on a steam bath (fumecupboard). Slowly add petrol (25 cm^3) to the warm solution with stirring. Allow to cool to room temperature, filter the purple product and dry it at the pump. Record the infrared spectrum of the compound.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write balanced equations for the formation of the complexes and give your yields.
4. Tabulate the IR spectra, assigning ν(NO).

5. What is the point group symmetry at the metal centre for $Fe(NO)(S_2CNEt_2)_2$ and for $NiBr(NO)(PPh_3)_2$?
6. Comment on the ESR spectrum of the complex (available from a demonstrator) and answer the questions below.
7. What oxidation state are the metals in your complexes; are the M-NO group linear or bent (see Vaciago, *et al*., *J.C.S. Chem. Commun.*, **1967**, 584); do the complexes obey the 18 electron rule?
8. Write a short conclusion.

Hand in with the report:	Samples of $Fe(NO)(S_2CNEt_2)_2$ and $NiBr(NO)(PPh_3)_2$	
	Infrared Spectra of both samples	
	Assigned ESR Spectrum	
Allocation of marks (Total = 100):	Experimental write-up/presentation	20
	Samples (quality/yields)	20
	Spectra (quality/interpretation	20
	Questions/discussion/conclusions	40

Reference

M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago and L. Zanbonelli, *J. Chem .Soc., Chem. Commun.*, **1967**, 583.

Questions to Accompany the ESR Spectrum of Fe(NO)(dithiocarbamate)$_2$.

Electron spin resonance is a form of magnetic resonance in which an unpaired electron in a magnetic field is excited from one spin to another by a quantum of energy in the microwave region of the electromagnetic spectrum. It is entirely analogous to nuclear magnetic resonance but the appearance of the spectrum is usually rather different because it is normally presented as the first derivative of the absorption with respect to field, plotted against field. In practical terms what this means is that a peak position is precisely measured by the field value at which the derivative crosses the baseline. The spectrum is characterised by two parameters, g and a.

The *g* Value. This is analogous to chemical shift in NMR. The free electron value is 2.0023; the value for a free radical in which the unpaired electron is centred on carbon is usually around 2.003; and if centred on nitrogen around 2.006. Metal ions can have very different g values (in general between about 1 and 8) but if there is only one unpaired electron the shift away from 2.0023 is often no more than about 0.2.

Calculate the g value from the field position of the central line using the formula $h\nu = g\beta B$ which gives $g = 0.0714484\ \nu(GHz)/B(tesla)$.

The *a* Value. This is the symbol for the isotropic hyperfine coupling constant which arises when a nearby nucleus interacts with the electron; it is analogous to the spin-spin coupling constant in NMR. In your molecule the unpaired electron clearly interacts with a nitrogen nucleus which has spin I = 1 having three projections along the magnetic field characterised by M_I = +1, O, -1. The isotropic hyperfine coupling constant a_N may be measured in field units by measuring the separation between two adjacent lines. To convert to frequency units use $a\ (MHz) = g \times 13.99626 \times a(mT)$.

Question 1. What can you say about your molecule from its g value?

Question 2. Given that an unpaired electron situated entirely on a free nitrogen atom has an isotropic hyperfine coupling constant a_o of 1540 MHz, calculate by direct ratio of the coupling constants the percentage probability of finding an unpaired electron on nitrogen in your molecule. What does this value tell you about the electronic structure?

EXPERIMENT 7

Nitration of cobalt(III) acetylacetonate.

Introduction

Coordination of organic molecules to metal ions frequently modifies the nature of the chemical reactions which they can undergo. In this experiment coordinated acetylacetone can be readily nitrated.

Safety Information

Acetic anhydride is an irritant. Avoid contact, handle in a fume cupboard.
Chloroform should be used in a fume cupboard.

Experimental

Preparation of Cobalt(III) acetylacetonate

A mixture of cobalt(II) carbonate (1.25 g) and 2,4-pentanedione (acetylacetone) (10 cm^3) in a 100 cm^3 conical flask is heated to 90 to 100 ˚C. Heating is stopped while 12% hydrogen peroxide (provided in the refrigerator) - *avoid skin contact* - (15 cm^3) is added dropwise with rapid stirring over a period of 10-15 min. (Do not add the hydrogen peroxide rapidly or the heat evolved will cause frothing). When addition is complete, cool the mixture in an ice-bath and then filter off the green solid and dry it at 110 ˚C. Dissolve the product in the minimum amount of hot toluene, filter if necessary, and then add 80-100 petroleum ether (*ca*. 75 cm^3) to the warm toluene solution. Cool in an ice-bath and filter off and air-dry the dark green crystals. Record the m.p.

Nitration of Cobalt(III)acetylacetonate

A mixture of finely ground copper(II)nitrate trihydrate (2.7 g) and acetic anhydride (50 cm^3) is stirred for 15 min. at 0^{o}C in a conical flask fitted with calcium chloride drying tube. To the resulting slurry add cobalt (III) acetylacetonate (1.25 g) and then stir for 2 hrs at 0^{o}C, followed by l h at room temperature. The blue green solution is then mixed with water (150 cm^3), ice (150 g), and sodium acetate (4 g). Stir the two-phase liquid for 2 hours, during which time a finely divided green precipitate appears. Continue stirring until any gummy substance has gone (the mixture should consist of a green solution and a fine green powder). Filter off the green solid, wash it with two portions of water (15 cm^3) and one portion of cold ethanol (15 cm^3) and then air-dry it. Dissolve the dry solid in boiling chloroform (10 cm^3) in a beaker (in a fume cupboard as chloroform is toxic and inflammable). Add hot ethanol (10 cm^3) and boil the mixture carefully, allowing the chloroform to distil off until crystals appear in the solution. Allow the mixture to cool, chill in an ice bath and then filter off the green solid. Wash with two portions of cold ethanol (5 cm^3) and air dry. Record the decomposition point of the product.

Record the IR spectrum of both complexes and make band assignments.[1] Collect the ^{1}H-NMR spectra of both complexes in $CDCl_3$ from a demonstrator.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write balanced equations for both reactions giving yields and m.p. of the products.

4. Tabulate the IR spectra of both complexes and give full band assignments.[1,2]
5. What are the point groups for both $Co(acac)_3$ and the product from the nitration ?
6. Tabulate and fully assign the ^1H NMR of both complexes.
7. Write a short conclusion

Hand in with the report:	Samples of Cobalt(III)acetylacetonate and its nitration product Infrared Spectra of both samples Fully labelled NMR Spectra of both samples	
Allocation of marks (Total 100):	Experimental write-up/presentation	10
	Samples (quality/yields)	20
	NMR (interpretation)	20
	IR (quality/interpretation)	20
	Point group	10
	Conclusion / Results and Discussion	20

References

1. J. P. Collman, R. L. Marshall, W.L. Young and S.D. Golby, *Inorg. Chem.,* **1962**, 1, 704 .
2. K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc*., **1961**, 83, 1066.

EXPERIMENT 8

Influence of ligand field tetragonality on the ground state spin

Introduction

Regularly octahedral first transition element complexes of configuration d^n (n = 4-7) may either be high- or low-spin depending primarily on the strength, Δ of the ligand field. For distorted ligand fields a wider range of possibilities exists for changes in ground state spin. Changes in spin can have important effects, *e.g*., high spin octahedral iron(II) complexes are much more labile than their low-spin counterparts. Moreover, the haem complexes that are involved in haemoglobin, catalase, cytochrome C, *etc*., contain the iron atom in either a high- or low-spin state, depending on the axial ligand.

The effects of changes in the axial ligands, X, on the electronic properties of a tetragonally distorted complex *trans*-ML_4X_2, are well illustrated by the magnetic properties and d-d spectra (and hence colours) of a series of nickel(II) complexes of formula $Ni(Et_2en)_2X_2$, where Et_2en = *N,N*-diethylethylenediamine ($Et_2NCH_2CH_2NH_2$) and X = Cl^-, I^-, NCS^-, Br^-, *etc*.

Safety Information

N,N-diethylethylenediamine has an unpleasant smell. Use it in the fume-cupboard and treat it as a potentially toxic compound. Make sure you do not use ethylenediamine or diethylamine by mistake. Also wear gloves when working with solutions of the nickel salts and their complexes, to avoid the possibility of heavy metal skin allergy.

Experimental

Preparation of $Ni(Et_2en)_2(NCS)_2$

Prepare an ethanolic solution of nickel thiocyanate (0.6 g) by dissolving the required amounts of nickel nitrate hexahydrate and potassium thiocyanate separately in hot absolute ethanol and mixing the two solutions. (For your guidance the solubility of nickel nitrate in hot ethanol is ca. 50 g/100 cm^3 and that of powdered potassium thiocyanate is *ca*. 10 g/100 cm^3). Keep the volume of solution to a minimum and allow the mixture to cool thoroughly before filtering off the precipitated potassium nitrate. Using a syringe, add 1 cm^3 of Et_2en to the filtrate with shaking and filter off the percipitated complex. Keep *ca*. 0.4 g of the dry crude product for the magnetic measurements (see below) and recrystallise the remainder from methanol (record the m.p., the yields of crude and of purified products).

Preparation of $Ni(Et_2en)_2I_2$

Prepare an ethanolic solution of nickel iodide (*ca*. l g) using nickel nitrate and sodium iodide (solubility of NaI in hot ethanol *ca*.16 g/100 cm^3) as for the nickel thiocyanate above. Add Et_2en (l cm^3), filter off the product, wash it with a little ethanol but do not attempt to recrystallise it.

Preparation of $Ni(Et_2en)_2Br_2$ and $Ni(Et_2en)_2Br_2.2H_2O$

The nickel bromide complexes of Et_2en exist in two forms; the anhydrous complex is orange and diamagnetic but it readily forms a blue paramagnetic dihydrate.[1] Slurry nickel bromide (1.5 g) (available in the lab.) in hot ethanol (20 cm^3) and, using a syringe, add Et_2en (1.5 cm^3) with stirring. Collect the solid product, wash it with a little ethanol and dry it in a dessicator. Record your observations at all stages.

Depending on the reaction conditions your product may be the orange anhydrous complex, the blue hydrated form or a mixture of the two. You should aim to hand in both the orange and the blue products separately. Samples of orange compound (or a mixture) can be converted to the dihydrate by moistening with alcohol and exposure to the air for several hours. Samples of the dihydrate (or a mixture) can be dehydrated to give the orange form by heating in a drying pistol at *ca*. 80 - 100 ˚C.

Measurements

$Ni(Et_2en)_2I_2$ is reported[1] to be diamagnetic and you do not need to measure its susceptibility. First read the background theory, procedure, and method of calculation of magnetic susceptibilities given in the Appendix to this experiment. (Make sure that you understand how to apply the tube correction and the corrections for the diamagnetism of the Et_2en ligand). Then measure the magnetic properties of $Ni(Et_2en)_2(NCS)_2$, using the dry crude product and also the recrystallized sample if the latter consists of small, fine crystals (crushing tends to cause problems with electrostatic charge). Record the IR spectrum of $Ni(Et_2en)_2(NCS)_2$ and identify the CN stretch of the NCS groups.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write balanced equations for the formation of the complexes giving your yields and m.p.
4. Report the magnetic susceptibility of $Ni(Et_2en)_2(NCS)_2$ and identify its CN stretch from the IR spectrum.
5. Report your observations about the formation of the nickel bromide complexes. Suggest how you might confirm that the colour changes in the bromide involve the uptake and loss of water molecules.
6. Draw the crystal field diagram for a tetragonally distorted octahedron and account for your observations in parts 4 and 5; you may assume that the anion in the 'thiocyanate' complex is bonded via N, *i.e.*, it is an iso-thiocyanate complex. This fact can be demonstrated by its IR spectrum.
7. To which point groups do the products that you have made belong?
8. Write a short conclusion.

Hand in with the report:	Samples of $Ni(Et_2en)_2(NCS)_2$, $Ni(Et_2en)_2I_2$, $Ni(Et_2en)_2Br_2$ and $Ni(Et_2en)_2Br_2.2H_2O$	
	Infrared Spectrum of $Ni(Et_2en)_2(NCS)_2$	
Allocation of marks (Total 100):	Experimental write-up/presentation	10
	Samples (quality/yields/m.p.)	34
	Spectra (quality/interpretation)	6
	Calculations/discussion/conclusion	50

References

1. D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, **1963**, 616.

Appendix

Magnetic Susceptibility Balance with Direct Digital Read-out

This involves the same basic principle as in the Standard Gouy method, but in this apparatus it is the force that the sample exerts on the magnet that is measured. Two magnets (samarium-cobalt alloy; field strengths 0.44T are used. These are mounted back-to-back and suspended from beryllium-copper torsion strips. When a sample tube is placed between the poles of one of the magnets, the system tilts, and a metal 'flag' moves between two opto-interruptors. The resultant signal from the opto-interruptors is amplified, and fed back, via a standard resistance, through a coil mounted between the poles of the other magnet. This feedback current tends to restore the magnets to their original position.

An equilibrium is reached in which the current through the coil exerts a force exactly equal to that of the sample. This current is read off from a digital voltmeter connected across the standard resistance. An electrical zero is provided by a variable voltage applied to a second coil.

Packing the sample tube

When packing a special sample tube to a length of approximately 2.5 cm, it is important that the column of substance in the tube should be uniformly packed. This is best achieved by placing the substance in the tube a little at a time and tapping the tube gently on a rubber bung between each addition. Crystalline specimens may require powdering, but the grinding process may cause the sample to gain electrostatic charge and this will prevent accurate measurements on the balance. To minimise this samples should be ground using a plastic spatula and then left for at least 15 minutes after grinding to allow the static charge to subside before packing. An antistatic gun may be used if available.

Operation of the magnetic susceptibility balance

1) Turn the left-hand knob to RANGE 1, and allow 5-10 min. for the apparatus to warm up. [If the apparatus is to be used frequently, it should be left on all day].
2) Adjust zero knob until display reads 000.
3) Gently place the sample tube into the holder and take reading $\mathbf{R_0}$ in cm^2. This value should be negative since glass is diamagnetic.
4) Weigh the sample tube.
5) Pack the sample tube as explained above and weigh the combination of sample tube and sample to obtain the sample mass, **m**, in g.
6) Gently place the sample tube into the holder and take reading **R** in cm^2. If the measurement goes off scale, remove the sample tube turn the RANGE knob to X10 (measurement divided by 10). Rezero the instrument. Reinsert the sample tube and record the reading. Multiply the reading by 10.
7) Remove the tube and gently tap the tube on a rubber bung.
8) Place the tube back in the balance and record the reading.
9) Repeat steps 8) and 9) until a constant reading is obtained.
10) Measure sample length, **l**, in cm. Record the ambient temperature, **T**, in K.

Calculations

The mass susceptibility χ_g (c.g.s. units) is calculated from the following equation:

$$\chi_g = \frac{C(R-R_0)l}{10^9 m}$$

where **l** is sample length (cm); **m** is sample mass (g); $\mathbf{R_0}$ is the empty tube reading; **C** is the dimensionless calibration constant (involving the field strength etc).

This value can then be converted to the molar susceptibility χ_m ($cm^3\ mol^{-1}$) by multiplying by the formula weight.

Next, in order to get a value that is related to the number of unpaired electrons pulling the sample into the magnetic field, the effect of all the diamagnetic pairs repelling it must be removed, including the paired electrons in the paramagnetic atom itself to give the corrected molar susceptibility, χ'_m. Note that since the diamagnetic repulsions oppose (weaken) the paramagnetic attraction, χ'_m is always larger than χ_m. A table of these diamagnetic corrections can be found next to the balance or in most good chemistry databooks.

Finally, the effective magnetic moment μ_{eff} (BM units) can be calculated using the following equation:

$$\mu_{eff} = (8\ \chi'_m\ T)^{½}$$

where χ'_m is the corrected molar susceptibility ($cm^3\ mol^{-1}$) and **T** is the temperature in K.

EXPERIMENT 9

[Co(dinosar)]Cl_3: An Encapsulation Complex prepared by a Template Reaction.

Introduction

Reactions of ligands coordinated to metal centres are of great synthetic importance. One such type of reaction is the template reaction in which the metal coordination sphere acts as a shape former, bringing appropriate parts of the ligands into close contact to allow subsequent reaction with each other or with an external agent and thus minimising unfavourable entropy contributions to reaction energies. The natural syntheses of many metalloproteins and metalloenzymes are based on template reactions. In some cases the new molecule will decoordinate from the metal, however in this experiment the resulting macrobicyclic species, dinosar (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-6.6.6-eicosane) - formed from a template "capping" on three 1,2-diaminoethane (ethylenediamine, en) ligands - completely encapsulates the cobalt.

Safety Information

Hydrogen peroxide is a powerful oxidant and its aqueous solutions cause skin damage rapidly. Avoid any contact. Formaldehyde is toxic and carcinogenic and any solutions containing it must be handled in a fume cupboard. All other reagents and products (namely the cobalt complexes, 1,2 diaminoethane, and nitromethane) should be regarded as toxic. Avoid ingestion via nose, skin or mouth and wear gloves. Hot acetic acid and concentrated hydrochloric acid are corrosive and noxious. Wear rubber gloves and work in a fume cupboard. Ethanol, acetic acid and nitromethane are flammable.

Experimental

Preparation of [$Co(en)_3$]Cl_3

Dissolve $CoCl_2.6H_2O$ (6.0 g) in water (17.5 cm^3). Whilst dissolution is in progress, add anhydrous 1,2-diaminoethane (4.5 cm^3) to water (12.5 cm^3) in a conical flask, cool the mixture in ice and then cautiously introduce 6M aqueous HCl (4.5 cm^3; concentrated hydrochloric acid is approximately 12M). With continuous stirring, add the $CoCl_2$ solution to the diaminoethane solution, followed by 30% aqueous H_2O_2 (5.0 cm^3). Continue stirring for several minutes until effervescence has ceased then place the flask on a hot plate (in a fume cupboard) and boil gently. When the solution has evaporated to a volume of approximately 30 cm^3 (but no less, otherwise a green byproduct may be recovered), add an equal volume of concentrated hydrochloric acid, followed by ethanol (60 cm^3). Cool in ice and filter off the precipitate under suction. Wash with ethanol (2 x 20 cm^3) and two of diethylether (20 cm^3) and air-dry the product. Record the yield and measure the electronic spectrum (300-600 nm) of an aqueous solution of your product. [NB you should use a known concentration since you must report extinction coefficients].

Preparation of [$Co(dinosar)$]Cl_3

Dissolve [$Co(en)_3$]Cl_3 (2.45 g) and Na_2CO_3 (1.2 g) in water (25 cm^3) in a conical flask. With continuous stirring, add 40% aqueous formaldehyde (18 cm^3 CAUTION) followed by nitromethane (2.85 g). Then, either (a) maintain the mixture at 30-40 ˚C (water bath on hotplate) for 60-90 minutes or (b) allow to stand at ambient temperature for (at least) 5 hours. If no precipitate appears, addition of a small quantity of ethanol (5 cm^3) should encourage it. The resulting solid is filtered under suction and cautiously dissolved in the minimum volume (*ca*. 7 cm^3) of hot 3 M hydrochloric acid. (Note that you may actually need to use slightly more than this). Cool this solution in ice/water and add ethanol (20-25 cm^3). Filter the recrystallised product under suction, air dry and place in a vacuum desiccator.

Record the electronic spectrum of a known concentration (300-600 nm) of an aqueous solution and the infrared spectrum of a nujol mull. High field NMR spectra (^{1}H **and** ^{13}C) are available from a demonstrator.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Give balanced equations for both stages together with yields of the products.
4. Report the electronic spectra of both complexes.
5. Tabulate the NMR data for $[Co(dinosar)]Cl_3$ and assign the spectra.
6. Assign the characteristic vibrations in the IR spectrum.
7. What is the point group symmetry at Cobalt?
8. Briefly suggest a plausible mechanism for the capping reaction.
9. Write a short conclusion.

Hand in with the report:	Samples of $[Co(en)_3]Cl_3$ and $[Co(dinosar)]Cl_3$
	Electronic Spectra for both samples
	Fully assigned ^{1}H and ^{13}C NMR spectra of $[Co(dinosar)]Cl_3$
	Fully assigned infrared spectrum of $[Co(dinosar)]Cl_3$

Allocation of marks (Total 100):	Experimental write-up/presentation	25
	Samples (quality/yields)	25
	Spectra (quality/interpretation)	25
	Conclusion / Results and Discussion	25

Reference

R. J. Geve, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, **l984**, 106, 5478, and references therein.

EXPERIMENT 10

Anomalous Paramagnetism in some Iron(III) Chelates Studied by the Evans NMR Method

Introduction

Crawford and Swanson have described the use of the Nuclear Magnetic Resonance technique to determine magnetic moments in solution.[1] The method relies on measuring the separation (Δf) in the resonance positions of two identical protons in two solutions. One of the solutions contains the paramagnetic material and the other contains pure solvent. The separation, Δf in Hertz, is related to the mass susceptibility, χ_g, of the dissolved paramagnetic substance by the following relationship

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_o \qquad \textbf{(1)}$$

where f is the frequency of operation of the machine, m is the concentration of paramagnetic substance (g/cm^3) and χ_o is the mass susceptibility of the pure solvent. The magnetic moment is then calculated using eqns **2** and **3**.

$$\chi_M = \chi_g . M \qquad \textbf{(2)}$$

where χ_M is the molar susceptibility and M is the molar weight of the complex. This gives your answer in c.g.s. units.

$\chi_M{}'$ is obtained from χ_M by including a diamagnetic correction for the ligands. This is done by summing the diamagnetic corrections for each ligand atom.[2] Finally, the effective magnetic moment μ_{eff} can be calculated using the equation **3**.

$$\mu_{eff} = (8\ \chi_M{}'\ T)^{1/2} \qquad \textbf{(3)}$$

where T is the temperature of the NMR probe.

In this experiment the technique is applied to the study of the anomalous paramagnetism of iron(III) *N,N*-dialkyldithiocarbamates. These complexes are anomalous in that their behaviour is neither "high spin" nor "low spin".[3,4] Depending on the nature of the alkyl substituents on the ligand, the value of the magnetic moments can be pure low spin, pure high spin, or intermediate between these values.

The explanation is that the ligand field energies for these complexes lie close to the crossover between the high-spin, weak field ground state configuration, ($t_{2g}^3 e_g^2$) and low-spin strong-field (t_{2g}^5) states. Thus the spin pairing energy for these complexes must be close to the ligand field strength. The high-spin configuration has 5 unpaired electrons and the low-spin configuration has one unpaired electron. For $Fe(S_2CNR_2)_3$ complexes, the low-spin case occurs for R = isopropyl, and isobutyl, and high spin for 2R = pyrrolidyl. Intermediate magnetic moments are observed for R = methyl, ethyl, benzyl. A spin equilibrium is suggested for these complexes.[3,4]

The iron dithiocarbamates also have the advantage of being easy to prepare and purify and of having good solubility in solvents such as chloroform. As paramagnetic shift, Δf, in eq. 1 depends on concentration, it

is an advantage to have as high a concentration as possible for accurate measurement of the shift. For these complexes, shifts of 5-40 Hz are observed for 0.02 g/cm^3 chloroform solutions.

Safety Information

Chloroform should be used in a fume cupboard. Carbon disulfide is toxic and must be used in a fumecupboard (wear gloves too). Both amines are irritating to eyes, face and respiratory system, again use gloves and work in a fumecupboard.

Experimental

Make $Fe(S_2CNR_2)_3$ for NR_2 = N,N-dicyclohexyl and N,N-dibenzyl as follows: Solutions of sodium salts of the ligands are prepared by adding CS_2 (0.05 mol; density = 1.266) to a stirred solution of the amine (0.05 mol) in ethanol (50 cm^3). 6 M NaOH (10 cm^3) is then added with stirring.

The complexes are prepared by mixing 0.017 mol of 60% w/v $FeCl_3$ aqueous solution with the solution from the ligand preparation. A black-brown precipitate immediately forms. This should be recovered by vacuum filtration, the precipitate washed with ethanol and air-dried. The complex is recrystallized by dissolution in hot $CHCl_3$ (30 cm^3) (**in a fume hood**), vacuum filtration, and addition of ethanol (30 cm^3) to the filtrate. Black or dark brown crystals form on cooling; the crystals are recovered by vacuum filtration and are washed with ethanol and air-dried.

The magnetic moments are determined by preparing a chloroform solution of accurately known concentration of the complex (ca. 0.1 g in ca. 0.5 cm^3 - use a pipette). An internal reference is used by placing a sealed capillary containing pure $CHCl_3$ in an NMR tube containing the complex solution. The NMR spectrum (in this case on a 270 MHz NMR machine) is then recorded in the region of the $CHCl_3$ peak. A large, broad solvent peak is observed due to paramagnetic broadening by the complex and a smaller, sharp peak is observed downfield to this peak. The magnetic moments can then be calculated.[1,2]

[NB] For the purposes of this experiment you may calculate the susceptibility of the solvent relativity using the values in reference 2 or see experiment 8.

Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Give balanced equations for the formation of the complexes and yields.
4. Give the magnetic moments (as determined by the Evans NMR method) of the two complexes. Comment on the values obtained.
5. What are the point groups of the compounds that you have made?
6. What sources of both systematic and random error are there in this experiment? Which are most significant errors and how might they be minimised?

Hand in with the report: Samples of both iron(III) chelates
NMR Spectra for both samples

(continued overleaf)

Allocation of marks (Total 100):	Experimental write-up/presentation	10
	Samples (quality/yields)	20
	Spectra (quality/interpretation)	20
	Discussion/conclusions	25
	Calculations	25

References

1. T. H. Crawford and J. Swanson, *J. Chem. Ed*., **1971**, 48, 382.
2. B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry*; Lewis and Wilkins, Eds., Interscience, New York, 1960, Ch. 6; J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw Hill, **1959**, chapter 2. [See also expt. 8]
3. A. H. White, R. Roper, E. Kokot, H. Waterman and R. L. Martin, *Aust. J. Chem*., **1964**, 17, 294.
4. A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem*837.