

# CHEMISTRY DEPARTMENT



## LABORATORY MANUAL

### SIC3021 PRACTICAL OF INORGANIC CHEMISTRY III

## Emergency Telephone Numbers

Further information in the details of the safety and health practice in the Universiti Malaya can be found at:



Occupational Safety &  
Health and Environment  
(OSHE), Universiti Malaya



Universiti Malaya Safety  
Handbook

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarize yourself with the safety aspects of your laboratory work.

### **Emergency Telephone Numbers:**

- |   |                              |
|---|------------------------------|
| • National Emergency Number                                       | 999 (Mobile phone, dial 112) |
| • Universiti Malaya Security Office                               | +603 7967 7070               |
| • Universiti Malaya Medical Centre (UMMC)<br>Emergency Department | +603 7949 2892               |
| • Universiti Malaya Students' Health Clinic                       | +603 7967 6445               |
| • Occupational Safety & Health and Environment<br>(OSHE)          | +603 7967 6597               |
| • Department of Chemistry Office                                  | +603 7967 4204               |
| • Pantai Fire Station (Jalan Pantai Baru)                         | +603 2282 4444               |
| • Pantai Police Station (Jalan Pantai Baru)                       | +603 2282 2222               |

(The numbers given above are working telephone numbers, as of 5<sup>th</sup> October 2022)

## CONTENTS

NO.	EXPERIMENT	PAGE
1	SYNTHESIS OF NICKEL COMPLEX WITH MIXED LIGAND SYSTEM	4
2	THE PREPARATION AND CHARACTERIZATION OF MESITYLENETRICARBONYLMOLYBDENUM(0)	6
3	MAGNETIC SUSCEPTIBILITY	8
4	ELECTRONIC SPECTRA OF NICKEL(II) COMPLEXES (A $d^8$ SYSTEM)	18

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## SYNTHESIS OF NICKEL COMPLEX WITH MIXED LIGAND SYSTEM

### INTRODUCTION

Hydrazones are prepared from the condensation of hydrazides with aliphatic or aromatic aldehyde-ketones. These compounds form metal complexes, featuring nitrogen, and oxygen donor atoms, showcasing intriguing stereochemical, electrochemical, and electronic properties. They have diverse applications across biological, inorganic, analytical, and catalytic processes.

On the other hand, phosphine-based compounds find broad pharmacological utility, serving as antiviral, antioxidant, antifungal, anticancerogenic, antibacterial, and antitumor agents.

In the realm of anticancer drug research, the stabilization of nickel(II) and palladium(II) complexes with bulky ligands like triphenylphosphine can prevent the formation of highly reactive species, enabling interactions with pharmacological targets such as DNA. Additionally, tertiary phosphine complexes of nickel, palladium, and platinum play a significant role in catalysis as homogeneous catalysts. Notably, nickel catalysis is particularly appealing due to its cost-effectiveness.

### LEARNING OUTCOME

- Students will be able to prepare and characterize mixed ligand metal complexes.

### METHODOLOGY

#### a) Synthesis of dichlorobis(triphenylphosphino)nickel(II), $\text{NiCl}_2(\text{PPh}_3)_2$

**NOTE: PLEASE HANDLE GLACIAL ACETIC ACID WITH CARE AND DO IT IN THE FUME CUPBOARD**

In a round-bottom flask, melt 5.25 g of triphenylphosphine in a water bath. Weigh 2.38 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and add 50 mL of glacial acetic acid to the nickel salt. A slurry will form. Pour the slurry into the stirring molten triphenylphosphine. Remove the flask from the bath and continue stirring at room temperature for 3 hours. Filter the product, wash with about 20 mL of hot glacial acetic acid to remove traces of free triphenylphosphine and keep in a vacuum desiccator. Run IR for the prepared compound.

#### b) Synthesis of Schiff base, benzoic acid-(2-hydroxy-benzylidene)-hydrazide

Dissolve 0.136 g of benzoylhydrazide in 30 mL of ethanol and pour the solution into a 250 mL round bottom flask. Dissolve 0.122 g of salicyldehyde in 20 mL of ethanol. While stirring the benzoylhydrazide solution, pour salicyldehyde into the first solution. Reflux the mixture for 4.5 hours. Then, cool the reaction mixture to room temperature. If solids do not appear, dry off the solvent on a rotary evaporator until yellow solid is seen. Pour water into the round bottom flask, swirl several times and filter the solid. Recrystallize the solid from hot ethanol to afford the pure ligand. Analyze the prepared Schiff base on IR and  $^1\text{H}$  NMR (in  $\text{DMSO-d}_6$ ).

**c) Synthesis of organophosphine nickel(II) Schiff base complex,  $\text{NiCl}_2(\text{PPh}_3)_2$  + Schiff base**

Reflux  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.653 g) with the Schiff base (0.226 g) in 40 mL of methanol in the presence of an equivalent amount of KOH for 5 hours. Cool the reaction mixture to room temperature. Filter the precipitate, wash with methanol and dry in a vacuum desiccator. Recrystallize to obtain the red crystal in dichloromethane. Run IR for the prepared compound.

**QUESTIONS**

1. Rationalize the utilization of molten  $\text{PPh}_3$  over its solution. State the nature of the  $\text{PPh}_3$  in most organic solvents.
2. Explain the denticity of each ligand ( $\text{PPh}_3$  and Schiff base) towards formation of nickel complexes. Predict the possible geometries in your explanation.
3. Propose a mechanism for the nickel complex formation with the synthesized mixed ligands that is obtained in this experiment (proof from the spectroscopic data).

**REFERENCES**

1. H.A. Tayim, A. Bouldoukian, F. Awad, *J. Inorg. Nucl. Chem.*, 1970, 32, p 3799-3803.
2. P. Krishnamoorthy, P. Sathyadevi, P.T. Muthiah, N. Dharmaraj, *RSC Adv.*, 2012, 2, p 12190-12203.

## Experiment 2

## Practical of Inorganic Chemistry III

### THE PREPARATION AND CHARACTERIZATION OF MESITYLENETRICARBONYLMOLYBDENUM(0)

#### INTRODUCTION

Isolated organometallic compounds of the transition elements have been known for a long time (e.g., Zeise's salt – 1827). However, it was not until the 1950's, following the accidental discovery of ferrocene, that the organometallic chemistry of the transition metals became a major area of inorganic research.

Perhaps the most versatile starting materials for the laboratory synthesis of transition metal organometallic compounds are the metal carbonyls. In this experiment, molybdenum hexacarbonyl is reacted directly with an organic aromatic (mesitylene). In general, the reaction can be represented as:



#### LEARNING OUTCOME

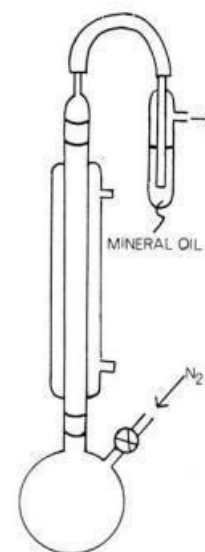
- Students will be able to prepare and characterize air- and moisture-sensitive compounds.

#### METHODOLOGY

**NOTE: THIS PREPARATION MUST BE PERFORMED IN A FUME HOOD. METAL CARBONYLS ARE VERY TOXIC.**

Assemble the apparatus as shown in the diagram using a 50 mL two-neck round bottom flask and a simple reflux condenser (water need not be circulated through the condenser: air cooling is sufficient).

Add 1.8 g  $\text{Mo}(\text{CO})_6$  to the flask followed by 10 mL of mesitylene, 10 mL decalin and 5-10 mL of toluene or hexane (This facilitates the sublimed  $\text{Mo}(\text{CO})_6$  to return back to the reaction mixture during refluxing at  $186^\circ\text{C}$ ). Flush the apparatus with a moderate stream of nitrogen for about 5 min. After the nitrogen flow is turned off and the stopcock closed, bring the mixture to a moderate boil with the heating mantle. Reflux for 2-3 hours (yield improves with stirring), then turn off the heat and immediately flush with nitrogen to prevent the mineral oil in the bubbler from being sucked back into the reaction vessel.



The apparatus for the preparation of mesitylene tricarbonyl molybdenum (0).

Allow the reaction mixture to cool to room temperature, then filter using a Buchner funnel. For purification, dissolve the filtered crude product in a minimum amount of  $\text{CH}_2\text{Cl}_2$  (FUME CUPBOARD), pass the solution through a medium frit loaded with ~2-3 cm Celite (aspirator pump). Transfer the filtrate to a rotary evaporator and evacuate to dryness. Remove the resulting fine lemon-colored crystals with a spatula and weigh. Further purification of the recrystallized product may be achieved by vacuum sublimation (100°C, high vacuum).

(a) Characterization

i. IR Spectrum.

Record the IR spectrum of the product over the whole range and assign the important bands. Also record the IR spectrum of the compound in solution in  $\text{CHCl}_3$  in the region 1800-2000  $\text{cm}^{-1}$ . Comment on the differences between the two spectra in this region.

ii. NMR Spectrum.

Prepare 0.5 mL of a saturated solution of the product in the specially purified  $\text{CHCl}_3$  (obtainable from the Laboratory Assistant) and record the NMR spectrum. Comment on the spectrum particularly the information it provides about the structure and bonding of the complex. Explain why free mesitylene shows two peaks at 2.25 and 6.78 ppm (vs. TMS in  $\text{CDCl}_3$  of relative intensity 9:3).

## QUESTIONS

1. Use spectral data to determine the structure of the complex.
2. To what symmetry group does the complex belong?
3. Discuss the differences in the stretching frequencies of CO in  $\text{Mo}(\text{CO})_6$  and the product.

## REFERENCES

1. G. E. Coates, M. L. H. Green and K. Wade: *Organometallic Compounds Vol. 11. (The Transition Elements)* 1968.
2. B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, (1959) 551.
3. F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann., *Advanced Inorganic Chemistry*, 6th Edition, Wiley-Interscience: New York, 1999.
4. R. J. Angelici, *J. Chem. Ed.*, 45 (1968) 119.

### MAGNETIC SUSCEPTIBILITY

#### INTRODUCTION

Magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field. If magnetic susceptibility is positive, then the material can be paramagnetic, ferromagnetic, ferrimagnetic, or antiferromagnetic. Measurements of magnetic properties have been used to characterize a wide range of systems from oxygen, metallic alloys, solid state materials, and coordination complexes containing metals. Most organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. All the transition metals have at least one oxidation state with an incomplete d subshell. Magnetic measurements, particularly for the first-row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about the oxidation state and electron configuration. The aim of the experiment is (1) to acquaint the student with two of the experimental techniques involved in magnetochemical measurements, *viz*, the Gouy method for solids and the Evans' method for solutions, and (2) to examine the magnetic behavior of a complex in the solid and solution state, and to gain information about stereochemical changes if any. The latest techniques include SQUID, (superconducting quantum interference device) a very sensitive magnetometer used to measure extremely subtle magnetic fields, based on superconducting loops containing Josephson junctions. Commercial SQUID magnetometers are available for temperatures between 300 mK and 400 kelvins, and magnetic fields up to 7 tesla.

#### LEARNING OUTCOME

- Students will be able to correlate the magnetism of a metal complex with its electronic configuration and ligand strength.

#### METHODOLOGY

To a stirred solution of 4.0 g of manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) and 10.2 g of sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) in water (150 mL) slowly add acetylacetone (18.8 mL). Follow by adding slowly, with stirring, a solution of potassium permanganate (0.80 g in 40 mL of water) and a few minutes later in small amounts, a solution of sodium acetate trihydrate (10.0 g in 40 mL of water). Heat on a water bath for 20 minutes at about  $60^\circ\text{C}$ , cool in ice-cold water and filter off the dark solid. Wash the product with ice-cold water, and dry in a vacuum desiccator over anhydrous calcium sulphate.

Dissolve the dry chelate in warm toluene (20 mL), filter and re-precipitate the complex by cooling and adding petroleum ether ( $40\text{-}60^\circ\text{C}$ ) (about 75 mL). Dry in a vacuum desiccator. Calculate the percentage yield.



- a) Measure the paramagnetic susceptibility of the complex as a solid (see Appendix 3A, p. 9-12).
- b) Run the NMR spectrum of a  $\text{CHCl}_3$  solution containing a known concentration of the complex (ca. 0.01 g/mL). Insert a capillary tube containing pure  $\text{CHCl}_3$  as external reference (see Appendix 3B).
- c) From the frequency separation of the proton resonance in the  $\text{CHCl}_3$  solution relative to the external reference of pure  $\text{CHCl}_3$ , calculate the magnetic susceptibility of the complex in solution.

**Notes:**

NMR spectra of these solvent mixtures are provided. See Appendix 3C for the calculation of the mass susceptibility  $\chi_o$  of these solvent mixtures.

Diamagnetic correction of solvent: The frequency separation for the methyl resonance in the solvent mixture relative to the pure toluene capillary is a measure of the solvent susceptibility, hence this frequency shift is equivalent to a diamagnetic correction and must therefore be subtracted from the overall frequency separation measured for the metal complex.

From the corrected frequency separation calculate  $\chi_g$ ,  $\chi_M$ , and  $\chi_M^{\text{corr}}$  (corrected for the diamagnetism of the ligands, See Appendix 3D), and hence the solution Bohr Magnetron Number,  $\mu_{\text{eff}}$ . (see Appendix 3B).

**QUESTIONS**

- 1) Describe under what conditions spin-only formula will be useful to calculate  $\mu$  of the complexes (Appendix 3A).
- 2) What conditions should be satisfied by a complex whose magnetic susceptibility we wish to determine in solution? Are there any restrictions to the type of reference solvent we could use? On the basis of your answer, discuss the feasibility of determining  $\mu_{\text{eff}}$  for the following:
  - a.  $\text{Fe}(\text{CN})_6^{3-}$  in aqueous solution using the tert-butanol methyl resonance as reference.
  - b.  $\text{CuCl}_4^{2-}$  in pyridine using the toluene methyl resonance as reference.
  - c.  $\text{Ni}(\text{DMG})_2$  in benzene using the methyl resonance of 4-methylpyridine as reference (DMG = dimethylglyoxime).

**REFERENCES**

1. F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann., Advanced Inorganic Chemistry, 6th Edition, Wiley-Interscience: New York, 1999.
2. M. Greenaway and L. E. Trail. J. Chem. Educ., (1983), 60 (8), p 681.

## APPENDIX 3A

### THE MEASUREMENT OF MAGNETIC SUSCEPTIBILITY

#### THEORY AND DEFINITIONS

Magnetic susceptibility is defined as the ratio of the intensity of magnetism induced in a substance to the magnetizing force or intensity of field to which it is subjected. It provides important electronic structural information of the transition and rare earth metal complexes.

Traditionally, measurement of magnetic susceptibility has been made using the Gouy and the Faraday methods. The original instruments were originally made from conventional laboratory balances and large permanent magnets. The magnets were brought towards the sample and the positive or negative change of apparent weight was noted. The balances and sample holder were free of ferromagnetic materials. The systems that evolved were very large relying on heavy magnets, fixed in position, and a moving sample.

The late Professor Evans of Imperial College London introduced an innovative step to the measurement. Instead of measuring the apparent weight loss or gain of a suspended sample, the force acting upon a suspended magnet was detected, thereby turning the method on its head. The advantage realized by this step led to the development of the light and inexpensive magnetic susceptibility balance, which is the MSB-MKI. The model used in our laboratory is MSB-AUTO which has many improved features, and which still relies on the advantage first obtained by Professor Evans.

The three most common ways that magnetic susceptibility values are expressed are with reference to the volume of sample, the weight of sample, and the moles of sample. These terms are commonly referred to as volume susceptibility, mass susceptibility, and molar susceptibility. The equations relating these terms are provided below:

#### VOLUME SUSCEPTIBILITY

The volume susceptibility,  $\chi_v$  designated is expressed by the following formula:

$$\chi_v = \frac{I}{H}$$

where  $I$  is the intensity of magnetism included in the substance and  $H$  is the intensity of the applied external magnetic field

The volume susceptibility can be quite variable due to changes in the density of the substance, particularly when the sample is a gas or solid. The mass susceptibility,  $\chi_g$ , introduces a density factor in the following manner:

## MASS SUSCEPTIBILITY

$$\chi_g = \frac{\chi_v}{d}$$

where  $d$  is the density of the substance, Note that  $\chi_g$  has units of reciprocal density,  $\frac{\text{cm}^3}{\text{g}}$

## MOLAR SUSCEPTIBILITY

The most common way of reporting a magnetic susceptibility value in the literature is by molar susceptibility, designated as  $\chi_M$ . The relationship of molar susceptibility to mass susceptibility is shown below:

$$\chi_M = \chi_g \times MW$$

where  $MW$  is the molecular weight of the substance.

The  $\chi_M$  is the best value to use when comparing different materials qualitatively or assessing the potential of a quantitative applications since the value of the term is not subjected to variations due to the method of measurement or to sample density.

Since the Auto, like other methods, measures Volume Susceptibility and the literature is quoted in Molar Susceptibility, the conversion between the two values is quite common in magneto chemical studies. *The initial step in the conversion, that is obtaining a  $\chi_g$  value from  $\chi_v$ , is done within the Auto provided the length and weight of the sample are known and can be entered into the unit.*

## Calculation of magnetic moment

The molar susceptibility obtained has to be corrected for the inherent diamagnetic contribution ( $\chi^{\text{dia}}$ ) from the ligands and metal ions using the table of Pascal's constants.

$$\text{i.e. } \chi_M^{\text{corr}} = \chi^{\text{exp}} - \chi^{\text{dia}}$$

The relationship between molar susceptibility and effective magnetic moment,  $\mu_{\text{eff}}$  is

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \text{ T}} \quad \text{Bohr Magnetron}$$

It can also be shown that the effective magnetic moment,  $\mu_{\text{eff}}$  is given by,

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

[Note: A system obeying Curie law would have no or negligible orbital contribution towards the magnetic moment].

For the details on the operation of the MSB-AUTO magnetobalance, please refer to the operating manual.

### **Cleaning and storage of sample tube**

[Note: The sample tube used in this magnetobalance is a high precision tube made of silica. It is expensive and should be treated with care!]

The good maintenance of the sample tubes is essential for good results. Sample tubes can be cleaned with conventional detergents and/or organic solvents, depending on the nature of their sample. In difficult cases, strong acids, viz. HCl or HNO<sub>3</sub> may be required. Pipe cleaners have proven to be a useful tool. Similarly, an aerosol can of ethylene dichloride, supplied with a plastic capillary spout (available for degreasing electronic components) has proven invaluable in removing oil from the tubes when analyzing for wear metals.

The tube should be stored in a dust-free environment and its susceptibility should be measured before introducing a sample. As a final precaution, the outside of the tube should be wiped with a dust free wiper just prior to introducing it to the balance, particularly if it has been allowed to lay on the bench.

### **Packing sample into the tube**

The tube is packed as follows. The solid to be measured is ground to a fine powder in a mortar and pestle. HgCo(NCS)<sub>4</sub> forms very fine crystals and can usually be used without grinding. Note that the greatest source of error in Gouy measurements is in homogeneous packing. It is essential that an effective routine for the packing of the powder into the tube is developed and adhered to. Good packing requires time and patience.

A small amount of the compound is picked up from the mortar, placed in the flared mouth of the tube, and tapped to the bottom of the tube. The closed end of the tube is tapped for about a minute on two sheets of filter paper on a wooden bench. (See a demonstrator about this). This process is continued until the tube is filled to the mark - make sure that the sample does not pack down with further tapping. Wipe away any excess compound from the mouth of the tube to remove excess moisture.

### Standard to calibrate the balance

Several standards can be used for checking the calibration of the balance. Perhaps one of the most reliable trouble free standard is water ( $10^6 \chi_g = -0.720$ ), since it is readily available in pure form. A singly distilled water sample should suffice.

$\text{HgCo(SCN)}_4$  ( $10^5 \chi_g = +1.644$  at  $20^\circ\text{C}$ ) is considered one of the best solid standards. At other temperature, use the relation

$$\frac{d\chi_g}{d\tau} = -0.05 \times 10^{-6} \text{ cgs/K}$$

to obtain the exact  $\chi_g$  value.

The ethylenediamine salts of nickel,  $\text{Ni(en)}_3 \text{S}_2\text{O}_3$  ( $10^5 \chi_g = +1.104$ ) is also a useful secondary standard.

Many solid samples of paramagnetic substances, if properly dried and ground and packed, usually give within 2% of their literature value.

If it is necessary to recalibrate, please refer to Section 5.2 of the original operator's manual.

## APPENDIX 3B

### EVANS' METHOD FOR MAGNETIC SUSCEPTIBILITIES

(Extracted from J. Chem. Ed., 46, 1969, 167)

This method is based on the principle that the position of a given proton resonance in the spectrum of a molecule is dependent on the bulk susceptibility of the medium in which the molecule is found. The shift of a proton resonance line of an inert substance due to the presence of paramagnetic ions is given by the theoretical expressions<sup>5</sup>.

$$\frac{\delta\nu}{\nu_0} = \frac{2\pi}{3} (\chi_v - \chi'_v) \quad (1)$$

where  $\delta\nu$  is the shift,  $\nu_0$  is the applied field,  $\chi_v$  is the volume susceptibility of the solution containing paramagnetic ions, and  $\chi'_v$  is the volume susceptibility of the reference solution. For example, if an aqueous solution of paramagnetic substance with 3% of t-butyl alcohol as an inert reference substance is placed in the inner tube of a concentric cell, and an identical solution without the paramagnetic substance is placed in the annular section of the cell, two resonance lines will usually be obtained for the methyl protons of the t-butyl alcohol due to the difference in the volume susceptibilities of the solutions. This is in accord with eqn. (1). The gram susceptibility,  $\chi_g$  of the dissolved substance is given by the expression<sup>5</sup>.

$$\chi_g = \frac{3 \delta\nu}{2\pi\nu_0 m} + \chi_o + \chi_o \left( \frac{d_o - d_s}{m} \right) \quad (2)$$

where  $\delta\nu$  is the frequency separation between the two lines in cycles/sec,  $\nu_0$  is the frequency at which the proton resonances are being studied in cycles/sec,  $m$  is the mass of substance contained in 1 cm<sup>3</sup> of solution,  $\chi_o$  is the mass (gram) susceptibility of the solvent ( $-0.72 \times 10^{-6}$  cc g<sup>-1</sup> for dilute t-butyl alcohol solutions),  $d_o$  is the density of the solvent, and  $d_s$  that of the solution. For highly paramagnetic substances, the last term can often be neglected<sup>5</sup>. The molar susceptibility, the effective magnetic moment and the "spin only" number of unpaired electrons may be calculated by the same procedure used for the Gouy measurements (See Appendix 3A).

## APPENDIX 3C

### MASS SUSCEPTIBILITY OF SOLVENT MIXTURES

For a mixture of non-interacting components,

$$\text{Mass susceptibility, } \chi_o = \sum m_f(i) \cdot \chi_o.$$

where  $m_f = \frac{m_i}{\sum_i m_i}$  which is the mass fraction of the i-th component

Use of this equation and the table below would enable us to calculate the mass susceptibility of the solvent mixtures used in this experiment.

**TABLE**

SOLVENT	MASS SUSCEPTIBILITY $\chi_o \times 10^{-6}$ (c.g.s. or Gaussian units)	DENSITY ( $\text{gcm}^{-3}$ )
Benzene	-0.702	0.876
Toluene	-0.7176	0.863
Pyridine	-0.622	0.981
Chloroform	-0.497	1.49

## APPENDIX 3D

### DIAMAGNETIC CORRECTIONS

When making diamagnetic corrections, an addition to the measured value is made for each atom present in the molecule.

The relevant diamagnetic susceptibilities are given in the table below:

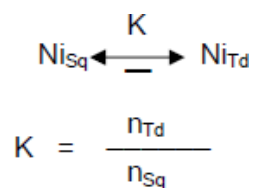
**TABLE**

<b>DIAMAGNETIC CORRECTIONS</b> (c.g.s. units) (All values x 10 <sup>-6</sup> /g atom)	
Element / ion	Diamagnetic correction values
H	-2.93
C	-6.00
C (aromatic)	6.24
O (alcohol)	-4.61
O (carbonyl)	+1.73
N (C=N)	-5.57
Mn <sup>3+</sup>	-10.0
Ni <sup>2+</sup>	-12.8



## APPENDIX 3E

Consider at equilibrium we have  $n$  mol of each of the square planar and tetrahedral forms present, each with a MOLAR magnetic susceptibility of  $\chi_M$ , then for the equilibrium:



We can write,

$$\chi_M^{\text{obs}} = \frac{n_{\text{sq}}}{\Sigma n} \cdot \chi_M^{\text{sq}} + \frac{n_{\text{Td}}}{\Sigma n} \cdot \chi_M^{\text{Td}}$$

But since

$$\chi_M^{\text{obs}} = 0, \quad \text{then,}$$
$$\chi_M^{\text{obs}} = \frac{n_{\text{Td}}}{(n_{\text{Td}} + n_{\text{Sq}})} \cdot \chi_M^{\text{Td}}$$

Now

$$\mu_{\text{eff}} = 7.977 \times 10^2 [\chi_M (\text{SI}) \cdot T]^{1/2}$$

i.e.,  $\mu_{\text{eff}}^2 = \text{constant} \times \chi_M$  at a given temperature, thus we can write

$$\mu_{\text{eff}}^2 = \frac{n_{\text{Td}}}{(n_{\text{Sq}} + n_{\text{Td}})} \mu_{\text{eff}}^2(\text{Td})$$

Assuming that the maximum Bohr Magnetron Number,  $\mu_{\text{eff}}$ , for a tetrahedral  $[\text{Ni}(\text{salen})_2]$  complex in solution is about 3.3 (See Reference 1), it is then possible to obtain an expression for  $K$  which can be solved using the observed value for  $\mu_{\text{eff}}$ , (obs) which you calculate from your data.

ELECTRONIC SPECTRA OF NICKEL(II) COMPLEXES, A  $d^8$  SYSTEM

## INTRODUCTION

Tanabe-Sugano (TS) diagrams are correlation diagrams that depict energies of electronic states of the complexes (or Terms) as a function of the strength of the ligand field. Ligand field is the electric field that is created by the ligands around a metal ion when the complex is formed. The strength of the ligand field is measured by the parameter  $Dq$ , which is related to the octahedral crystal field splitting by  $10Dq = \Delta_o$ . The energy of an electronic state in a TS diagram is denoted by  $E$ .

Figure 1 shows  $d^8$  diagram. In the diagrams the term energies,  $E$ , are expressed as  $E/B$  and plotted against  $\Delta_o/B$ , where  $B$  is the Racah parameter.

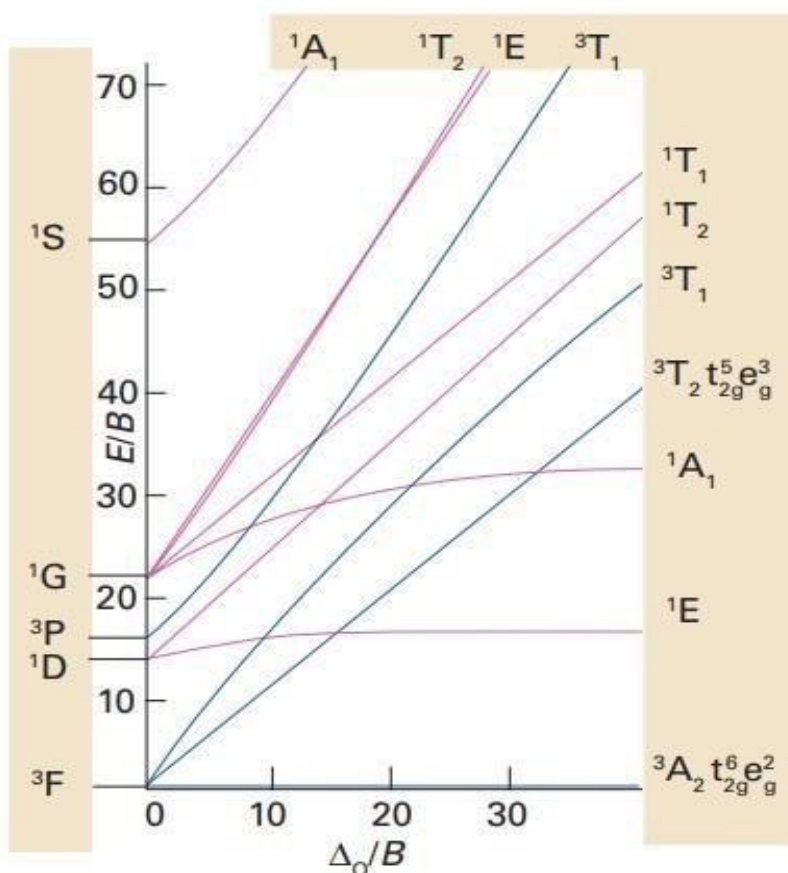


Figure 1: TS diagram for  $d^8$  system (Shiver & Atkins, 2010).

The lowest energy term is set to 0, and all other states are defined relative to the ground state. The terms for  $d^8$  configuration include  $^3F$ ,  $^1D$ ,  $^3P$ ,  $^1G$  and  $^1S$ . Since the  $^3F$  is the ground state we will assume that the two transitions observed in the absorption spectrum arise from the  $^3F$  and  $^3P$  states. (Note that spin allowed transitions ( $\Delta S = 0$ ) will be the most intense). Electron-electron repulsion splits the term into components with different energies as shown in Figure 2.

Atomic term	Number of states	Terms in $O_h$ symmetry
S	1	$A_{1g}$
P	3	$T_{1g}$
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$

Figure 2: Splitting of free-ion terms in octahedral field (Shriver & Atkins, 2010).

The purpose of the experiment is to extract the value of the ligand-field splitting parameters from the electronic absorption spectrum of a complex with more than one d electron, when electron-electron repulsions are important.

The strategy involves fitting the observed transitions (UV visible spectra) to the correlation lines in a Tanabe-Sugano diagram and identifying the values of  $\Delta_o$  and B.

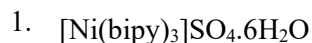
## LEARNING OUTCOME

- Students will be able to explain the effect of ligand strength on the electronic spectra of metal complex by using the Tanabe-Sugano diagram.

## METHODOLOGY

Preparation of Nickel(II) Complexes:

*\*obtain complex 1 from the lab assistant and prepare complexes 2, 3, 4 and 5.*



Warm an aqueous solution containing 15 g of 2,2-bipyridyl and 6 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . Cool and filter. Dissolve 5 g of the chloride and add  $5 \text{ cm}^3$  of a 1 M solution of  $\text{Na}_2\text{SO}_4$ .  $\text{Ni}(\text{bipy})_3\text{SO}_4$  crystallizes out.

Reference: J. Chem. Soc., 1971 (A), 1637, 1640.

2.  $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Add 3.0 mL of 70% aqueous ethylenediamine to a solution of 2.38 g (0.01 mol)  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 100 mL of water. Filter the purple solution to remove the small amount of anhydrous iron oxide which precipitates and is then evaporated to a volume of 40 to 50 mL on a steam bath.

Add two drops of ethylenediamine, and cool the solution in an ice bath. Collect the orchid-colored crystals by suction, wash twice with 95% ethanol, and air-dried. The yield is *ca.* 2.86 g (80%). Several more grams may be recovered from the mother liquor by adding ethanol and cooling.

3.  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$

Dissolve 2 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 3 mL water. Add 6 mL  $\text{NH}_3$  and heat for 10 min. but do not boil. (Use fume-hood.) Then cool the solution in an ice bath and slowly add 6 mL ethanol while stirring. Filter with suction. Wash the precipitate with ethanol and acetone; and air-dried. Record your yield.

4.  $[\text{Ni}(\text{DMSO})_6]\text{Cl}_2$

Dissolve 2 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in minimum ethanol (approx. 3-4 mL) and mix with the same volume of ether, followed by 4.0 mL of dimethylsulfoxide (DMSO). Cool the mixture in the refrigerator until crystals are formed. Filter and dry in a vacuum desiccator.

Reference: J. Inorg. Nucl. Chem., (1961), 16, 219.

5.  $\text{K}_4[\text{Ni}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$

Dissolve 0.01 mole of  $\text{Ni}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  and KSCN in water (Work out appropriate amounts). Evaporate to dryness. Extract with absolute alcohol. Filter off the  $\text{K}_2\text{SO}_4$  and concentrate on the alcoholic solution to obtain the complex.

Reference: Inorg. Chem. 4 (1965), 715, 823.

Prepare solutions as described in Table 1.

Table 1: Solutions of complexes to be prepared.

<u>Complex</u>	<u>Solvent and Blank</u>	<u>Concentration</u>
1. $[\text{Ni}(\text{bipy})_3]\text{SO}_4 \cdot 6\text{H}_2\text{O}$	Water	0.05 M
2. $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	20% en	0.05 M
3. $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$	Aqueous $\text{NH}_3$	0.05 M
4. $[\text{Ni}(\text{DMSO})_6]\text{Cl}_2$	DMSO	0.05 M
5. $\text{K}_4[\text{Ni}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$	10 M KSCN in water	0.05 M

bipy = 2,2-bipyridyl ; en = ethylenediamine ; DMSO = dimethylsulfoxide

Record the spectrum of each solution in the region 200 - 1100 nm and calculate  $\Delta_0$  and  $B$ , for each ligand.

## QUESTIONS

1. Determine all the spin-allowed electronic transition for  $d^8$  system.
2. Arrange the ligands in the spectrochemical series, that is in order of increasing  $\Delta_o$ .
3. Assign the 2 bands in the observed spectrum of complex 5 and estimate the frequency of the missing band.
4. Estimate the frequency of the absorption maximum for the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transition in complex 1. Why is it not possible to get this directly from the spectrum? (Do not include limitations of instrumentation as a valid reason).
5. The energy versus  $\Delta$  correlations for  ${}^3T_{1g}(P)$  and  ${}^3T_{1g}(F)$  deviate from linearity, why?

## REFERENCES

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