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| **KWAME NKRUMAH UNIVERSITY OF**  **SCIENCE AND**  **TECHNOLOGY** |
| **CHEM 280**  **PRACTICAL CHEMISTRY I**  **ELECTRONIC ABSORPTION SPECTRA OF SOME Cu(II) COMPLEXES** |
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**OBJECTIVES**

* To measure the electronic absorption spectra for some complexes of Cu (II) complexes.
* To determine crystal field splitting energies of some Cu (II) complexes.
* To learn to operate the ultra-violet/visible spectrophotometer.
* To improve upon acquired skills for titration.

**INTRODUCTION**

Transition metals are elements with partially filled d-orbital. Transition metals exhibit a wide range of features which makes them unique and different from other metals on the periodic table. One of such features is the formation of coloured compound. When transition metals absorb energy, they become excited and very unstable; as a result they soon de-excite to release energy in the form of electromagnetic radiations with a particular wavelength. The process of energy absorption, excitation and de-excitation usually occur in the visible region of the electromagnetic spectrum and hence the compounds appear coloured to the eye.

There are several theories that are used to relate electronic absorption spectra to electronic structure. One of these is the **Crystal Field Theory** **(CFT)** which relates electronic absorption spectra to electronic structure by giving account for both the colour and magnetic properties of many coordination compounds.

This theory explains the bonding in complex ions purely in terms of electrostatic forces. The d-orbitals have different orientations, but in the absence of external disturbance, they all have the same energy (degenerate). In the presence of these electrostatic field generated by the ligands, the degenerate d-orbitals split between two energy levels: a higher level with two orbitals (dx2-y2and dz2) which form the axial set and represented by the symbol eg and a lower level with three equal energy orbitals (dxy, dyz and dxz) forming the inter-axial set represented by the symbol t2g.

eg

Metal d orbital

t2g

The energy difference between the two sets of d-orbitals is called **the crystal splitting energy** and is given the symbol Δ0. The magnitude of ∆0depends on the metal and the nature of the ligands; it has a direct effect on the colour and magnetic properties of complex ions. For an octahedral complex with the electronic configuration of d1 the ground state configuration is (t2g) 1.

The electronic absorption spectrum for the complex consist of a single absorption band corresponding to the transition (t2g) 1→ (eg) 1. The d9 system is complementary to that of d1. For a given metal ion in an octahedral field, the value of Δo

depend on the nature of the ligand. Different ligands cause different degrees of splitting of the d orbitals. The list of ligands in order of their capacity to cause d orbital splitting is known as spectrochemical series. In this experiment, the electronic absorption spectra of some Cu (II) complexes are going to be measured and recorded and their crystal field splitting energies would be determined.

**APPARATUS AND CHEMICALS**

1. Ultraviolet Visible spectrophotometer 1. 1M copper (II) nitrate solution.
2. An electric burner 2. 1M ammonia solution
3. Beakers 3. 2M ammonia solution
4. Measuring cylinder 4. 3M ammonia solution
5. Volumetric flask 5. 2M ammonia nitrate solution
6. Fume chamber 6. Concentrated ammonia solution

7. Distilled water

8. EDTA (ethylenediamine solution)

9. Solid glyci

**PROCEDURE**

**(a) Preparation of complexes of [Cu(NH3)n(H2O)6-n]2+, n=0.**

Using a burette, 1.0 cm3 of 1moldm-3 Cu(NO3)2 was drawn into a 50cm3 volumetric flask and diluted to the 50cm3 mark. For n=1, 1 cm3 of 1moldm-3 Cu(NO3)2 solution is drawn into a small beaker and 2.8g of solid ammonium nitrate added. This was then stirred and warmed to about 30. 1 cm3 of 1moldm-3 NH3 solution was added to this solution and the whole thing was diluted to 50.0cm3. For n=2 and n=3, the same method for n=1 was used but replacing 1moldm-3 NH3 with 2 and 3 moldm-3 NH3 respectively. For n=4, 1 cm3 of concentrated NH3 was added to 1cm3 of 1 moldm-3 of Cu(NO3)2 and then diluted to 50.0cm3.

**(b) Preparation of the complex of [Cu(en)2(H2O)2]2+.**

1cm3 of 1moldm-3 Cu(NO3)2 was drawn into a 50cm3 volumetric flask and EDTA was added to give a concentration of 0.04 moldm-3 ethylenediamine . This was then diluted to the 50.0cm3 mark.

**(c) Preparation of the complex [Cu(gly)2(H2O)2.**

Draw 1.0cm3 of 1 moldm-3 of Cu(NO3)2 into a 50.0cm3 volumetric flask and add glycine to give a concentration of 0.04 moldm-3. Add 20 cm3 of 0.1 moldm-3 NaOH and make to the mark with distilled water.

**(d ) Recording spectra**

Ask the demonstrator to explain the use of the UV-visible recording spectrophotometer. Record the visible spectra over the range of maximum abundance for each complex.

**TABLE OF RESULTS**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| n | Absorbance | | Wavelength/nm | | ∆o/cm-1 |
| 0 | 0.969 | | 447 | | 22371 |
| 1 | 1.240 | | 450 | | 22222 |
| 2 | 1.235 | | 500 | | 20000 |
| 3 | 1.236 | | 600 | | 16667 |
| 4 | 1.260 | | 700 | | 14286 |
| en | 1.257 | | 447 | | 22371 |
| gly | | 1.283 | 447 | 22371 | |

**DISCUSSION**

A simple glance at the graph above reveals the splitting energy (∆o) decreasing as the value of n increases (i.e. the number of substituted NH3 molecules), with the highest value occurring at n=0, only water molecules being the ligands. Clearly the introduction of the NH3 tends to reduce the splitting energy. An explanation for this observation may involve factoring in the properties of the ligand in question, which may include size, stability, polarity, distribution of electrons in valence shells among many others.

Looking at the table of results the ligands, en and gly shared the same value of splitting energy with n=0,

this in fact cannot be true because the properties of the involved ligands are far from near and therefore should not have the same effect on the splitting of orbitals. For example, water is inorganic and much polar compared to organic en and gly. This experiment should therefore be scrutinized for errors.

Answer to Question 3

H2O, en, gly, NH3 decreasing order of capacity to split

**Precautions**

1. I ensured that all volumes were read from the meniscus to reduce error by parallax.
2. I also ensured that the fume chamber was used for the boiling of the solution.
3. I ensured that the solutions were handled with care to avoid solution spillage on the tables

**References**

Marr and Rockett, p.102; Cotton and Wilkinson, p.673, 906.