

# EXPERIMENT 6

## INFLUENCE OF LIGAND FIELD TETRAGONALITY ON THE GROUND STATE SPIN OF NICKEL(II) COMPLEXES

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### Special Safety Precautions

*N,N*-Diethylethylenediamine should be stored and used in a fume cupboard and any skin contact with it avoided; wear rubber gloves when using it. Also wear rubber gloves when working with solutions of the nickel salts and their complexes, to avoid the possibility of heavy metal skin allergy.

Regularly octahedral, first series transition-metal complexes of electronic configuration  $d^n$  ( $n = 4-7$ ) may be either high- or low-spin depending, primarily, on the strength,  $\Delta$  or  $10 Dq$ , of the ligand field. For distorted ligand fields, a wider range of possibilities exists for changes in the 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 heme complexes involved in hemoglobin, 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  $trans\text{-ML}_4\text{X}_2$  are well illustrated by the magnetic properties and  $d-d$  spectra of a series of nickel(II) complexes of formula  $\text{Ni}(\text{Et}_2\text{en})_2\text{X}_2$ , where  $\text{Et}_2\text{en} = N,N$ -diethylethylenediamine ( $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) and  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ , etc.

In the following experiment, a number of compounds of this type can be made and their spin-states determined by magnetic susceptibility measurements, supplemented, if possible, by their solid state (reflectance)  $d-d$  spectra.

## Experimental

### a) $\text{Ni}(\text{Et}_2\text{en})_2(\text{NCS})_2$

Prepare an ethanol solution of nickel thiocyanate by dissolving nickel nitrate hexahydrate (2.0 g) and finely powdered potassium thiocyanate (1.3 g) separately in hot absolute ethanol and mixing the two solutions. Keep the volume of solution to a minimum and cool the mixture thoroughly before filtering off the precipitated potassium nitrate. (For your guidance, the solubility of nickel nitrate in hot ethanol is *ca.* 50 g/100 ml, and that of powdered potassium thiocyanate is *ca.* 10 g/100 ml).

To the resulting solution of nickel thiocyanate, add 2 ml of  $\text{Et}_2\text{en}$  by means of a syringe, and stir or shake the solution during the addition. Filter off the precipitated complex, wash it with a little cold ethanol, and dry it (air dry or vacuum desiccator). Record the yield of crude product and then recrystallise it from methanol. Record the yield of pure, crystalline product and take its m.p.

### b) $\text{Ni}(\text{Et}_2\text{en})_2\text{I}_2$

Prepare an ethanol solution of nickel iodide containing *ca.* 2 g  $\text{NiI}_2$  from ethanol solutions of the appropriate amounts of nickel nitrate hexahydrate and sodium iodide (solubility of  $\text{NaI}$  in hot ethanol *ca.* 16 g/100 ml). (Again, cool the solution well before filtering off the precipitated sodium nitrate). Add  $\text{Et}_2\text{en}$  (2 ml) using a syringe and filter off, wash (ethanol) and dry the precipitated complex. Do not attempt to recrystallise it. (Alternatively, or additionally, the analogous nickel nitrate complex can be made by simple addition of  $\text{Et}_2\text{en}$  to a concentrated ethanol solution of nickel nitrate).

### b) Physical measurements

Measure the magnetic susceptibilities of the complexes and, in the case of the thiocyanate complex, also calculate the magnetic moment. If the thiocyanate complex has formed large crystals, it may be necessary to powder some of the sample to achieve good packing in the Gouy (or Evans) tube used for the magnetic measurements.

Obtain the IR spectrum of the thiocyanate complex and identify the bands due to the NCS group, which coordinates to the nickel via the nitrogen atom, i. e. it is an isothiocyanato complex. If you have access to a spectrometer capable of measuring the reflectance spectra of solid samples in the UV-vis region, record the spectra of the complexes and relate the spectra to the colors of the compounds.

c) Other complexes

The analogous complexes with nickel chloride and nickel bromide exist as dihydrates as well as anhydrous compounds. Investigate the formation of these compounds by dissolving 1 g of nickel chloride or bromide respectively, in ethanol and adding Et<sub>2</sub>en (1 ml) to each of these solutions. Observe the colours of the initial precipitates and any colour changes that take place when the products are filtered off, washed with ethanol and air dried. Put a small amount of each compound in a melting-point tube, record the melting point or decomposition point and note any colour changes that occur prior to that point.

If you have isolated both anhydrous and hydrated forms of each complex, record their infrared spectra (using *dry* Nujol) and identify additional bands from the water molecules. If time permits, the weight loss when one of the dihydrates is converted to its anhydrous analogue can be determined, for example, by heating in an oven or a drying pistol at ca. 100 °C, or on prolonged storage in an evacuated desiccator over a good drying agent.

### Exercises

Draw the crystal field splitting diagram expected for a tetragonally elongated octahedron and use it to explain why some of the compounds you have made are diamagnetic and the others are paramagnetic with magnetic moments indicative of two unpaired electrons per nickel atom.