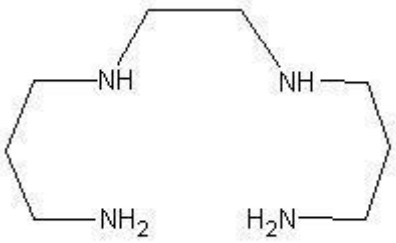
Octahedral to Square Planar Transition in Nickel Chelates

Experiment Overview

The experiment investigates the equilibrium between the octahedral and square planar geometries in a nickel(II) complexes coordinated by 1,2-bis(3-aminopropylamino)ethane (BAP), a tetradentate ligand containing four nitrogen donors.



1,2-bis(3-aminopropylamino)ethane (BAP)

The octahedral complex ion $[Ni(OH_2)_2BAP]^{2+}$ forms readily in solution with the aqua ligands taking the axial positions. In the formation of the square planar geometry these aqua ligands are removed. In aqueous solution an equilibrium between the two forms is observed:

$$[Ni(OH_2)_2\,BAP]^{2+} \rightleftharpoons [Ni\,BAP]^{2+} + 2H_2O$$

The equilibrium is shifted using both temperature and electrolyte concetration and is investigated using uv/vis spectroscopy.

Learning Experience

The experiment is robust, can be carried out easily in a three hour laboratory session and helps to support theory on a number of important aspects of physical inorganic chemistry. The experiment investigates the equilibrium between two complexes of differing coordination sphere geometries; as such, the experiment allows the investigation of the thermodynamics of the equilibrium and the application of crystal field theory to the understanding of the transformation. Additionally, the experiment provides (further) exposure to the use of uv/vis spectroscopy as an analytical tool. The experiment, therefore, covers a number of chemical concepts in physical and inorganic chemistry and can be used in either subject area.

Aims and Objectives

As this experiment is part of a subject on inorganic chemistry focussing of the fundamentals of aqueous transition metal chemistry, its aim is primarily to investigate the transformation between octahedral and square planar geometries in nickel chelates and help develop an understanding of the application of crystal field theory to the transformation. Students have already undertaken a course in physical chemistry and have covered the introductory theory in equilibrium thermodynamics. The experiment in its current form applies this knowledge and relates it to the relative stability of the complexes in equilibrium, thus reinforcing previously gained knowledge.

The experiment helps to develop analytical laboratory skills. The quality of the data depends on the diligence of students in the preparation of their solutions and in the acquisition of spectra, though the experimental data remains viable for most sets of data acquired.

The experiment also aims to develop data manipulation skills. Excel solver is used to calculate the molar absorptivities as all of the solutions studied contain both of the complex ion species (and, therefore, no solution contains a single species of know concentration for direct application of the Beer-Lambert law).

Level of Experiment

The experiment, in its current form, is aimed at second year Stage 4 students. Students should have an appreciation of the concepts of equilibria and transition metal complex formation and should be familiar with uv/vis spectroscopy and the application of the Beer-Lambert law.

Keyword Descriptions of the Experiment

Domain
Inorganic Chemistry (and Physical Chemistry)

Specific Descriptors
crystal field theory, octahedral and square planar nickel (II) complexes, polydentate ligands, chemical equilibria, isosbestic point

Course Context

The experiment is part of a second year Stage 4 subject on fundamentals of inorganic chemistry focussing on aqueous transition metal chemistry.

Prerequisite Knowledge and Skills

Students should have a basic understanding of the physical chemistry and thermodynamics of chemical equilibria and understand complex formation. Students should also be familiar with uv/vis spectroscopy and the application of the Beer-Lambert Law.

Time Required to Complete

Prior to Lab: 1 hour
In Laboratory: 2 hours
After Laboratory: 3 hours

Experiment History

The experiment has been run as part of the laboratory program of the undergraduate Stage 4 subject Inorganic Chemistry 1 at UTS since Spring Semester 2006.

References

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3. P.W. Atkins, 'Elements of Physical Chemistry', 2nd Ed Chapter 3.5 and Chapter 11.1

4. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry' Chapter 17 in 6thEdition: 'Elements of the First Transition Series – Nickel'

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