Preparation of solutions of copper and nickel en and dien complexes- an illustration of the Jahn-Teller effect

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Abstract. With the advent of methods that effectively solve the problems of modeling metal ions in the gas, water, and solid phases, computational tools are becoming increasingly important in chemical research. Here we consider both quantum and classical strategies for modeling systems containing metal ions that have been developed over the past few decades. This experiment was performed to study solutions of copper (II) and Nickel (II) complexes containing the following ligands, such as ammonia, diene, ene, and water in molar ratios, and to characterize the visible spectrum of the prepared solutions. The research was divided into three parts. In the first part, Nickel complexes were prepared and their formulas were determined using the job method. The second part of the experiment was performed to obtain EN-complexes of copper (II), and in the last part diene complexes were obtained. Dien and en were used as ligands.

1. Introduction
Metals and metal ions are widely distributed in nature and make up a huge chemical diversity. In the periodic table, from element 1 (H) to the new elements that complement this table, there are 84 metals, 7 metalloids, and only 18 nonmetals. The sum of Al, Fe, Ca, Na, K, Mg, and Ti contents in the earth's crust is ~ 25%. Metals are well-known substances in our daily lives that make up objects from coins to bridges, but the metal objects we touch are metal crystals or alloys. Having a low electronegativity, metals are easily ionized and have a high reactivity, which allows them to participate in many unique reactions or catalytic processes. In many fields, including chemistry, Geochemistry, biochemistry, and materials science, metal ions play an important role. Computational methods offer an understanding of the atomic / molecular and electronic level that is difficult or impossible to obtain experimentally. New molecules can be quickly constructed and characterized for desired properties before expensive synthetic efforts begin. Computing is playing an increasingly important role in structure-based drug design and discovery, as well as in the field of material design. Computational tools for creating structure-based drugs have contributed to the discovery of new compounds for treating diseases including HIV, cancer, and hypertension. He also contributed to the development of new materials for use in solar cells, solid catalysts, semiconductors, and superconductors. Unlike s- and p-block elements, TM have d- or f-orbitals as their extreme orbitals, which can also participate in chemical bonding. Compared to s- and p-orbitals, d- and f-orbitals have more electrons and a more complex shape (due to their higher angular moments), resulting in more complex chemical bond characteristics. Based on the above, TM-containing species have more than complex samples of chemical bonds than their organic counterparts, which largely determines their ability to have a flexible General-purpose solutions have...
been developed for organic species and biopolymers that describe their behavior in General terms. However, metal ions present much more complex modeling problems due to their large coordination numbers, relatively labile chemical bonding, and variety of electronic States. For metal elements of the main group, their chemical bond is more ionic, which leads to the fact that they have both higher and more flexible than elements of non-metals of the main group. Unfortunately, experimental data on TM types are limited, which slows down the development of accurate theoretical methods for modeling TM-containing compounds. For example, both the number and accuracy of experimentally obtained values of heat of formation for molecules containing HM are modest compared to what is available for organic compounds. Copper complexes have a 3d10 closed-shell configuration and, therefore, must be studied by methods, and dynamic coordination environment. Chemical bonds are often characterized by a continuum from covalent to ionic: on the one hand, bonds are based on electrons shared between two atoms, while on the other hand, electrons are held exclusively by one atom or another, and the Association is electrostatic. Non-metallic elements of the main group usually have stable binding patterns due to the nature of their covalent bonds. For example, hydrogen and halogen atoms usually form only one bond with other atoms, whereas oxygen atoms usually have one double bond or two single bonds with other atoms. A maximum of two carbon atoms can form a triple bond, which can be understood as one σ bond and two π bonds between a pair of atoms. Although the chemical bond in organic species has its own nuances, many chemical models involving electron ionization or transitions to higher-energy free valence orbitalsxx [1-3].

2. Methods and results

In the octahedral crystal field, the t2g orbitals appear at a lower energy than the eg orbitals. This is a reflection of the orientation of the orbitals, since t2g are directed between the bond axes, and the eg point is along the bond axes. The shielding effect this has on electrons is used to explain why the Jahn-Teller effect is usually only important when the eg level is filled with an odd number [4,5]. The Jahn-Teller distortion effect is best documented for Cu (II) complexes (with 3 electrons at the eg level), where it was found that most of the complexes are elongated along the z axis. Nickel (II) chloride (or just nickel chloride), is the chemical compound NiCl2. The anhydrous salt is yellow, but the more familiar hydrate NiCl2·6H2O is green. In general nickel (II) chloride, in various forms, is the most important source of nickel for chemical synthesis. The nickel chlorides are deliquescent, absorbing moisture from the air to form a solution.

Copper (II) chloride is the chemical compound with the formula CuCl2. This is a light brown solid, which slowly absorbs moisture to form a blue-green dihydrate. The copper(II) chlorides are some of the most common copper(II) compounds, after copper sulfate.

Ethylenediamine (1,2-Diaminoethane) abbreviated as en when a ligand is the organic compound with the formula C2H4(NH2)2. This colorless liquid with an ammonia-like odor is a strongly basic amine. Diethylenetriamine (abbreviated DETA) is an organic compound with the formula HN(CH2CH2NH3)2. This colourless hygroscopic liquid is soluble in water and polar organic solvents, but not simple hydrocarbons. Diethylenetriamine is structural analogue of diethylene glycol. Its chemical properties resemble those for ethylene diamine, and it has similar uses. It is a weak base and its aqueous solution is alkaline. DEET is a by-product of the production of ethylenediamine from ethylene dichloride [6-8].

In this part, nickel chloride was used to supply the Ni2+ ion. 1,2-diaminoethane (en) was used as the ligand. A solution of nickel (II) chloride with a volume of 0.3 mol dm-3 was obtained by dissolving 17.827 g of nickel (II) -6-water chloride in deionized water and bringing it to a volume of 250 cm3. A 0.3 mol dm-3 solution of 1,2-diaminoethane (en) was prepared by dissolving 5 ml of 1,2-diaminoethane (en) in deionized water to a volume of 250 cm3.

From each of them, 11 stock solutions were prepared as shown in Tables 1,2,3 below.

Nickel chloride itself is yellow, in hydrated NiCl2 *6H2O it is green.
Table 1. Preparation of dien complexes (the tridentate ligand, diethylenetriamine) complexes.

| Volume of solutions/cm³ | Volume of solutions/cm³ | Complete: Mole ratio Ni²⁺  
| i.e. volume Ni²⁺/total volume |
|-------------------------|-------------------------|------------------------|
| En or Dien              | Ni²⁺(or Cu²⁺)           | 0                      |
| 0                       | 20                      | 20/20=1                |
| 7                       | 13                      | 13/20=0.65             |
| 8                       | 12                      | 12/20=0.60             |
| 9                       | 11                      | 11/20=0.55             |
| 10                      | 10                      | 10/20=0.50             |
| 11                      | 9                       | 9/20=0.45              |
| 12                      | 8                       | 8/20=0.40              |
| 13                      | 7                       | 7/20=0.35              |
| 14                      | 6                       | 6/20=0.30              |
| 15                      | 5                       | 5/20=0.25              |
| 16                      | 4                       | 4/20=0.20              |

Table 2. Preparation of dien complexes (the tridentate ligand, diethylenetriamine) complexes.

| Volume of solutions/cm³ | Volume of solutions/cm³ | Complete: Changing the colours of made stock solutions |
|-------------------------|-------------------------|------------------------------------------------------|
| En                      | Ni²⁺                    | Mole ratio Ni²⁺  
| i.e. volume Ni²⁺/total volume |
| 0                       | 20                      | 20/20=1 Light green                                  |
| 7                       | 13                      | 13/20=0.65 Light blue                               |
| 8                       | 12                      | 12/20=0.60 Light blue                               |
| 9                       | 11                      | 11/20=0.55 Blue                                     |
| 10                      | 10                      | 10/20=0.50 Blue                                     |
| 11                      | 9                       | 9/20=0.45 Dark blue                                 |
| 12                      | 8                       | 8/20=0.40 Dark blue                                 |
| 13                      | 7                       | 7/20=0.35 Violet                                    |
| 14                      | 6                       | 6/20=0.30 Light purple                              |
| 15                      | 5                       | 5/20=0.25 Purple                                    |
| 16                      | 4                       | 4/20=0.20 Dark purple                               |

Table 3. Preparation of dien complexes (the tridentate ligand, diethylenetriamine) complexes.

| Volume of solutions/cm³ | Volume of solutions/cm³ | Complete: Changing the colours of made stock solutions |
|-------------------------|-------------------------|------------------------------------------------------|
| En                      | Cu²⁺                    | Mole ratio Cu²⁺  
| i.e. volume Cu²⁺/total volume |
| 0                       | 20                      | 20/20=1 Light green                                  |
| 7                       | 13                      | 13/20=0.65 Light blue                               |
| 8                       | 12                      | 12/20=0.60 Blue                                     |
3. Conclusion

The procedure was continued by using the same steps as in the part one and two; however, 1,2-diaminoethane(en) was replaced to Diethylenetriamine(dien). And the 11 stock solutions were prepared. En and dien were used as are ligands in all parts. The visible spectrum of twenty-two stock solutions was measured in 450-700nm wavelength.

The first methods include photoelectron spectroscopy, in which the valence or core electron is ionized by a photon with a known energy, and the flow of electrons with a given kinetic energy is recorded directly. The latter method is x-ray absorption spectroscopy at the K-edge of Cu (I), where the 1s electron is excited to 4p levels of Cu. Since s → p transitions are resolved by electric dipoles, they create intense absorption features that are sensitive to the Cu (I) ligand environment. XAS is usually performed using synchrotron radiation emitted by electrons orbiting at relativistic speeds. It has a continuous energy range providing wavelengths in UV, soft and hard x-rays, and is polarized in the ring plane. Third-generation synchrotron sources produce extremely intense beams (many orders of magnitude higher than conventional x-ray tubes, which produce only discrete energies). Cu (II) has a 3d9 configuration that results in a 2Eg ground state. This is orbitally degenerate, which leads to the Jahn-teller distortion, which lowers the symmetry of the complex, splits the orbital degeneracy, and reduces the total energy of the system. This usually results in tetragonal distortion, that is, elongation along the z axis and compression in the x, y plane, as well as a bounding square planar structure. A key feature of LFT is that the energy splitting of d-orbitals is sensitive to the ligand environment in the metal center. For the flat-square limit, this leads to a center splitting pattern where the half of the occupied orbital with the highest energy is dx2 - y2, since its lobes are oriented along the ligand-metal bonds and thus has the most repulsive (i.e. Loosening) interaction with the ligands. The structural coordinate that plays an important role in Cu (II) (bio) inorganic chemistry is the distortion of the flat square to distorted tetrahedral structure of D2d. 12 This involves lifting two TRANS ligands above and two TRANS ligands below the plane of the molecule. Note that in the tetrahedral limit, the complex will have a 2T2 ground state, which is again degenerate and unstable with respect to the Yang-teller distortion of the D2d structure. In a distorted tetrahedral D2d node, the ground state is still the half-occupied dx2-y2 orbital [9]. A that the energy splitting of d-orbitals in the D2d structure is significantly reduced compared to that in the square planar structure. This reflects the fact that the 10Dq of an approximately tetrahedral structure is -4/9 10Dq of an octahedral (or connected square planar) structure. Finally, note that in square planar structures, the dz2 level is often lower in energy than predicted by LFT.13 It has the fact that metal 4s mixes with the 3dz2 level in planar structures, an interaction that is not directly included in LFT, but is present in molecular structures. orbital theory.

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