QUANTUM CHEMICAL STUDY OF CHANGES
IN THE MAGNETIC STATE OF Ni(AA)2 AND Ni(ktf)2
ADSORBED ON THE SURFACE OF NATURAL SILICA

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For nickel(II) bis-acetylacetonate [Ni(AA)2] and nickel(II) bis-trifluoroketoiminate [Ni(ktf)2], quantum chemical cluster modeling of the effect of chelate node distortion and changed coordination number of the central atom on the magnetic state of the molecules adsorbed on the surface of hydrated natural oxide on silicon by the SCF-Xα-SW method is reported. Differences between the energies of the lowest singlet and triplet states are obtained for the clusters. It is shown that the diamagnetic state of Ni(ktf)2 molecules changes to paramagnetic when the coordination number of the central atom increases due to its donor-acceptor interaction with the Si-O groups of the real surface of silicon provided that the molecules are adsorbed by the planes of the chelate rings.

INTRODUCTION

The mechanism of adsorption of Cu(II) and Ca(II) dipivaloylmethanates (dpm) on the surface of SiO2 was studied in [1] by IR and EXAFS spectroscopy; it was concluded that, irrespective of the type of metal, adsorption of the complexes is determined by the interaction of the ligand with the OH groups lying on the surface of SiO2. The MO4 chelate node does not participate in adsorption and does not experience a spatial rearrangement.

This conclusion conflicts with our discovery of a change in the magnetic susceptibility of Ni(II) trifluoroketoiminate molecules due to their adsorption on the surface of hydrated natural oxide on silicon. In the crystalline state the Ni(ktf)2 molecule is diamagnetic and has a square-planar chelate node NiO2N2. In its structure the chelate node of Ni(ktf)2 is a close analog of the CuO4 chelate node of Cu(dpm)2. On the periphery of the ligands of Ni(ktf)2 and Cu(dpm)2, CH3 and CF3 radicals are replaced by C(CH3)3 radicals, which are unessential for adsorption, as follows from [1]. Thus the mechanism of Ni(ktf)2 adsorption must be analogous to the one presented for Cu(dpm)2 [1].

The magnetic properties of Ni(ktf)2 adsorbed on the surface of silicon powder were investigated by Faraday's method. The initial solid complex Ni(ktf)2 is diamagnetic and has magnetic susceptibility \(-0.34 \times 10^{-6} \text{ cm}^3/\text{mole}\). The Ni(ktf)2 complex dissolved in chloroform was deposited in small portions onto the silicon powder. As a result, the diamagnetic state of the complex changed to paramagnetic. The silicon-free complex recrystallized from chloroform remained diamagnetic. Figure 1 presents the dependence of the paramagnetic contribution of Ni(ktf)2 adsorbed on the surface of silicon on the relative content of the complex \(x = m(\text{Ni(ktf)2})/m(\text{Si})\). At large values of \(x\), the surface of silicon is saturated with the adsorbed complex. Probably, the change to the paramagnetic state of adsorbed Ni(ktf)2 indicates an electronic rearrangement of its chelate node.

This rearrangement may result from a spatial distortion of the node due to chemisorption or an increase in the coordination number of the central atom due to its donor–acceptor interactions with the Si–O or Si–OH groups of the real surface of silicon.

Here we investigate the role of chelate node rearrangement and changed coordination number of the central atom in the appearance of paramagnetism in the model clusters NiO4 and NiO6 and chelates Ni(NH2–CH2–CH2–CH2–O)2 and Ni(NH2–CH2–CH2–CF2–O)2. This investigation permits us to trace the effect of the far and near atomic environment of the central (Ni) atom on the diamagnetic–paramagnetic transition. The influence
of the crystal structure and defective surface of silicon on the appearance of paramagnetism in adsorbed Ni(II) \( \beta \)-diketonate molecules is not treated here.

QUANTUM CHEMICAL MODELING AND CALCULATION PARAMETERS

As is known, the square-planar NiO\(_4\) clusters of \( D_{4h} \) symmetry are diamagnetic. The electronic structure of the valence shell of the clusters is characterized by elimination of the antibonding molecular orbital (MO) of \( b_{1g} \) symmetry (Ni3d\(_x^2-y^2\)) from the other MOs by \( \approx \) 1 eV. This MO of \( b_{1g} \) symmetry is unoccupied, the total spin of the system is zero, and the complex is diamagnetic. Can any symmetry distortion lead to an approach of the unoccupied MO to valence MOs [this will make the configuration with parallel spins on the partially filled highest valence and lowest unoccupied MOs energetically more favorable than the configuration with opposite spins (analog of Hund’s rule)]? If so, the system would become paramagnetic.

On the other hand, it is known that octahedral clusters of NiO\(_6\) type are paramagnetic. The highest doubly degenerate unoccupied orbital of \( e \) symmetry (two electrons) is not completed, and the state with spin \( S = 1 \) is energetically more favorable than the state with \( S = 0 \). When the octahedron is distorted, the \( e \) orbital is split into two singly degenerate orbitals. When a certain degree of deformation is achieved, the splitting becomes sufficient for the system to pass to the diamagnetic state \( (S = 0) \).

The \( X_\alpha\)-SW method [2] (spin-polarized version) was chosen as the principal method of investigation; the INDO method [3] in a UHF approximation served as an auxiliary method. Regrettably, neither the \( X_\alpha\)-SW nor any semiempirical method give the required accuracy of total energy calculations of the system in any of its states. Yet one can reveal some tendencies in variation of the total energy differences between homologous chemical compounds. We believe that combining these two different methods will allow one to obtain more reliable results.

This paper considers the following distortions of the square-planar NiO\(_4\) and octahedral NiO\(_6\) clusters (Fig. 2): deviation of the metal atom from the square plane (1A), diminishing of two opposite angles O–Ni–O (1B), and lengthening of two (1C) and one (1D) oppositely directed Ni–O bonds. When the two opposite bonds are sufficiently

![Fig. 2. Variants of distortion of the square-planar (1A, 1B) and octahedral (1C, 1D) complexes [NiO\(_4\)]\(^{6-}\) and [NiO\(_6\)]\(^{10-}\).](image-url)