

Complex formation of 1D-coordination polymers based on arendiyl-bisphosphinic acid

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Abstract. Within the framework of the density functional theory and the *ab initio* pseudopotential, we have obtained the spatial distributions of the valence electrons density, the electron energy spectra and the atom charge states of 1D-coordination polymers based on arendiyl-bisphosphinic acids and metal ions. Formation of one-dimensional polymer chains takes place under participation of strong intermolecular bonds.

Keywords: coordination polymers, arendiyl-bisphosphinic acids, metal ions, density functional theory, electronic-structural properties.

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1. Introduction

Coordination polymers (CPs, the kind of supramolecular polymers) are highly-molecular compounds composed by repetition of organic molecules, metal ions and linked due to intermolecular interactions [1–3]. One of the strongest types of these interactions is the coordination bond between donor centers in an organic molecule (ligand – L) and a metal ion (M). If the ligand contains several donor sites, located in the molecule divergently, then it can participate in the binding of several metal centers into one supermolecule. Translation of these linked (L-M) fragments in one, two or three directions leads to formation of 1D, 2D or 3D CPs [4]. CPs are functional hybrid materials with original redox, luminescent, nonlinear optical, magnetic, sorption, catalytic, ion exchange, sensory and other properties [5–7]. Most of the currently known coordination polymers are constructed using di- and polycarboxylic acids as ligands. Coordination polymers based on di- and three-phosphinic acids are currently represented by large extent compounds containing a flexible spacer between phosphorus atoms, which ensures the conformational mobility of these systems. The complexing properties of arendiyl-bisphosphinic acids remain practically unexplored [8–10]. Our work is devoted to the theoretical study of the one-dimensional coordination polymers based on arendiyl-bisphosphinic acids. We studied their electronic-structural properties and charge states of centers in an organic molecule and a metal ion by the methods of the density functional theory in local approximation, the *ab initio* Bachelet–Hamann–Schlüter pseudopotential and

the authors' software [11–14]. These potentials written in a convenient form for application are transferable for different atomic environments and have been successfully tested many times by the authors of this paper for substances of various structures and chemical compositions.

2. Results and discussion

The basic states of the electron-nuclear systems have been detected by means of the self-consistent solution of the Kohn–Sham equations. Electronic variables only were determined with the atomic cores fixed. Our calculations were made under the following conditions: the Brillouin zone summation was changed by calculation at the Γ -point. The self-consistency iterations were terminated, if the results of the current iteration calculation coincided with the previous one with a predetermined error. Their number varied depending on the object being calculated, but usually, our results coincided after 3–5 iterations. The number of plane waves in the expansion of the wave function was truncated by trial calculations and evaluation of the physicality of the obtained results (the spatial distribution of electron density, the magnitude of the gap in the energy electron spectrum between the last occupied state and the first unoccupied, general ideas about the simulated nanostructure) or evaluation of the obtained results in comparison with those obtained by other authors. Often, the number of plane waves was chosen to be equal to 20–25 waves per base atom. The atomic basis was not optimized. As the calculation algorithm envisages translational symmetry in the explored atomic system,

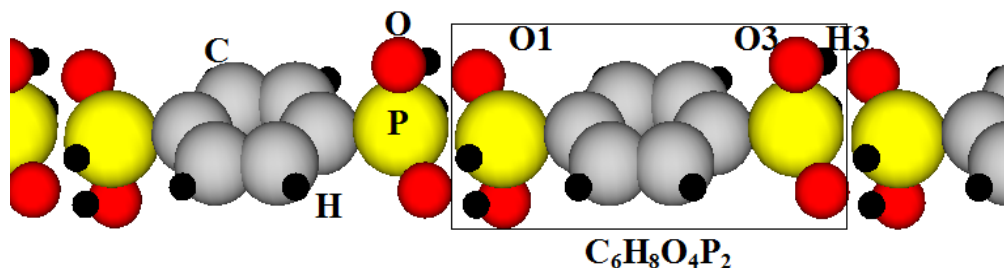


Fig. 1. Formation of one-dimensional polymer chain due to intermolecular interaction of hydroxyl groups of 1,4-benzenediyl-bis(H-phosphinic) acid ($C_6H_8O_4P_2$) molecules.

initially, the orthorhombic type artificial superlattice was created. The research object defined parameters of the superlattice and the atomic base. For simulation of an endless polymer chain or a single molecule, the lattice parameters along the Z, X and Y axes have been correlated accordingly.

The geometry of tectons (these are supramolecular building blocks capable of self-assembly) predetermines the structure of coordination polymers. We have chosen arendiyl-bisphosphinic acid, which contains 1,4-benzenediyl as a linker between the phosphinate groups, for which one can expect formation of linear one-dimensional polymeric chains [$C_6H_8O_4P_2$] $_n$ (Fig. 1).

According to the literature data, phosphinic acids in the crystalline state form strong intermolecular interactions between the protons of the hydroxyl group and the oxygen of the phosphoryl group [15, 16], which leads to formation of one-dimensional polymer chains. Quantitative electronic characteristics of the intermolecular interaction between the proton of the hydroxyl group (H3) and the oxygen of the phosphoryl group (O1) are shown in Fig. 2.

The geometric characteristics of the region of intermolecular interaction were as follows: the distance between the O1 atom and the H3 atom was 1.52 Å, the distance between the O1 atom and the O3 atom was 2.41 Å, and the spatial angle O1-H3-O3 was 153.9°. The charge values were evaluated (the unit of measurement is the electron charge) in the neighborhood (with a radius of 1.33 Å) of the O1 and O3 atoms for different atomic environments. As for the energy characteristics, the HOMO-LUMO gap for a single molecule was 27.2 eV, and for a molecular chain 16.6 eV, respectively.

Thus, the presence of a second phosphoryl group in diphosphinic acid ($C_6H_8O_4P_2$) leads to formation of the one-dimensional polymer chain with the participation of strong intermolecular non-covalent bonds. The maximum directed densities of valence electrons are preserved between the atoms of the phosphoryl group within the molecule. Smaller, but quite significant, valence electrons densities are formed between the phosphoryl groups of neighbor molecules.

We have studied the electronic properties of supramolecular structures of salts of arendiyl-bisphosphinic

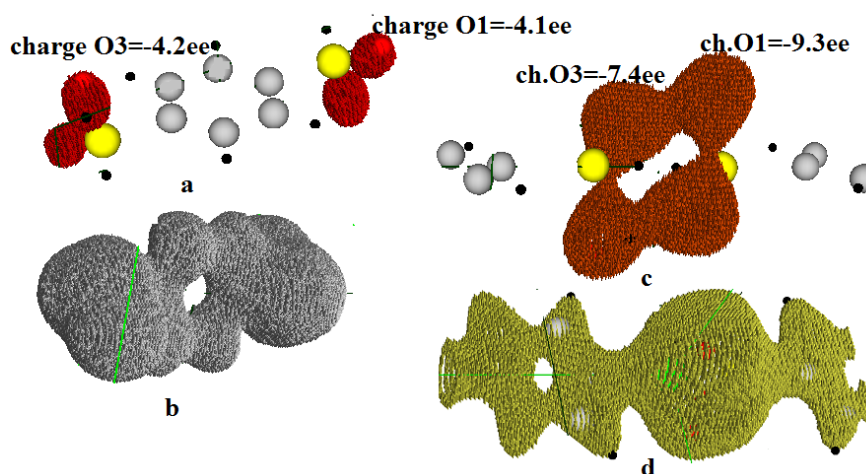


Fig. 2. Spatial distributions of the valence electrons density on 1,4-benzenediyl-bis(H-phosphinic) acid ($C_6H_8O_4P_2$) molecule (a, b) and one-dimensional polymer chain (c, d) within the interval of 0.9...0.8 of the maximum value (a, c), within the interval of 0.2...0.1 of the maximum value (b) and within the interval of 0.5...0.4 of the maximum value (d).

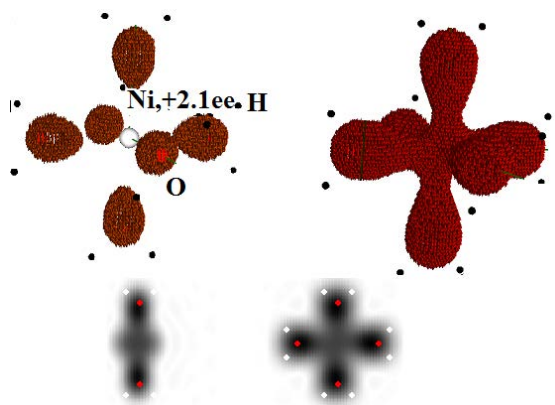


Fig. 3. Spatial distributions of the valence electrons density on the complexes of six-coordination nickel within the interval of 0.9...0.8 of the maximum value (top left), within the interval of 0.8...0.7 of the maximum value (top right) and cross sections of the spatial distributions of the valence electrons density (down). The charge value is given (the unit of measurement is the electron charge) in the neighborhood (with the radius close to 1.01 Å in the image) of the Ni atom.

acids and Ni. Nickel (II) is characterized by formation of complex compounds, in which it exhibits the coordination numbers of the complexing agent equal to 6 or 4. The complexes of six-coordination nickel are built according to the octahedron type (Fig. 3).

The nickel (II) ion of the polymer has a properly octahedral coordination sphere formed by two water molecules in equatorial positions, two water molecules in axial positions, and two oxygen atoms of two phosphoryl groups in equatorial positions.

Thus, in the coordination polymer under consideration, only one oxygen atom of the phosphoryl group takes part in binding to the metal ion. At the same time, the charge value is given in the neighborhood (with the radius close to 1.33 Å) of O atom amounted to a value equal to (-7.5 ee). Each diphosphine ligand binds to two metal ions; each metal atom in turn binds to two phosphine ligands, resulting in 1D chain (Fig. 4).

One-dimensional polymer chains can be cross-linked into a three-dimensional supramolecular structure by numerous hydrogen bonds between the solvate water molecules and phosphine oxygen atoms not involved in bonding with metal ions.

3. Conclusions

Within the framework of the density functional theory and the *ab initio* pseudopotential, we have obtained the spatial distributions of the valence electrons density, the electron energy spectra and the atom charge states of 1D-coordination polymers based on arendiyl-bisphosphinic acids and metal ions. Formation of the one-dimensional polymer chains takes place under participation of strong not hydrogen intermolecular bonds.

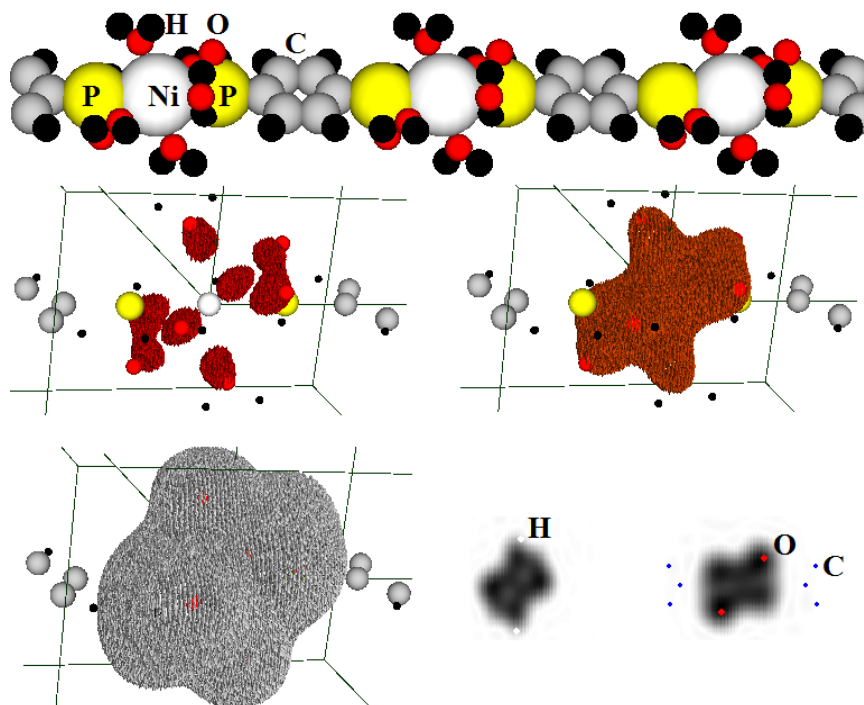


Fig. 4. Structure of one-dimensional coordination polymer (top row). Spatial distributions of the valence electrons density in the area of the junction of phosphoryl groups and nickel complex (bottom rows) within the interval of 1.0...0.9 of the maximum value, within the interval of 0.9...0.8, within the interval of 0.2...0.1, and cross sections of the spatial distributions of the valence electrons density, respectively. The charge value is given (the unit of measurement is the electron charge) in the neighborhood (with the radius close to 1.01 Å) of Ni atom amounted to the value equal to (-3.19 ee).

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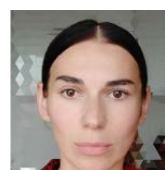
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M.V. Yatsiuta: investigation, writing – editing, project administration, visualization.

Комплексоутворення 1D-координаційних полімерів на основі арендііл-бісфосфінової кислоти

Р.М. Балабай, О.О. Бондаренко, М.В. Яцюта

Анотація. У рамках теорії функціоналу густини та *ab initio* псевдопотенціалу отримано просторові розподіли густини валентних електронів, енергетичні спектри електронів і зарядові стани атомів 1D-координаційних полімерів на основі арендііл-бісфосфінових кислот та іонів металів. Утворення одновимірного полімерного ланцюга відбувається за участю міцних міжмолекулярних зв'язків.

Ключові слова: координаційні полімери, арендііл-бісфосфінові кислоти, іони металів, теорія функціоналу густини, електронно-структурні властивості.