

Transition Metal Bis(Dicarbollide) Complexes in Design of Molecular Switches

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Abstract : Design of molecular machines is an extraordinary growing and very important area of research that it was recognized by awarding Sauvage, Stoddart and Feringa the Nobel Prize in Chemistry in 2016 'for the design and synthesis of molecular machines'. Based on the type of motion being performed, molecular machines can be divided into two main types: molecular motors and molecular switches. Molecular switches are molecules or supramolecular complexes having bistability, i.e., the ability to exist in two or more stable forms, among which may be reversible transitions under external influence (heating, lighting, changing the medium acidity, the action of chemicals, exposure to magnetic or electric field). Molecular switches are the main structural element of any molecular electronics devices. Therefore, the design and the study of molecules and supramolecular systems capable of performing mechanical movement is an important and urgent problem of modern chemistry. There is growing interest in molecular switches and other devices of molecular electronics based on transition metal complexes; therefore choice of suitable stable organometallic unit is of great importance. An example of such unit is bis(dicarbollide) complexes of transition metals $[3,3'-M(1,2-C_2B_9H_{10})_2]^{n-}$. The control on the ligand rotation in such complexes can be reached by introducing substituents which could provide stabilization of certain rotamers due to specific interactions between the ligands, on the one hand, and which can participate as Lewis bases in complex formation with external metals resulting in a change in the rotation angle of the ligands, on the other hand. A series of isomeric methyl sulfide derivatives of cobalt bis(dicarbollide) complexes containing methyl sulfide substituents at boron atoms in different positions of the pentagonal face of the dicarbollide ligands $[8,8'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$, $rac-[4,4'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ and $meso-[4,7'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ were synthesized by the reaction of $CoCl_2$ with the corresponding methyl sulfide carborane derivatives $[10-MeS-7,8-C_2B_9H_{11}]^-$ and $[10-MeS-7,8-C_2B_9H_{11}]^-$. In the case of asymmetrically substituted cobalt bis(dicarbollide) complexes the corresponding *rac*- and *meso*-isomers were successfully separated by column chromatography as the tetrabutylammonium salts. The compounds obtained were studied by the methods of 1H , ^{13}C , and ^{11}B NMR spectroscopy, single crystal X-ray diffraction, cyclic voltammetry, controlled potential coulometry and quantum chemical calculations. It was found that in the solid state, the *transoid*- and *gauche*-conformations of the 8,8'- and 4,4'-isomers are stabilized by four intramolecular $CH\cdots S(Me)B$ hydrogen bonds each one (2.683-2.712 Å and 2.709-2.752 Å, respectively), whereas *gauche*-conformation of the 4,7'-isomer is stabilized by two intramolecular $CH\cdots S$ hydrogen bonds (2.699-2.711 Å). The existence of the intramolecular $CH\cdots S(Me)B$ hydrogen bonding in solutions was supported by the 1H NMR spectroscopy. These data are in a good agreement with results of the quantum chemical calculations. The corresponding iron and nickel complexes were synthesized as well. The reaction of the methyl sulfide derivatives of cobalt bis(dicarbollide) with various labile transition metal complexes results in rupture of intramolecular hydrogen bonds and complexation of the methyl sulfide groups with external metal. This results in stabilization of other rotational conformation of cobalt bis(dicarbollide) and can be used in design of molecular switches. This work was supported by the Russian Science Foundation (16-13-10331).

Keywords : molecular switches, NMR spectroscopy, single crystal X-ray diffraction, transition metal bis(dicarbollide) complexes, quantum chemical calculations

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