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STRUCTURAL DISTORTIONS OF COORDINATED KETENE MOLECULE INDUCED BY THE PSEUDO JAHN-TELLER EFFECT

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Abstract. It is demonstrated that the only reason of structural distortions of ketene molecule coordinated in the complexes VCp_2-H_2C_2O (**I**) and $Pt(PPh_3)_2$-H_2C_2O (**II**) is the pseudo Jahn-Teller effect (PJTE) induced by the orbital charge transfers (OCTs) by coordination. It is shown that the η^2-(C-O) coordination and the in-plane b_2-type distortion of ketene in the complex (**I**) is due to the PJTE induced by the back donation to its LUMO $3b_2$ (π_{CO}*). The η^2-(C-C) coordination mode, as well as the out-of-plane b_1-type distortion of the molecule in the complex (**II**) is caused by two OSTs: from the HOMO $2b_1(\pi_{CC})$ to the metal, and from the d_{xy}- atomic orbital (AO) of the atom of Pt to the vacant $3b_1(\pi_{CC}$*) molecular orbital (MO) of ketene, thus being the result of the diorbital Pt-ketene interaction. The necessary parameters of the PJTE were estimated by considering the excited states of free ketene molecule, and the values of the OSTs were obtained from the electronic structure calculations of the complexes.

Keywords: Pseudo Jahn-Teller effect, orbital charge transfers, ketene excited states, metal ketene complex.

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