

ELECTRON SPIN STATES AND STRUCTURES OF LANTHANIDE (Ce, Pr, and Nd) COMPLEXES OF CYCLOOCTATERAENE

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1,3,5,7Cyclooctatetraene (COT, C_8H_8) is one of the most versatile ligands used in organometallic chemistry, with coordination modes ranging from η^2 to η^8 . COT is anti-aromatic with a tub conformation in its ground state; however, the dianion ($C_8H_8^{2-}$) is aromatic and planar. In this paper, we report a study of $M(COT)$ ($M = Ce, Pr, \text{ and } Nd$) using pulsed-field ionization zero electron kinetic energy (ZEKE) spectroscopy and density functional theory. The ZEKE spectra of the Ce, Pr, and Nd-COT complexes show multiple electronic transitions from the neutral ground state to various ion states, and each transition exhibits a major metal-ligand stretching progression. From the ZEKE spectra, the neutral ground states were determined as triplet, quartet, and quintet, and the ion states were doublet, triplet, and quartet for $M = Ce, Pr, \text{ and } Nd$, respectively. In both neutral and ion states, the complexes are in C_{8v} symmetry, and COT is planar. The conformational change of COT from a tub shape to a plane is induced by two electron transfer from the metal atoms to the ligand orbitals. It is noted that the spectra of these complexes are very much different from those of the Sc, Y, La, and Gd complexes previously studied in our group, for which only single transition was observed.^{ab}

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