HALF-SANDWICH COMPLEXES OF GROUP III (Sc, Y, and La) METALS WITH CYCLOOCTATERAENE

SUDESH KUMARI, JUNG SUP LEE, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*.

1,3,5,7 – Cyclooctatetraene (COT, C_8H_8) is one of the most versatile ligands used in organometallic chemistry, with coordination modes of η^2, η^4, η^6, and η^8. COT is non-aromatic with a tub conformation; however, its dianion (C_8H_8) is aromatic and planar. In this work, we have studied group III M-COT (M = Sc, Y, and La) 1:1 complexes using pulsed field ionization - zero electron kinetic energy (ZEKE) photoelectron spectroscopy and density functional theory. The ZEKE spectra of these complexes show a strong 0-0 transition and a major metal-ligand stretching progression. The ionization energies are measured to be 42261(5), 40747(5), and 36641(5) cm^{-1}; and the M^+-COT stretching frequencies are 338, 300, and 278 cm^{-1} for the triad. The ionization energies of the metal complexes decrease down the group as expected from those of the bare metal atoms. The metal-ligand stretching frequencies decrease with increasing the mass of the metal atoms. In coordination with theory, the neutral and ionized complexes are determined to be in C_{4v} point group, with M/M^+ in η^8 binding to the planar COT; the observed transition is assigned to $^1A_1 \leftarrow {}^2A_1$. The conformation change of the COT molecule upon metal coordination is associated with the metal to ligand electron transfer and metal-ligand orbital interaction.