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

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1,3,5,7–Cyclooctatetraene (COT, C₈H₈) is one of the most versatile ligands used in organometallic chemistry, with coordination modes of η², η⁴, η⁶, and η⁸. COT is non-aromatic with a tub conformation; however, its dianion (C₈H₈⁻) 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 C₄ᵥ point group, with M/M⁺ in η⁸ binding to the planar COT; the observed transition is assigned to ¹A₁ ← ²A₁. The conformation change of the COT molecule upon metal coordination is associated with the metal to ligand electron transfer and metal-ligand orbital interaction.