

Synthesis and Optical Properties of Metal Complexes with Azulene Derivative as Ligands

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Azulene is known as a unique compound that exhibits blue coloration with a simple structure. Azulene and its derivatives have attracted attention in the fields of organic synthesis and photochemistry because of their unique reactivity derived from their electronic states and optical properties ^{1), 2)}. However, there are few reports on metal complexes with azulene derivatives as ligands, and their structures and optical properties are of great interest. Therefore, we investigated the synthesis of metal complexes with azulene derivatives, diethyl 2-aminoazulene-1,3-dicarboxylate (**DEAA**) and diethyl 2-hydroxyazulene-1,3-dicarboxylate (**DEHA**), as ligands according to the scheme in Fig. 1.

When **DEAA**, an azulene derivative having amino group, was used as a ligand, stable complex was formed only with Pd. On the other hand, **DEHA**, an azulene derivative having hydroxy group, gave stable complexes with Co, Ni, Cu, Zn, and Pd. In the Co, Ni, and Zn complexes, hetero-complexes with Cs⁺, originated from a base, were formed. In the synthesis of Zn complexes, when the base was changed from Cs₂CO₃ to Rb₂CO₃, K₂CO₃, and Na₂CO₃, coordination polymers were formed for Cs, Rb, and K, respectively. In the case of Na, the complex had a cluster structure. No fluorescence was observed for Pd, Cu, Co, and Ni complexes. Fluorescence was observed for Zn complex. The complex having **DEHA** showed S₂ emission, whereas Zn complexes showed S₁ emission as shown in Fig. 2.

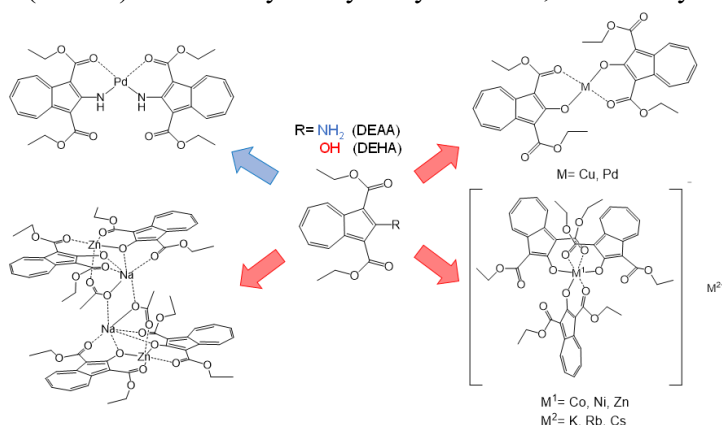


Fig. 1 Synthesis of metal complexes with DEAA and DEHA

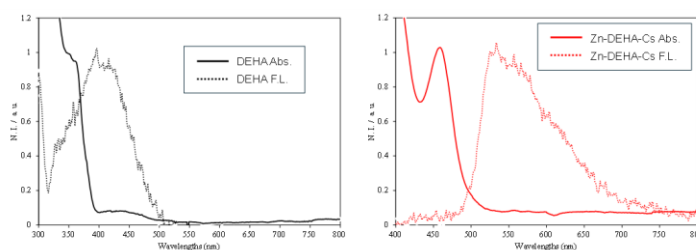


Fig. 2 UV-Vis and fluorescence spectra in CH₂Cl₂ (Left; DEHA, right; Zn-DEHA-Cs)

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