THERMODYNAMIC AND SPECTRAL PROPERTIES OF MONONUCLEAR 1,3-DIKETONATES

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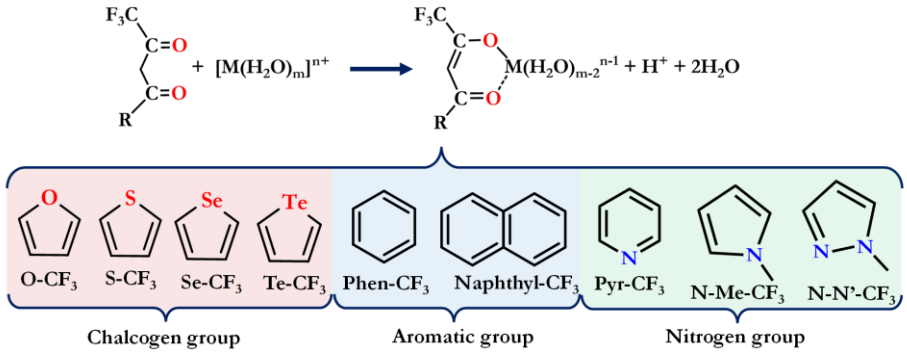
Dicarbonyl ligands and their derivatives play a critical role in "aqueous" coordination chemistry of rare earth and transition metals. π-Conjugated complexes of β-dicarbonyl ligands are chelates that exhibit pronounced luminescent and optical properties, which make it possible to study their formation using electronic absorption spectroscopy. Herein, we present a large dataset of stability constants for mononuclear chelates of non-symmetric fluorinated diketones with rare earth and transition metal ions. We demonstrate that the metal–diketone bond has a semi-ionic nature and can be quantitatively estimated through derivatives of thermodynamic parameters and the ionic potential of metal ions.



General scheme of studied reaction

Analysis of the spectral dataset has shown that the main absorption band of dicarbonyl complexes corresponds to an intraligand π-π* transition within the delocalized orbitals of the dicarbonyl fragment. The absorption band of the complexes is always shifted to the red region of the spectrum relative to that of the ligand, and the magnitude of this shift depends on the nature of the metal ions. DFT modeling shows that the red shift of the main absorption band of dicarbonyl complexes is related to charge redistribution in the HOMO orbitals. As the ionic radius of the metal ions increases, electron density is transferred from the molecular orbitals of the dicarbonyl fragment to the multiple bonds of the substituted heterocyclic ring.

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