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Phosphorescence of Group IVB metal complexes

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An interest in chemistry of Group IVB metals (Ti, Zr, and Hf)[1] especially increased recently due to their wide use, including catalysis.[2]

In this work, we describe for the first time the phosphorescence properties of isostructural molecules containing zirconium(IV) and hafnium(IV) and present the results of comparative examination of the low-energy excited states in the triad of Group IVB metals for their π-complexes $Cp_2M^{IV}Cl_2$ [Cp = η^5-C_5H_5; M = Ti (**1**), Zr (**2**), Hf (**3**)] (Table 1). The compounds under study (content of the main substance ≥98, Aldrich) were purified by known procedures,[3,4] and their concentrations in solutions were 10^{-5}—10^{-4} mol L^{-1}. Spectral measurements were carried out according to the previously described procedure.[5]

In homologs **1**—**3**, the low-energy absorption in the UV-visible region corresponding to the Franck-Condon charge transfer from the π-ligand to the metal[6] (HOMO→LUMO[4]) results in the high-lying excited states in which the metal ion is formally reduced: $M^{4+}Cp_2^{2-} \rightarrow M^{3+}Cp_2^{-*}$. The data on intense emission allow the estimation of the position of the lowest excited state in **1**—**3**. The quantum yield of the low-temperature (77 K) emission (determined by comparison with those for anthracene and Rhodamine B) is high: ~1.0 (**2**), 1.0 (**3**), and 0.09 (**1**). The radiation lifetimes are of millisecond range, which indicates the forbidden radiation transition of the $T_1 \rightarrow S_0$ type. The phosphorescence spectra virtually coincide with the absorption spectra and are independent of the wavelength of the exciting light. The radiation lifetime (λ_{exc} = 337 nm) of $T_1 \rightarrow S_0$ transitions in the isostructural triad depends strictly on the metal nature: Zr, ~2 ms (longest); Ti, ~0.8 ms; and Hf, ~0.3 ms (shortest). The excitation and phosphorescence spectra of complexes **2** and **3** are substantially broadened as compared to those of **1**. The phosphores-

Table 1. Comparative characterization of absorption and luminescence in isostructural complexes of Group IVB metals

Compound	Matrix	LMCT*-absorption (20 °C)		Emission (77 K)				Refs.
		cm^{-1}	ε/M cm^{-1}	max/cm^{-1}	(0—0)/cm^{-1}	τ/ms	φ	
Cp_2TiCl_2	Toluene	25600 19450	— —	15400	16800	0.80	0.09	**
	Dichloromethane	25510 19080	2300 193	—	—	—	—	7
	EtOH : MeOH	—	—	14880	16460	0.73	—	7
	MC	—	—	—	—	0.80	—	**
Cp_2ZrCl_2	3-MH	35100 30200	— —	21700	24300	2.00	1.0	**
	Toluene	34500 30100	— 950	21800	24300	1.70	—	**
	MC	—	—	—	—	1.50	—	**
	MC	—	—	22120	—	—	—	8
Cp_2HfCl_2	3-MH	38400 32600	— —	23300	26100	0.30	1.0	**
	Toluene	32500	1200	23550	26300	0.30	—	**
	MC	—	—	—	—	0.30	—	**
	MC	—	—	23420	—	—	—	8

Note. MC is microcrystalline sample; 3-MH is 3-methylheptane.
* Ligand-to-metal charge transfer.
** This work.

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cence spectra exhibit a new fine structure as a broad maximum for molecules **2** and **3** and shoulders in **1—3**.

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