

Mendeleev 2024

XIII International Conference on Chemistry for Young Scientists

BOOK OF ABSTRACTS



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SPECIFICITY OF COMPLEXATION AND PHOTOINDUCED RECOORDINATION OF BIS-AZA-18-CROWN-6-CONTAINING DIBENZYLIDENECYCLOPENTANONE WITH ALKALI AND ALKALINE-EARTH METAL

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Various derivatives of mono-aza-crown ethers are considered as prototypes of smart photoactive molecular devices, sensors for optical and electrochemical detection of metal cations [1].

In this work, the features of the complexation process and the specifics of the photoinduced recoordination in complexes of ditopic bis-aza-18-crown-6-containing dibenzylidenecyclopentanone (1) with alkali and alkaline earth metal cations of various stoicheometry $1^{(M^{n+})}$, $1^{(M^{n+})}$, $(M^{n+})^{*}$ 1* (Mn+)2 were thoroughly studied. Spectral-kinetic features of investigated complexes (1) with metal cations were obtained in MeCN (Table 1).

Cation	Log[Ks(dm ³ *mol ⁻¹)]			ε _a ^{max} / dm ³ *mol ⁻¹ *cm ⁻¹			λ _a ^{max} /nm			Cation
	(1:1)	(1:2)	(1:3)	(1:1)	(1:2)	(1:3)	(1:1)	(1:2)	(1:3)	radius/Å
H+	3.65	3.60	-	36400	45500	-	448	341	-	-
Li+	2.10	-	1.30	63400	-	62600	463	-	500	0.68
Na⁺	3.00	-	-0.30	59800	-	73900	459	-	489	0.97
K+	3.08	2.70	_	55300	44800	-	459	452	-	1.33
Mg ²⁺	3.03	-	1.90	49700	-	54800	456	-	525	0.66
Ca ²⁺	3.90	3.05	-	49600	40400	-	453	422	-	0.99
Ba ²⁺	4.40	4.10	—	49600	39100	-	447	371	_	1.34

Table 1. Spectral-kinetic features of investigated complexes (1) with alkali and alkali-earth cations

In the process of investigation we found that the first stage of photoinduced recoordination takes place in complexes of (1) with Ba²⁺, Ca²⁺, K⁺. It was proved that the process of photoinduced recoordination could be effectively blocked in the PrCN cold matrix (at 77K condition). It was found that photoinduced recoordination occurs in range of no more than 100fs. Quantum-chemically calculated conformation curves that describe the process of recoordination in ground and excited state signifies that the process of photoinduced recoordination has potential barrier in both states. Moreover, it was established that the process of photoinduced recoordination is conjugated with the process of changing the solvate shell of metal cation that coordinated by aza-crown cavity (1) (Scheme 1).



Scheme 1. The process of photoinduced recoordination that takes place in complex (1) with Ba²⁺. Axial conformation of complex (left) proceeds to equatorial (right) – the result of the process of photoinduced recoordination

References

[1] Dalton Trans.2012, 41, 8767

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