

## Effect of the Hydration Shell on the Red Shift of Optical Absorption Bands of Diketonate Complexes

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### Supporting information

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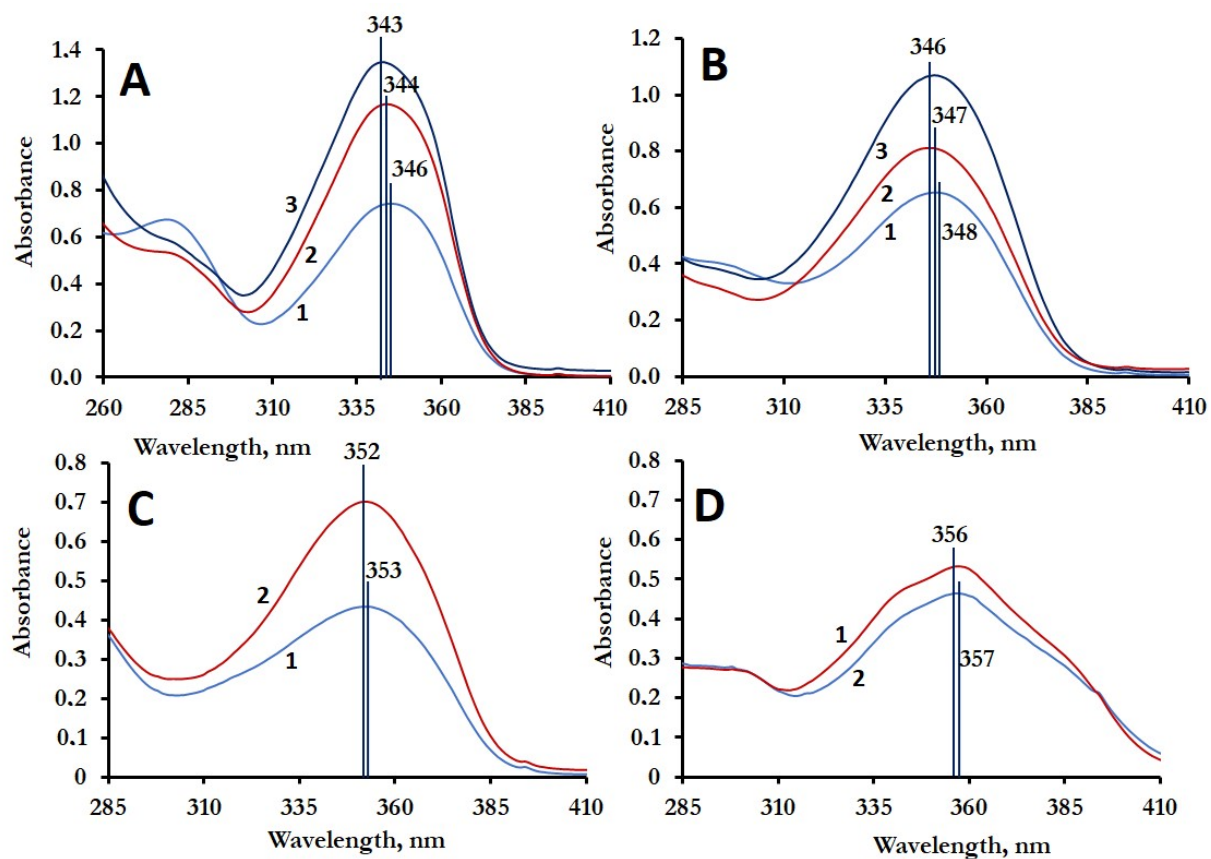
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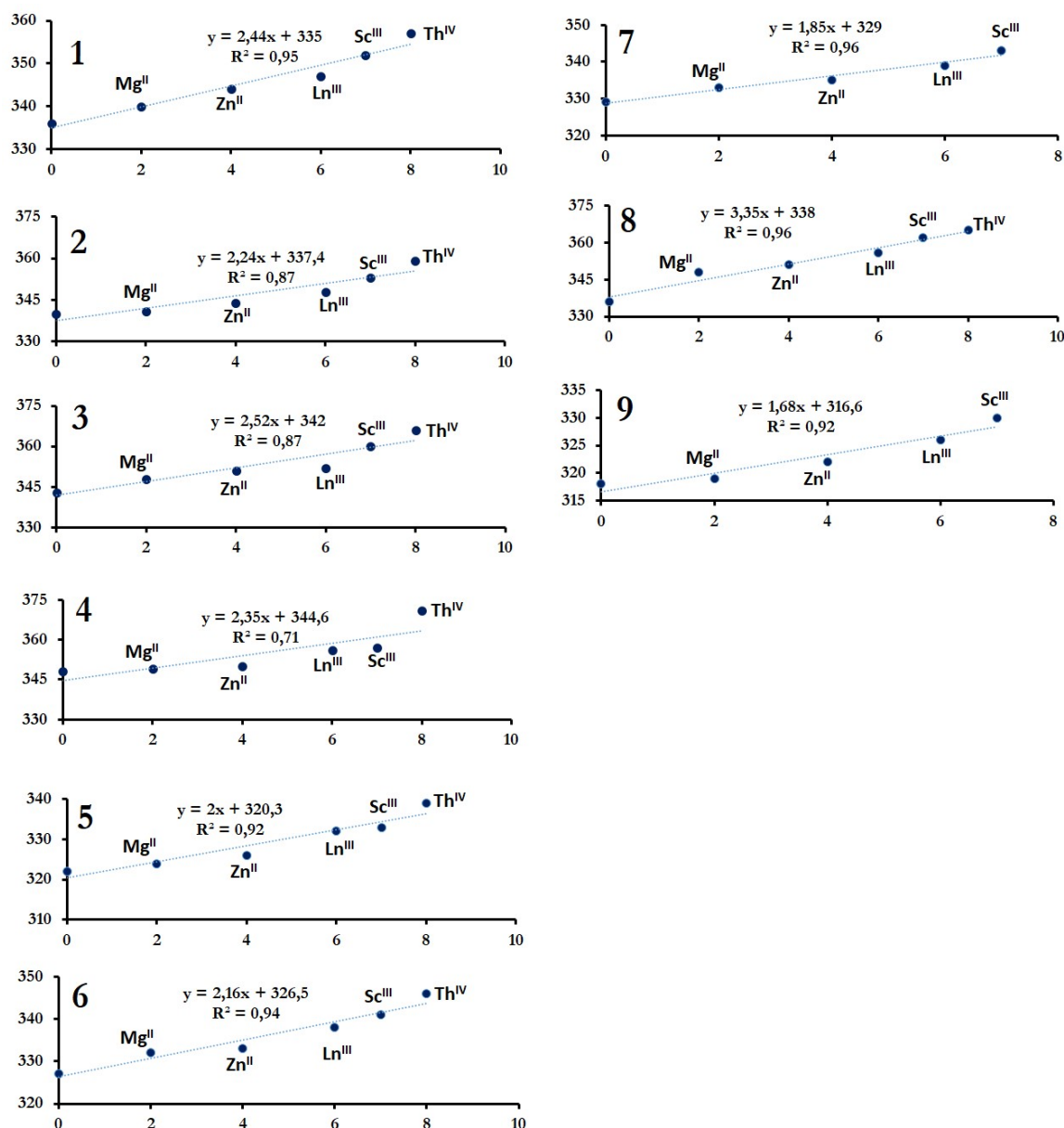
## Data used

In the discuss, we were using the data obtained in our previous works:

1. Lutoshkin, M.A.; Petrov, A.I.; Malyar, Y.N.; Kazachenko, A.S. Interaction of Rare-Earth Metals and Some Perfluorinated  $\beta$ -Diketones. *Inorg. Chem.* **2021**, 60 (5), 3291-3304.
2. Lutoshkin, M.A.; Taydakov, I.V. Selenoyl-trifluoroacetone: Synthesis, properties, and complexation ability towards trivalent rare-earth ions. *Polyhedron* **2021**, 207, 115383.
3. Lutoshkin, M.A.; Taydakov, I.V. A new Tellurium-bearing substituted  $\beta$ -diketone: Synthesis and properties; *Polyhedron* **2023**, 237, 116395.
4. Lutoshkin, M.A.; Taydakov, I.V. Complexation of Zn(II) and Cu(II) by Perfluorinated  $\beta$ -Diketones: Theoretical and Experimental Approaches and Potential Use as Copper-Eliminating Agents. *J. Sol. Chem.* **2023**, 52, 304–325.
5. Lutoshkin, M. A.; Taydakov, I. V.; Kuznetsov, B. N. Behavior of Some Perfluorinated Analogs of Thenoyltrifluoroacetone in Aqueous Solution. *J. Chem. Eng. Data* **2019**, 64, 2593–2600.
6. Lutoshkin, M. A.; Malyar, Y. N. Determination of Acid–Base and Complexing Parameters of Chlorine-Substituted Trifluorobenzoylacetone in Water Medium. *J. Chem. Eng. Data* **2020**, 65 (7), 3696–3705.
7. Lutoshkin, M. A. Revision and Analysis of the Formation Constants of Rare Earth Diketonates. *The Journal of Physical Chemistry A* **2023** 127 (40), 8383-8391.
8. Maxim A. Lutoshkin, Anastasia A. Patrusheva, Ilya V. Taydakov, Anatoly I. Rubaylo, Chelation of rare earth metals by perfluorinated  $\beta$ -diketones bearing nitrogen heterocycles rings, *Journal of Molecular Liquids*, 2024, 408, 125302.
9. Lutoshkin, M. A.; Taydakov, I. V.; Patrusheva A. A., Matveev P.I. Complexation of Thorium<sup>IV</sup> with Fluorinated Heterocyclic  $\beta$ -Diketones in Aqueous Hydrochloric Solutions; *Eur. J. Inorg. Chem.* 2024, e202400407
10. Maxim A. Lutoshkin and Yuriy N. Malyar; Study of Mono-fluorinated Derivative of Benzoyltrifluoroacetone, *Journal of Solution Chemistry*; 50, 1189–1203 (2021).



**Figure S1.** Spectra of Eu<sup>III</sup>-diketones system under different concentrations of ethanol: (a) O-CF<sub>3</sub> (1 – water, 2 – 40 % ethanol, 3 – 80% ethanol); (b) S-CF<sub>3</sub> (1 – water, 2 – 40 % ethanol, 3 – 80% ethanol); (c) Se-CF<sub>3</sub> (1 – water, 2 – 80% ethanol); (d) Te-CF<sub>3</sub> (1 – water, 2 – 80% ethanol);



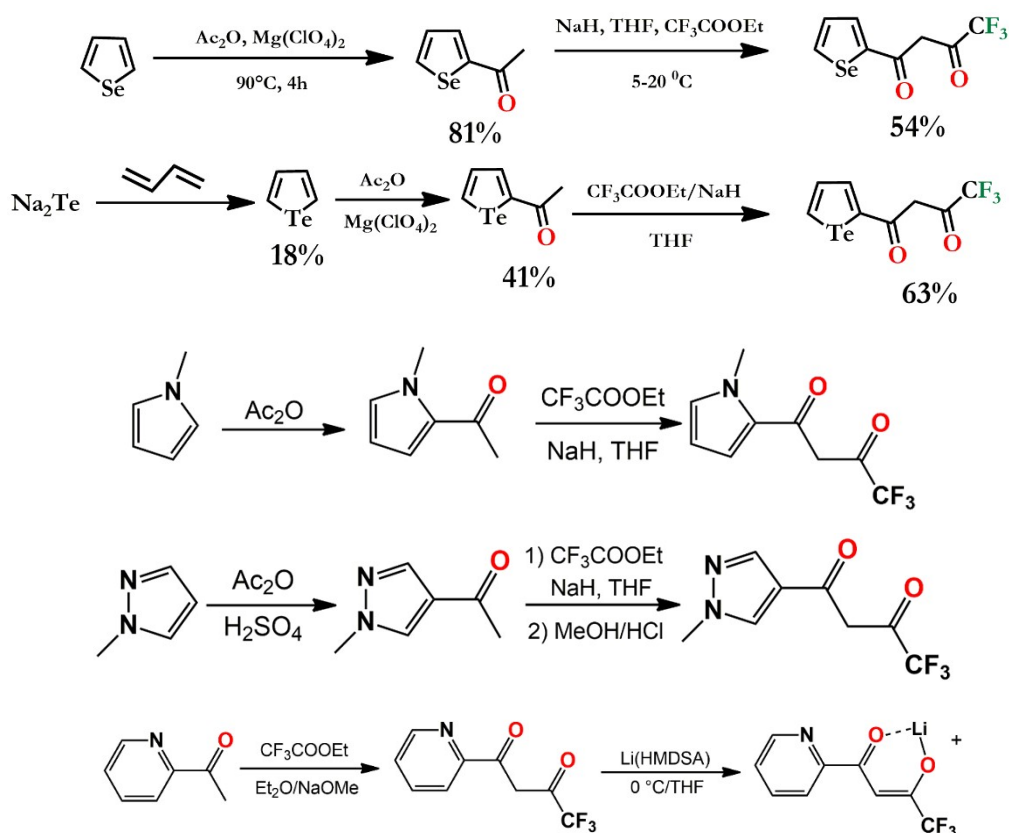
**Figure S2.** The correlation between maximum of absorbance wavelength (y-axis, nm) and typical number of water molecules (m) in solvation shell  $[M(H_2O)_mL]^{n+}$  (x-axis): **1** – O-CF<sub>3</sub>, **2** – S-CF<sub>3</sub>, **3** – Se-CF<sub>3</sub>, **4** – Te-CF<sub>3</sub>, **5** – Phen-CF<sub>3</sub>, **6** – Naphthyl-CF<sub>3</sub>, **7** – Pyr-CF<sub>3</sub>, **8** – N-Me-CF<sub>3</sub>, **9** – N-N'-CF<sub>3</sub>. Zero point for each graphics corresponds to the anionic form of ligand

**Table S1.** Wavelengths (nm) of maximum absorbance for ligands and their ML complexes. The number in brackets represents the number of coordinated water molecules in mono-complex species

Ligand	Anion (0)	Mg <sup>II</sup> (2)	Zn <sup>II</sup> (4)	Ln <sup>III</sup> (6)	Sc <sup>III</sup> (7)	Th <sup>IV</sup> (8)
O-CF <sub>3</sub>	336	340	344	347	352	357
S-CF <sub>3</sub>	340	341	344	348	353	359
Se-CF <sub>3</sub>	343	348	351	352	360	366
Te-CF <sub>3</sub>	348	349	350	356	357	371
Phen-CF <sub>3</sub>	322	324	326	332	333	339
Naphthyl-CF <sub>3</sub>	327	332	333	338	341	346
Pyr-CF <sub>3</sub>	329	333	335	339	343	-
N-Me-CF <sub>3</sub>	336	348	351	356	362	365
N-N'-CF <sub>3</sub>	318	319	322	326	330	-

## Synthesis of ligands

Some of studied ligands have been synthesized for the first time during our previous works by Claisen-type condensation (Scheme S1) and were identified using NMR, GC-MS, and elemental analysis. Corresponding spectra are contained in the ref. 2,3 and 8 from Data Used List (page S1)



**Scheme S1.** Synthesis of Se-CF<sub>3</sub> and Te-CF<sub>3</sub>, and nitrogen group of ligands (ref. 2,3, and 8)

## S2 Experimental section

Shimadzu 3600 Plus (Shimadzu, Japan) scanning spectrophotometer with grating-grating double monochromator and 1 cm quartz cell was used for recording electronic absorption spectra. All spectra were obtained within 220-450 nm and the spectral gap was set at 1 nm. Thermostating (298±0.1 K) was performed with a TCC-100 thermoelectrically temperature-controlled cell holder. The complexation with Mg(II) has been studied in the similar conditions which were used for studied complexation with Rare Earth Metals (REMs): acetate buffer (CH<sub>3</sub>COOH+CH<sub>3</sub>COONa), molar series method (excess of metal concentration under ligand content C<sub>M</sub>>>C<sub>L</sub>), constant ionic strength (I=0.5 M, background electrolyte – NaCl). Under used conditions, the formation of only mono-complexes species was observed (see literature references).

**The wavelength of maximum absorbance for complex species** has been estimated using nonlinear multi-wave regression analysis where maximum values of extinction (ε<sup>max</sup>) was determined as the variable parameters:

$$\sum_{i=1}^n (A_i^{\text{exp}} - A_i^{\text{calc}})^2 \xrightarrow{K_i, \epsilon_i} \text{minimum} \quad (1)$$

$$K' = \frac{[ML]}{[M][HL]} \quad (2)$$

$$[ML] = \frac{1}{2} \left[ \left( \frac{1}{K'} + C_{HL} + C_M \right) - \sqrt{\left( \frac{1}{K'} + C_{HL} + C_M \right)^2 - 4C_{HL}C_M} \right] \quad (3)$$

$$A_i = (\epsilon_{HL}(C_{HL} - [ML]) + \epsilon_M(C_M - [ML]) + \epsilon_{ML}[ML]) \quad (4)$$

The maximum value of molar extinction coefficient at corresponding wavelength

**The wavelength of maximum absorbance for Magnesium<sup>II</sup>** has been calculated as the maximum of the ΔA-λ curve, where ΔA is a difference of the optical density between spectrum of complexes (solution ligand+metal+buffer) and spectrum of ligand (free ligand in buffer) and metal (background absorption). To level the absorbance of ligand, the high concentration of Mg(II) was used, and all ligand was binding with metal ions. Based on the previous works, the conditions of the chelation were chosen for the predomination of ML complexes.

**The wavelength of maximum absorbance for complex species for high-resolution** spectra was measured using the resolution of double monochromators of 0.01 nm and a spectral gap of 0.5 nm. Each spectrum was recorded five times for two different concentrations of metals and equal concentrations of ligands (C(S-CF<sub>3</sub>)=6.05×10<sup>-5</sup> M). The final concentration of ethanol did not exceed 2% for each solution. Since in previous works we have determined all thermodynamic parameters of such systems, the concentrations of metals were taken in excess for full chelation of ligand. This allows us does not use the difference between the initial and final spectrum and to determine the diapason of maximum absorption directly from spectrum of solution. The region of maximum absorption was chosen as the sequence of wavelengths which have the highest values of absorption.

**Table S2.** The region of maximum absorption wavelength for S-CF<sub>3</sub>/Ln<sup>3+</sup> system

M <sup>3+</sup>	Hydration number	Diapason of maximum wavelength	Middle
Ce	9.1	347.5-347.9	347.7±0.2
Pr	9.2	347.0-347.3	347.2±0.2
Nd	8.9	347.3-347.4	347.4±0.1
Sm	8.5	346.9-347.3	347.1±0.2
Tm	8.1	346.4-346.8	346.6±0.2
Lu	8.0	346.6-347.1	346.9±0.3

**The wavelengths of maximum absorbance in water-ethanol mixture** were measured at the metal ion excess under ligand concentration to minimize the absorbance of other ions and the main absorption species was metal-ligand complex. Using previously acquired data, conditions (concentration of ligand, metal, pH and ionic strength) were selected for the predomination of mono-complex species ML. Excess of metal ions leads to the full chelation of ligand molecules, and the absorption peaks corresponding to the bands of the ML complex.

**Short comments about stability.** In this article, we have discussed about series of metals:  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $REMs^{3+}$ ,  $Sc^{3+}$ ,  $Th^{4+}$ . In this order, the coordination number of ions increases. However, the stability of diketone complexes (logK) also increases. One would assume that the spectral shift depends on stability constants. But according to the Born equation [The Born equation and ionic solvation; P. W. Atkins and A. J. MacDermott; Journal of Chemical Education 1982 59 (5), 359; DOI: 10.1021/ed059p359], the decrease of dielectric constants of media lead to the significant increase of stability constant. However, in solution with high ethanol concentration, we see a small spectral shift in short-wave region. This behavior corresponds to the change of the solvation shell and the decrease of the number of water molecules in solvation shell in  $Eu^{III}$  complexes in ethanol solution.

### S3 Quantum-chemical calculations

The quantum-chemical computations were performed using the GAMESS US program package on the cluster MVS-1000M of the Institute of computational modeling SB RAS. Geometry optimization was performed by density functional theory (DFT-D3) with PBE0 (under Grimme's empirical correction) and CAM-B3LYP functionals. The cc-pVDZ and Def2-SVP basis set functions were applied to C, H, O, S, Se, Mg and F atoms. The effective core potential CRENBL ECP was used for Te complexes. The solvent effects were evaluated using the SMD solvation model. UV-Vis absorption maximum wavelengths of complex species were reproduced from the vertical excitation energies for the first 12 singlet excited states by Time-Dependent Density Functional Theory (TD-DFT).

**Table S3.** Theoretical calculated values of wavelength (nm) of absorbance for  $Mg^{II}$  complexes (cc-pVDZ/PBE0/SMD)

Ligand	Complex				Exp
	$[MgL]^+$	$[Mg(H_2O)_2L]^+$	$[Mg(H_2O)_4L]^+$	$[Mg(H_2O)_6L]^+$	
O-CF <sub>3</sub>	348	342	332	331	340
S-CF <sub>3</sub>	347	341	334	333	341
Se-CF <sub>3</sub>	355	349	341	341	348
Te-CF <sub>3</sub>	357	352	343	342	349

For the clarification of the influence of explicit and implicit solvation models on the TD-DFT modeling, computations without the SMD model were performed (Table S4). As we can see, the combination of both solvation models gives the best results.

**Table S4.** Theoretical calculated values of wavelength (nm) of absorbance for  $Mg^{II}$  complexes for gas phase (cc-pVDZ/PBE0)

Ligand	Complex				Exp
	$[MgL]^+$	$[Mg(H_2O)_2L]^+$	$[Mg(H_2O)_4L]^+$	$[Mg(H_2O)_6L]^+$	
O-CF <sub>3</sub>	316	312	307	307	340
S-CF <sub>3</sub>	328	318	312	313	341
Se-CF <sub>3</sub>	326	318	321	320	348
Te-CF <sub>3</sub>	337	332	327	326	349