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New molecules prepared from a 1,3,4-thiadiazole derivative and chromone- or coumarin-3-carboxylic acid and their metal complexes

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Chromone and coumarin are natural compounds. They have been incorporated into bigger molecules to act as ligands in coordination chemistry. One of the reasons are the fluorescent properties of those molecules [1]. In this work, two molecules containing the chromone or coumarin skeletal were planned with the goal to explore their behavior as probes toward first-row transition metal ions. The chromone-3-carboxylic acid and coumarin-3-carboxylic acid were converted to the corresponding 3-carbonyl chlorides. They were reacted with 5-(methylthio)-1,3,4-thiadiazol-2-amine, yielding HL^1 and HL^2 (Fig. 1). The synthetic reaction for the obtention of HL^1 also produced an imine molecule (HL^{1b}) by ring transformation [2]. All the molecules were used for complexation reactions with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions. HL^1 reacted only with copper salts while HL^2 reacted with all ions except Mn^{II}. The use of copper acetate led to the formation of green complexes with formula $[Cu_2(L)_2(Ac)_2]$ (Fig. 1b). The use of copper chloride formed violet and green complexes, with probable composition of $[Cu(H_2O)_2(L^1)_2]$ and $[Cu_2(L^2)_2Cl_2]$, respectively. The cobalt, nickel and zinc complexes with HL^2 are probably similar to the copper compound. HL^1 has no solubility in common organic solvents (only in hot dimethyl sulfoxide). In the UV-Vis spectra, HL^2 has three absorption bands in dichloromethane (288, 311 and 343 nm) and a broad absorption band centered at 311 nm in *N*,*N*-dimethylformamide (DMF). In DMF, HL^{1b} changes the profile within the time, changing from bands at 266 and 349 nm (medium intensities) to 292 (low intense band) and 395 nm (broad band, high intensity). Complex $[Zn(dmf)_2(L^{1b})_2]$ has identical spectrum in DMF (bands at 292 and 395 nm). It suggests that the 4-hydroxycoumarin fragment in HL^{1b} slowly "deprotonates" and the molecule changes to a zwitterion (the solution changes from yellow to colorless) which is promoted by the polar aprotic solvent DMF. Complex $[Zn(dmf)_2(L^{1b})_2]$ is fluorescent when exposed to an external UV-A radiation source (λ 365 nm). HL^{1b} seems to be a good candidate to be used as probe for detection of metal ions.

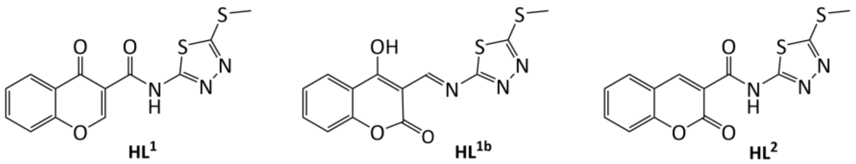

Figure 1. Chemical structure of the HL^1, HL^{1b} and HL^2 molecules.

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References

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