

MS43-P9 **Trans-keto*form emission in non photochromic *N*-salicylidene aminomethylpyridines: a structural study.** Pierre-Lod'c Jacquemin,^a François Robert,^a Bernard Tinant,^a Yann Garcia ^a*Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Belgium*
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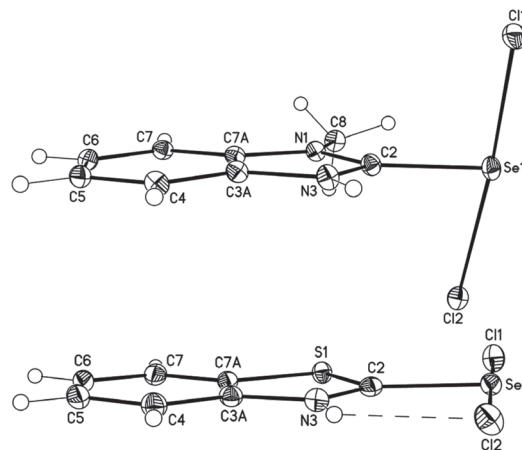
Among the rare classes of molecules that exhibit both reversible thermo and photochromism in the crystalline state, *N*-salicylidene aniline aminopyridine can be highlighted.^[1] In this work, we have studied the influence of the increase of flexibility and electronic conjugation loss among *N*-salicylidene aminopyridine derivatives on the optical properties after the introduction of a methylene spacer. Five *N*-(5-chloro)salicylidene aminomethylpyridine derivatives were successfully synthesized and their structural and solid state optical properties analyzed. Yellow crystalline powders of CH_2L^3 and $\text{CH}_2\text{L}^{3-4}\text{Cl}$ present both thermo- and photochromism whereas CH_2L^2 and CH_2L^4 do not show any switching properties, as probed by diffuse reflectance spectroscopy. Contrary to structural-optical expectations, non-photochromic CH_2L^2 molecule (*P21/n*) shows an open crystal structure, and photochromic molecules $\text{CH}_2\text{L}^{3-4}\text{Cl}$ (*P21/c*) present a closed crystal packing, revealed by single crystal X-ray diffraction, which is typical of exclusively thermochromic molecules. After UV irradiation, *trans*-keto* emission observation in CH_2L^2 and CH_2L^4 indicates the unexpected formation of *trans*-keto form, in these non photochromic anil molecules. Radiative relaxation of the *trans*-keto* form is in addition detected, for the first time, by fluorimetry for all *N*-salicylidene molecules of the series, whatever their switchable chromic properties. Thus, the absence of photochromism in diffuse reflectance spectroscopy after light irradiation thus does not imply the impossibility of *trans*-keto formation.^[2]

- [1] Robert, F., Naik, A. D., Tinant, B., Robiette, R. & Garcia, Y. (2009). *Chem. Eur. J.* **15**, 4327-4342. 15, 4327. Robert, F., Tinant, B., Clérac, R., Jacquemin, P.-L. & Garcia, Y. (2010). *Polyhedron* **29**, 2739-2746.
[2] Robert, F., Jacquemin, P.-L., Tinant, B. & Garcia, Y. (2012). *CrystEngComm*. DOI:10.1039/C2CE00006G.

Keywords: *N*-salicylidene aniline, anils, fluorescence, photochromism

MS43-P10 **Perpendicular versus coplanar conformation of SeCl_2 moiety in hypervalent T-shaped adducts.** Victor N. Khrustalev,^a Sheyda R. Ismaylova,^a Zhanna V. Matsulevich,^b Alexander V. Borisov,^b ^a*Nesmeyanov Institute of Organoelement Compounds, Russia*, ^b*Alekseev Nizhny Novgorod State Technical University, Russia*.
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N-methylbenzimidazole-2-selone-dichlorine (**1**) and benzothiazole-2-selone-dichlorine (**2**) have been synthesized by the treatment of the corresponding selones with sulfuryl dichloride in dichloromethane. The X-ray crystal structure determinations of **1** and **2** show their 10E3 T-shaped hypervalent chalcogen adduct natures. The both structures are essentially zwitter-ionic, a negative charge resides on the SeCl_2 moiety and a positive charge is supported by the nitrogen atoms. The CSe distances of 1.896(2) Å in **1** and 1.898(2) Å in **2** are representative of the single bonds. Interestingly, the almost linear Cl–Se–Cl systems in **1** [174.60(2)] and **2** [179.41(2)] are differently orientated in relative to the organic fragment plane. In **1**, the SeCl_2 moiety is roughly perpendicular to the benzimidazole plane [68.73(3)], whereas, in **2**, this moiety is approximately coplanar to the benzothiazole plane [3.0(1)] (see the figures below). Apparently, the observed planar conformation of **2** is explained by the absence of the steric hindrances, *i.e.*, bulky substituent in the 1-position of the five-membered ring, for the formation of the strong intramolecular N3H3...Cl2 hydrogen bond. In the case of **1**, the Cl2 chlorine atom forms the strong intermolecular N3H3...Cl2 hydrogen bond. Due to the hydrogen bonding interactions, the SeCl_2 moiety in **1** and **2** has the asymmetric geometry with the longer Se1Cl2 bond [2.5374(5) Å in **1** and 2.4622(6) Å in **2**] as compared to the Se1Cl1 bond [2.3352(5) Å in **1** and 2.3377(6) Å in **2**]. Thus, the structures of **1** and **2** clearly demonstrate the free rotation of the SeCl_2 moiety around the CSe bond that, in turn, confirms the absence of its significant double character.



Keywords: selenides; hypervalent compounds; X-ray crystallography