

MS23-P14 Non-covalent interactions in crystals of some heterocyclic compounds. Julia Voronina,^a A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
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It is known that non-covalent interactions play an important role in various physical and chemical properties. A detailed analysis of such interactions can explain, and in some cases, predict some properties of the test compound. Various biologically-active compounds are being investigated for a long time at the A.E. Arbuzov Institute. Among them the most interesting are the pyrimidine and isocyanurate derivatives, which are widely used as pharmaceuticals, and also the new derivatives of isoindigo. Within this work the non-covalent interactions in compounds of these classes are studied. The investigation of the crystal structure of the uracyl and isocyanurate derivatives has revealed the presence of two types of interactions - $Lp \dots \pi$ and $\pi \dots \pi$ - in the crystals of molecules, which are incapable of the formation of the H-bonds. The similarities and differences of $Lp \dots \pi$ interactions, depending on the nature of the heterocycle were analyzed. We have analyzed the $Lp \dots \pi$ interactions in the uracyl and isocyanurate derivatives, estimated their energy and charge on the oxygen atoms and heterocyclic fragments. However we are still assuming a substantial contribution of electrostatic forces in the nature of this interaction suggested by the prevalence of these interactions in crystals of isocyanurate derivatives, and this was confirmed by a detailed study of the crystal structures presented in CCDC. In the process, we found interesting examples of the influence of $Lp \dots \pi$ interactions in the direction of the chemical reaction in the derivatives of isocyanurate and crystallization processes of uracyl derivatives. For example, pseudopolimorphs for one of the compounds with different Z' were found. A detailed comparison of the molecular structure showed the implementation of $Lp \dots \pi$ intramolecular interactions in one of the molecules in the independent part, which led to some difference in the conformations and probably to the crystallization of the compound with two independent molecules in a unit cell. Also, the presence of intramolecular $Lp \dots \pi$ interaction in the sulfide derivatives of isocyanurate led to obtaining the unexpected oxidation products by the sulfide sulfur atom in the substituent. Also, the molecular structure of izoindigo derivatives in crystals was studied. Unexpectedly it was found that izatin fragments of isoindigo derivatives having the small alkyl or aryl substituents at the nitrogen atom according to X-ray analysis can be either in planar or non-planar conformation. The performed quantum-chemical calculations showed that for the isoindigo in the gas phase is the most energetically favorable is the non-planar conformation, what is surprising, because isoindigo is a conjugated heterocyclic system. Interestingly, the non-covalent interactions differ in crystals formed by planar and non-planar molecules. Thus, the planar molecules are linked by stacking interactions of izatin fragments, but non-planar ones - only through $CH \dots O$ interactions. This work was supported by RFBR (project a 12-03-00898-a) and the Russian Ministry of Education (GK No. 14.740.11.1027).

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MS23-P15 Amide hydrogen bonding vs. coordination? Marijana Đaković, Ana Filošević, Zora Popović, Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

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Amide moiety is already well known as a robust and reliable supramolecular connector in organic systems. Even though there are quite a number of reports where amide hydrogen bonds were used in a deliberate strategy for connecting metal complexes into extended networks [1,2], a predetermination of supramolecular architectures and topologies of metal-organic systems is still a hard task.

Recently, we found for a series of picolinamide complexes of late 3d-block metal(II) ions that self-complementary amide motif [$R^2_2(8)$] is not the synthon of the first choice [3]. Instead, the motif involving other accessible hydrogen bonding acceptor atom(s) and the amide nitrogen as a double hydrogen bonding donor [$R^2_4(8)$] is more readily formed one, although it has been shown that the difference in energy between the two motifs is rather small. Furthermore, the problems encountered in optimisation of geometry of structures (Zn, Cu) suggested that formation of the motif might be one that is responsible for the determining of their coordination geometries.

Having this in mind, we wanted to give the system more freedom in realizing the optimal framework, so now we used a combination of different amide derivatives of pyridine and/or pyrazine ligands. As the result, here we report several complexes where the self-complementary hydrogen bonding is the synthon of the first choice due to exceeding some rigidity of the systems in hands.

- [1] Aakeröy, C. B., Beatty, A. M., Desper, J., O'Shea, M. & Valdés-Martínez, J. (2003). *Dalton Trans.*, 3956-3962.
- [2] Brammer, L. (2004). *Chem. Soc. Rev.* **33**, 476-489.
- [3] Đaković, M., Vila-Viçosa, D., Calhorda, M. J. & Popović, Z. (2011). *CrystEngComm*. **13**, 5863-5871.

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