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Our group was devoted to the research of metal string complexes in past decades. We believe that the thinnest metal wire could be applied to practical applications in molecular electronics in future. We successfully synthesized two kinds of ligand in order to extend the study of metal strings. First, the new decametal string complex $[\text{Ni}_{10}(\mu_{10}\text{-bdpdany})_4(\text{NCS})_2](\text{PF}_6)_2$ was successfully synthesized with $\text{H}_4\text{bdpdang}$ ligand. The crystal structure of $[\text{Ni}_{10}(\mu_{10}\text{-bdpdany})_4(\text{NCS})_2](\text{PF}_6)_2$ shows that all of the bdpdany^{4-} ligands bind metal in all-syn conformation and the X-ray structural studies reveal the internal Ni-Ni bond distance is ca. 2.36~2.23 Å. Second, the heteronuclear $[\text{Ru}_2\text{Ni}_2(\text{DAniDANy})_3(\text{OAc})_2\text{Cl}]$ complex was successfully synthesized with $\text{H}_2\text{DAniDANy}$ ligand. The crystal structure of $[\text{Ru}_2\text{Ni}_2(\text{DAniDANy})_3(\text{OAc})_2\text{Cl}]$ is shown in Figure 1b. Ru(1)-Ru(2) is about 2.288(1) Å. Ru(1)-Cl is 2.469(2) Å. Ru-N distances are 2.04-2.09 Å. Ru(2)-Ni(1) is 2.469(1) Å. This distance is close enough to have some overlap between Ru and Ni. Magnetic study shows it has three unpaired electrons. IVCT band at 890 nm indicates there exists an unoccupied δ^* which is similar to Ru_2 dimer. DFT study shows that the three magnetic orbitals are essentially Ru_2 based. Ru_2 and Ni_2 may have weak bonding interaction.

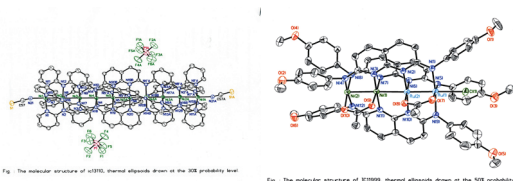


Fig. 1 The crystal structures of $[\text{Ni}_{10}(\mu_{10}\text{-bdpdany})_4(\text{NCS})_2](\text{PF}_6)_2$ and $[\text{Ru}_2\text{Ni}_2(\text{DAniDANy})_3(\text{OAc})_2\text{Cl}]$.

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Keywords: metal-metal bonds; crystallography; magnetic properties

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Insight into Crystal Structure/Optical Properties Relationships of New N-Salicylidene Anils. Bernard Tinant^a, François Robert^a, Anil D. Naik^a, Yann Garcia^a. ^aUnité de Chimie Structurale et des Mécanismes Réactionnels et Unité de Chimie des Matériaux Inorganiques et Organiques, Département de Chimie, Université Catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium.
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N-salicylidene aniline derivatives are highly versatile thermo- and photochromic molecules [1]. These are actively studied for many applications like non linear optics [2], biological activities [3], information storage and display

[4], etc. Thermo and photochromism occurring in the solid state thanks to reversible equilibria between the uncoloured *enol*, the yellow *cis-keto* and the red *trans-keto* forms [1] are the main interests of these compounds. All derivatives are described as thermochromic but only a few of them are photochromic. Many authors stress the importance of crystal packing [5] to explain these properties but the molecular environment is also to be considered [6]. Crystallographic study of N-salicylidene aniline derivatives is essential for the understanding of molecular properties in solution or in solid state. In this work, we have observed that the dihedral angle between aromatic rings and the crystal packing are not sufficient to predict the photochromism behaviour of the compounds [7]. This is clearly seen with the N-salicylidene 4-aminopyridine (L4) and 2-(3,5-bis(pyridin-2-yl)-1,2,4-triazole-4-ylimino-methyl)-phenol (ABS). L4, a highly twisted molecule, present an open structure with large intermolecular distances and weak CH- π and $\pi\pi$ stacking interactions. Photo-isomerisation to the *trans-keto* form should be easier thanks to the crystal packing. However, L4 is only thermochromic. In contrast, ABS crystal is formed with highly twisted molecules, packed very closely with strong supramolecular interactions ($\pi\pi$ stacking) but is only photochromic. This observation clearly disagrees with reported conclusions [5]. Finally, a novel interesting molecular conformation has been discovered with the N-salicylidene 4-amino-1,2,4-triazole (Hsaltraz) which is packed as supramolecular *zig-zag* double chains.

[1] Fujiwara T., Hadara J., Keiichiro O., *J. Phys. Chem. B* **2004**, 108,4035. [2] Plaquet A. *et al J. Phys. Chem. C* **2008**, 112, 5638. [3] Parashar R.K., Sharma R.C., Kumar A., Mohan G. *Inorg. Chim. Acta* **1988**, 151, 201. [4] Feringa B. L., Jager W. F., de Lange B. *Tetrahedron* **1993**, 49/37, 8267. [5] Hadjoudis E., Mavridis I.M., *Chem. Soc. Rev.* **2004**, 33, 579. [6] Haneda T., Kawano M., Kojima T., Fujita M., *Angew. Chem. Int. Ed.* **2007**, 46, 6643. [7] Robert F., Naik A.D., Tinant B., Robiette R., Garcia Y., *in press*

Keywords: supramolecular chemistry; crystal structure; optical properties

FA4-MS02-P24

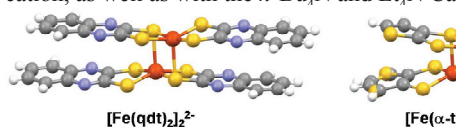
Cation and Ligand Roles in the Coordination of Fe^{III} Bisdithiolene Complexes. Isabel Corderio Santos^a, Ana Isabel S. Neves^a, Dulce Belo^a, Manuel Almeida^a. ^aDept. Química, I.T.N./CFMUL, P-2686-953, Sacavém, Portugal.

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Aiming at a better understanding of the role of the cation versus the role of the ligand in the coordination geometry of Fe^{III} bisdithiolene complexes we have been exploring either new $[\text{Fe}^{\text{III}}(\text{qdt})_2]^-$ salts (qdt=quinoxalinedithiolate) with different cations or new iron bisdithiolates complexes, such as $[\text{Fe}(\alpha\text{-tpdt})_2]$ ($\alpha\text{-tpdt}$ =2,3-thiophenedithiolate). At variance with the large diversity of coordination geometries and oxidation states of bisdithiolene complexes with most metals, the iron complexes with these ligands have been essentially restricted to one stable oxidation state, Fe(III), and until quite recently all were found to adopt in solid state the same square pyramidal, 4+1, coordination geometry due

to the formation of dimeric arrangements through two Fe-S bonds between distorted square based $[\text{Fe}(\text{S}_2\text{L})_2]^-$ units, $[\text{Fe}(\text{S}_2\text{L})_2]_2^{2-}$. The first, and so far unique, exception to this rule was the *n*-Bu₄N $[\text{Fe}(\text{qdt})_2]$ complex [1], displaying a perfectly square planar coordination geometry and a $S = 1/2$ spin state.

The crystal structure of the new $(\text{BrBzPy})_2[\text{Fe}(\text{qdt})_2]$ complex shows a rare weak Fe^{III} bisdithiolene dimerisation with unusual molecular planarity and long apical S-Fe distances, in an anion configuration intermediate between the only monomeric Fe bisdithiolene reported so far, and the common strong dimeric geometry also observed in other $[\text{Fe}(\text{qdt})_2]$ salts. The standard strong dimeric situation is also observed in the new $[\text{Fe}(\alpha\text{-tpdt})_2]$ salt with the same cation, as well as with the *n*-Bu₄N and Et₃N Cations.



[1] Simão D., Ayllón J.A., Rabaça S., Figueira M.J., Santos. I.C., Henriques R. T. and M. Almeida, *CrystEngComm*, **2006**, 8, 658.

Keywords: molecular compounds; Fe-bisdithiolene complexes; crystal engineering

FA4-MS02-P25

pH Indicators – Molecular Structure and Proton Distribution. Zofia Urbanczyk-Lipkowska^a, Przemysław Kalicki^a. ^a*Institute of Organic Chemistry, Polish Academy of Sciences. 01-224 Warsaw, Poland*
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A pH indicators are usually weak bases or weak acids that recognize selectively hydronium ions. In common organic solvents they exist as equilibrium of variously protonated forms and/or open/cyclic structures. Apart of common use in chemical laboratories, medical diagnostics and industry, solid state structural data on pH indicators are scarce [1-3]. Here we present X-ray structures of bromocresol purple, bromothymol blue, 4',5'-dibromofluorescein, and Congo red crystallized in different crystallization conditions and at different pH. Such problems like proton distribution and electronic structure of the molecules will be addressed.

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Keywords: pH indicators; lactones; electronic structure

FA4-MS02-P26

Enclathration by a Xanthenol Host via Solid-solid Reactions: Structures and Kinetics. Ayesha Jacobs^a, Luigi R. Nassimbeni^a, Kanyisa L. Nohako^a, Gaëlle Ramon^a, Jana H. Taljaard^b. ^a*Department of*

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The compound, 9-(4-methoxyphenol)-9H-xanthen-9-ol (H) has proved to be a versatile host and has included a variety of small organic guests [1,2]. Solid-solid reactions with this host and a series of polycyclic unsaturated hydrocarbons have also been reported [3]. In this study the host compound, H, has successfully included the solid guests 1-naphthylamine(NAPA), 8-hydroxyquinoline(HQ), triethylenediamine(TEDA) and acridine(ACR). The structures for all four inclusion compounds were solved in the space group P-1. Similar packing motifs were found for the NAPA and HQ inclusion compounds where neighbouring host molecules form dimers of the type (Host)-OH...O(Host). The TEDA and ACR guests hydrogen bond to the host molecule. In addition the compounds were also formed by direct grinding of the host with each of the guests and the kinetics of the solid-solid reactions determined using powder x-ray diffraction. The kinetics for all four reactions were modelled using the first order rate law: $f(\alpha) = \ln(1-\alpha) = -kt$ where α is the extent of the reaction.

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Keywords: solid-solid reactions; inclusion compounds; kinetics

FA4-MS02-P27

Existence Region of Type-I Clathrates in the System Ba-Ni-Ge. Umut Aydemir^a, Horst Borrmann^a, Cécile Hébert^b, Nguyễn Thị Kim Liên^a, Ulrich Burkhardt^a, Michael Baitinger^a, Yuri Grin^a. ^a*Max Planck Institute for Chemical Physics of Solids, Dresden, Germany.* ^b*Ecole Polytechnique Fédérale de Lausanne, Lausanne, France.*

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The formation of voids in the framework of Ge clathrates has a strong impact on their crystallographic and physical properties. In the binary system Ba – Ge, the composition of a hypothetical clathrate-I compound without defects is Ba₈Ge₄₆. Since a four-bonded framework Ge₄₆ can be already formed with uncharged Ge atoms, the additional valence electrons of the Ba atoms would occupy antibonding states. However, the formation of defects is more favorable for Ge clathrates. Each defect □ in a framework Ge_{46-x}□_x is surrounded by four three-bonded Ge atoms (3b)Ge¹⁻. Hence, the 16 valence electrons from 8 Ba atoms would be completely compensated by four defects surrounded by 16 (3b)Ge¹⁻. Actually, instead of the expected composition Ba₈Ge₄₂□₄, the binary clathrate was found to be Ba₈Ge₄₃□₃ with 4 conduction electrons per formula unit [1]. Ternary type-I clathrates Ba – TM – Ge can be obtained with