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Structure-property relationships in acenes and pyrenes for organic electronics.

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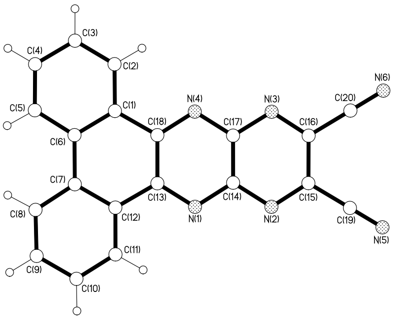
Compounds incorporating several fused, aromatic rings offer considerable promise in organic electronics. In the actual electronic devices the compounds are spun out as thin films. However, a knowledge of their structure from X-ray crystallography is vital in the on-going work to improve device performance. In collaboration with Dr. Jonathan Hill's MANA group at NIMS, Tsukuba, Japan, we are engaged in the synthesis and self-assembly of soluble oligoazaacenes [1,2]. One successfully targeted compound is 2,3–dicyanotetraazabenzotriphenylene, **1**. The crystal structure exhibits π-π stacking, C-H···N head-to-tail interactions resulting in a ribbon packing motif, and an exceptionally close intermolecular N···N separation. This latter feature, we believe, explains the *n*-type semiconductor properties of the compound.



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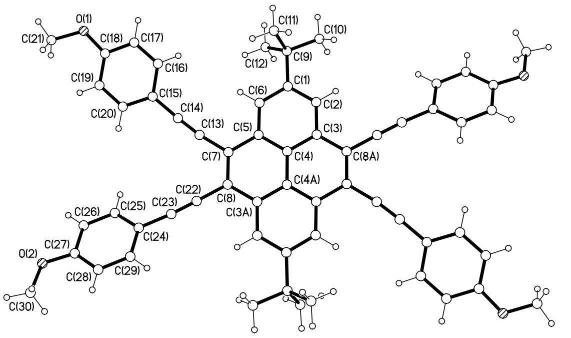
In collaboration with Prof. Takehiko Yamato's group at Saga Univ., Japan, we have investigated a variety of photoactive compounds, for example, the pyrene-based, cruciform-shaped compound, **2**. In this compound, the key feature is that the aromatic decks are **not** very closely stacked and it is this that is believed to be important in the light being emitted at the valuable blue end of the visible spectrum [3]. Diffraction data have been obtained for several other examples, some collected at the ALS synchrotron source, Berkeley, CA.



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[1] Richards G.J., Hill J.P., Okamoto K., Shundo M., Elsegood M.R.J., Mori T., Ariga K., *Langmuir*, 2009, 25, 8408. [2] Richards G.J., Hill J.P., Subbaiyan N.K., D'Souza F., Karr P.A., Elsegood M.R.J., Teat S.J., Mori T., Ariga K., *J. Org. Chem.*, 2009, 74, 8914. [3] Hu, J-Y. Era, M.; Elsegood, M.R.J., Yamato, T., *Eur. J. Org. Chem.,* 2010, 72.

Keywords: organic materials, electronic materials, photoemission.

FA4-MS33-P02

Possible polyamorphic relationship between liquid and crystalline phases in $\mathrm{SnI_4}$

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From in situ synchrotron x-ray diffraction measurements on liquid tin tetraiodide, which consists of $\mathrm{SnI_4}$ molecules at ambient pressure, we have established that the liquid forms existing above and below a break point pressure, 1.5 GPa, where the slope of the melting curve of the crystalline phase changes abruptly, have different structures [1]. This discovery offers evidence of thermodynamically stable polyamorphism in general compounds as well as in elements such as phosphorus. The vertex-to-face orientation between the nearest molecules plays a key role in the transition from the low-pressure to the high-pressure liquid phase [1].

The liquid-liquid critical point (LLCP) scenario, which presumes the existence of a critical point associated with the liquid-liquid phase transition, seems to be naturally applicable to describe the aspect observed in $\mathrm{SnI_4}$. Indeed, the LLCP scenario can consistently explain all our findings, including the stability limits of the two amorphous states. Our recent experimental investigation suggests that the LLCP is, if it exists, located close to the break point on the melting curve. Mean field treatments for the scenario allows us to estimate the differences in the molar entropy and volume, respectively, between the two liquid phases. Although the former is about 5 times larger than the corresponding value between the two amorphous states in ice, the latter is quite comparable with that found in ice, implying that the value represents a specific volume contraction upon collapsing a tetrahedral open network structure. Moreover, we infer that the vertex-to-face orientation correlation in the high-pressure liquid structure reflects a molecular arrangement in the high-pressure crystalline phase whose structure still remains unresolved.

[1] Fuchizaki K., *J. Chem. Phys.* 2009, 130, 121101. [2] Stokely, K.; Mazza, M. G.; Stanley, H. E.; Franzese, G. *Proc. Natl. Acad. Sci.* 2010, 107, 1301.

Keywords: liquid state, high pressure, synchrtorn X-ray diffraction

FA4-MS33-P03

$\mathrm{Co(pym)(VO_3)_2}$ and $\mathrm{Co(H_2O)_2(VO_3)_2.2H_2O}$: structure, magnetic properties and relationships.

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The use of organic molecules for the design of new inorganic materials has allowed the preparation of compounds with major technological applications[1]. In this context, vanadium derivatives seem to be good candidates to obtain new materials because of the versatile behaviour of this metal[2]. For this reason, our research has been focused in the synthesis and characterization of hybrid vanadates with aromatic and aliphatic amines[3]. In this work we present the comparative study of a hybrid vanadate, $Co(pym)(VO_3)_2$ (pym=pyrimidine) and an inorganic one $Co(H_2O)_2(VO_3)_2.2H_2O$ with closely related structures.

The three-dimensional $Co(pym)(VO_3)_2$, **1**, has been synthesized under mild hydrothermal conditions. The crystal structure of **1** was solved using single-crystal X-ray diffraction data, taking into account that the crystals are twins of two components. Compound **1** crystallizes in the monoclinic system, space group C2/c, a= 12.899(5) Å, b= 9.899(2) Å, c= 7.051(1) Å, β= 111.41(3) º, Z= 4. The crystal structure is built up from edge sharing VO_5 trigonal bipiramid double chains and $[CoO_4pym]_n$ chains. This resembles to the structure of the $Co(H_2O)_2(VO_3)_2.2H_2O$ compound[4], **2**. For this reason a comparative study of their properties was carried out.

Magnetic measurements of **1** reveal the existence of a ferromagnetic transition. This fact was confirmed with magnetization measurements. The ferromagnetic transition was also studied by specific heat measurements. However, **2** shows an antiferromagnetic behaviour with a metamagnetic transition at low temperature. The comparative study of the magneto-structural correlations reveals that the magnetic interactions in **1** are propagated via pyrimidine molecules, while in **2** the unique magnetic exchange pathway is the one extended by the vanadate groups.

[1] Gómez-Romero P., Sanchez C., *"Functional Hybrid Materials"*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Alemania, 2004. [2] Hagrman P.J., Hagrman D., Zubieta J, *Angew. Chem. Int. Ed*, 1999, 38, 2638. [3] Larrea E. S., Doctoral thesis, *"New Transition Metal Hybrid Vanadates. Hydrothermal Synthesis, Structural Study and of their Spectroscopic and Magnetic Properties"*, Universidad del País Vasco (UPV/EHU), 2009. [4] Avtamonova N.V.,.Trunov V.K, Bezrukov I.Ya., *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, 1990, 26, 346.

Keywords: Organic inorganic hybrid materials, Magnetic properties, Structure-magnetism relationships.

FA4-MS33-P04

Magneto-Structural D-Correlations in Metal Complexes.

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Determination of the molecular and crystal structure by X-ray diffraction is an important step in the course of the characterization of new molecule-based magnetic materials. In addition to determination of molecular geometry, in some cases a detail analysis of the structural properties can give relevant information on different magnetic phenomena itself. For example, the correlation of the isotropic exchange coupling constant J with the bridging angle in dinuclear complexes is well-known [1]. However, the relationship between structural properties and single-ion magnetic anisotropy of metal complexes is also of a great interest. Nevertheless, such correlation has not yet been clearly formulated.

Unlike magneto-structural J-correlations, our new magneto-structural D-correlation interrelates the zero-field splitting parameter D withdrawn from the magnetic data with the structural tetragonality D_{str}. The possibility of correlating these parameters has been outlined gradually [2, 3].

The correlation allows to predict that negative zero-field splitting occurs for the tetragonally compressed nickel(II) complexes. Cobalt(II) complexes in octahedral ligand-field have high-spin ground state with a distinct spatial symmetry and thus such a correlation shows a substantially different structure-magnetism relationship. Mn(II)/(III) complexes and systems with angularly distorted chromophores have been also investigated.

[1] Gorun, S.M.; Lippard, S.J. *Inorg. Chem.* 1991, *30*, 1625. [2] Boča, R.; Titiš, J.; Magnetostructural D-correlations for Zero-Field Splitting in Nickel(II) Complexes, in *Coordination Chemistry Research Progress*. Nova, New York, 2008, 247. [3] Titiš, J.; Boča, R. *Inorg. Chem.* 2010, in press.

Keywords: metal complexes, magnetic anisotropy, magneto-structural correlations

FA4-MS33-P05

The structure of poly[di-μ_3-acesulfamato-O,O:O';O':,O,O-di-μ-acesulfamato-O,O;N-di-μ-aqua-dicalcium(II)]: a two dimensional coordination polymer.

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The crystal structure of the title compound, $C_{32}H_{40}Ca_4N_8O_{36}S_2$, determinated at 293 K. The structure contains Alkali Earth Metal, Ca, and acesulfam ring. The crystal that is two dimension coordination polymer contain three intramolecular hydrogen bonds, but no signification intermolecular hydrogen bonds. The structure consists of sheets in the bc plane. The crystal structure with acesulfam ring and Ca ion is first polymeric structure.

Keywords: Alkali Earth Metal, Acesulfam

FA4-MS33-P06

Non-triglyceride structuring of edible oils and emulsions.

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The structure of oil-continuous products, such as margarine or butter, is based on a network of small crystallites of triglycerides (also known as triacylglycerols or TAGs). Low molecular weight structuring agents that can serve as an alternative to crystallising triglycerides in edible oils have raised considerable interest in recent years. The requirement that potential structurants should at least hold the promise to be allowed in food applications is a severe limitation. Nevertheless, several systems have been identified [1], amongst which the class of γ-oryzanol + sterol organogelators is the most intriguing representative [2].