to the formation of dimeric arrangements through two Fe-S bonds between distorted square based $[Fe(S_2L)_2]^-$ units, $[Fe(S_2L)_2]_2^{2-}$. The first, and so far unique, exception to this rule was the n-Bu$_4$N [Fe(qdt)$_2$] complex[1], displaying a perfectly square planar coordination geometry and a S = 1/2 spin state.

The crystal structure of the new (BrBzPy)$_2$[Fe(qdt)$_2$]$_2$ 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 [Fe(qdt)$_2$] salts. The standard strong dimeric situation is also observed in the new [Fe(α-tpdt)$_2$]$_2$ salt with the same cation, as well as with the n-Bu$_4$N and Et$_4$N Cations.

[Fe(qdt)$_2$]$_2^{2-}$ [Fe(α-t
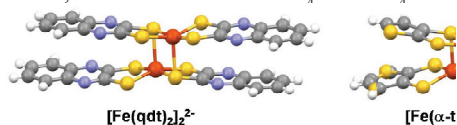
[1] Simão D., Ayllón J.A., Rabaça S., Figueira M.J., Santos. I.C., Henriques R. T. and M. Almeida, *CrystEngComm*, **2006**, 8, 658.

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.

[1] Hirasa M., Inagaki A., Akita M. J. *Organometallic Chem*. C50, **2007**, 93; [2] Ojala W.H., Sudbeck E.A., Lu L.K., Richardson T.I., Lovrien R.E., Gleason WB. *J A.C.S.* **1996**, 118, 2131; [3] Willner I., Eichen Y., Rabinovitz M., Hoffman R., Cohen S. *J.A.C.S.* **1992**, 114, 637.

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], Gaelle Ramon[a], Jana H. Taljaard[b]. *[a]Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa. [b]Sasol Technology, R&D, Klasie Havenga Road 1, Sasolburg, South Africa.*
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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 Clatrates in the System Ba-Ni-Ge. Umut Aydemir[a], Horst Borrmann[a], Cécile Hébert[b], Nguyên Thi 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 Ba$_8$Ge$_{46}$. Since a four-bonded framework Ge$_{46}$ 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 $\square$ in a framework Ge$_{46-x}\square_x$ is surrounded by four three-bonded Ge atoms $(3b)Ge^{1-}$. Hence, the 16 valence electrons from 8 Ba atoms would be completely compensated by four defects surrounded by 16 $(3b)Ge^{1-}$. Actually, instead of the expected composition Ba$_8$Ge$_{42}\square_4$, the binary clathrate was found to be Ba$_8$Ge$_{43}\square_3$ with 4 conduction electrons per formula unit [1]. Ternary type-I clathrates Ba – TM – Ge can be obtained with

transition metal elements TM = E8 – E10. In the system Ba – Ni – Ge, two homogeneity ranges with different Ni content are structurally characterized, which are both related to the clathrate-I structure. Compounds with low Ni content, $Ba_8Ni_xGe_{42\pm1}$ ($0 < x \leq 0.6$), can be considered as solution of Ni in the binary $Ba_8Ge_{43}\square_3$ (space group Ia–$3d$, a = 21.307(2) Å). The subcell with space group Pm–$3n$ is observed for the compositions $Ba_8Ni_xGe_{42\pm1}$ ($0.6 < x \leq 4.2$). The change in Ni content is associated with the respective change in lattice parameters (a = 10.657(1) - 10.681(1) Å), but also confirmed by microprobe analyses.

[1] Carrillo-Cabrera W., Budnyk S., Prots Y., Grin Yu., *Z. Anorg. Allg. Chem.*, **2004**, 630, 2267

Keywords: clathrate-I; defects; supercell

FA4-MS02-P28

Valence Tautomerism of a Novel Polymeric Mn(II) Species. <u>Francesco Caruso</u>[a], Elizabeth Chacon-Villalba[b], Miriam Rossi[c]. *[a]Istituto di Chimica Biomolecolare, CNR, Piazzale Aldo Moro 5, 00185, Rome, Italy. [b]CEQUINOR, U.N.L.P. La Plata 1900, Argentina. [c]Vassar College, Department of Chemistry, Poughkeepsie, NY, 12604-0484, USA.*
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$Mn(Lap)_2$, HLap = lapachol, is a polymeric compound showing extended conjugated double bonds, where the 3 O atoms of lapachol act in a novel way, two chelating one Mn and the 3rd generating a coordinative bond towards another metal unit. X-ray structure determinations at 125K, 197K and 300K describe the progressive trend of a Mn contribution to Mn-O1 bond length as a function of T. The Mn-O1 bond distance increases with temperature and may be therefore associated with a lapachol semiquinonate action at low T by the carbonyl O1 donor (and corresponding to Mn(III)). It transforms to a more classical coordinative bond at room T and stabilizes a Mn(II) species; this is a reversible phenomenon involving Mn(II)-Mn(III) oxidation states. A related UV-visible band shows in the near IR spectrum.
The extended network of mesomerism allows for potential transfer of charge through the whole crystal. There are few precedents of this phenomenon in the literature [1].

[1] AS. Attia, C. G. Pierpont, *Inorg. Chem.* **1998**, 37, 3051.

Keywords: Mn(II); valence tautomerism; electron transfer

FA4-MS02-P29

Structural Analysis, Magnetic Properties of the $Bi_2Sr_2Ca(Cu_{2-x}Co_x)O_{8+d}$ System. <u>N. Boussouf</u>[a], M. F. Mosbah[a], A. Amira[b], T. Guerfi[c]. *[a]Université Mentouri de Constantine, Laboratoire de Couches Minces et Interfaces, Campus de Chaabet-Erssas-25000 Constantine- Algérie. [b]Laboratoire des Essais Non Destructifs (LEND), Université de Jijel. B.P. 98, 18000 Jijel, Algeria. [c]Université de Boumerdes,*

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The effects of Co substitution on the structural and superconducting properties of the $Bi_2Sr_2Ca(Cu_{2-x}Co_x)O_{8+d}$ compound have been studied. as a function of doping concentrations. The $Bi_2Sr_2Ca(Cu_{2-x}Co_x)O_{8+d}$ samples were prepared by conventional solid state reaction method and characterized by X-ray diffraction (XRD), DC resistivity, AC susceptibility,. XRD investigations showed multiphase in the Co-substituted samples with slight reflection peaks of impurity and Bi2201 low-Tc (LTc) phase, these configurations suggest the insufficient ionic diffusion to form the superconducting crystals [1].The refinement result for XRD data shows that the a-axis expands, while the c-axis contract slightly with increasing of Co. The value Tc increased significantly with increasing the Co concentration in the system. The relation between Tc and the c-axis lattice parameter suggests that the change of Tc is correlated with a redistribution of holes between the Bi–O layers and the Cu–O planes [2].