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Keywords: MOFs, perovskites, structural analysis

MS24.P75

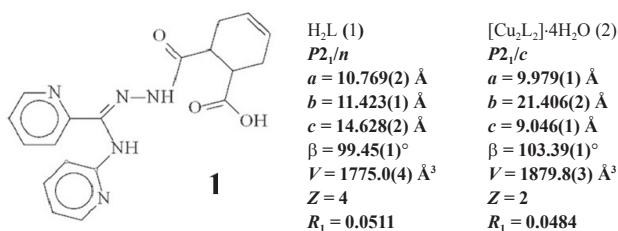
Acta Cryst. (2011) **A67**, C386

Novel amidrazone derivative and its Cu(II) complex: Crystal structure and antitumor activity

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Compounds with an open chain amidrazone system, N=C=N-N, (Scheme) constitute a unique group of ligands with their propensities to react with a wide range of transition metals in their neutral or ionic forms as well as diversity of their coordination modes [1]. Depending on the quality of the metal center and experimental conditions they can form mono-, bi- and poly-nuclear species. These properties make them useful in design and synthesis of novel functional materials. However, the most extensive studies of hydrazones are related to their pharmacological properties. It has been shown that some of them exhibit significant antibacterial and antitumor properties [2], [3].

X-ray diffraction analysis of 6-acetyl-cyclohex-3-enecarboxylic acid [1-pyridin-2-yl-1-(pyridin-2-ylamino)meth-(Z)-ylidene] hydrazide, H₂L, (1) and its copper(II) complex [Cu₂L₂]-4H₂O (2) has been carried out in order to elucidate the influence of coordination and amide protonation state on the geometry of the ligand.



Structural analysis shown that compound (1) exists in his amide-hydrazone form in the solid state. The central amidrazone moiety has a Z configuration with respect to the hydrazone C=N double bond. The N³-C²=N²-N¹-(C¹=O¹) chain, which adopts a cis,trans,cis conformation, is almost planar. All atoms of the acylamidrazone moiety may be regarded as sp² hybridized. Near-planarity of this unit may suggest a high level of π -electron delocalization. However, the X-ray data indicate, that there is a clear distinction between single and double bonds in this part of molecule.

The reaction of H₂L (1) with copper(II) acetate results in double deprotonation of the ligand, namely the carboxylic and amide groups. This induces considerable π -electron delocalization along the whole acylamidrazone system. Furthermore, the ligand configuration is found to be transferred from Z to E upon metal complexation. The elementary building units in crystal (2) are centrosymmetric binuclear species. Isomerization around the C=N bond allows the L²⁻ ions to chelate the Cu²⁺ ion through its pyridine-N, amide-O and imine-N

atoms. The carboxylate O atom from the adjacent, inversion-related ligand completes the square-planar donor arrangement around the metal center.

In cytotoxicity research, (2) shown a high in vitro cytotoxic properties against SW 948, CX-1 and A-431 cancer cell lines, whereas growth inhibition activity of the free ligand (1) was no significant.

This work was supported by the Polish Ministry of Science and Higher Education (project No. N204 546839).

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Keywords: amidrazone, copper complex, crystal structure

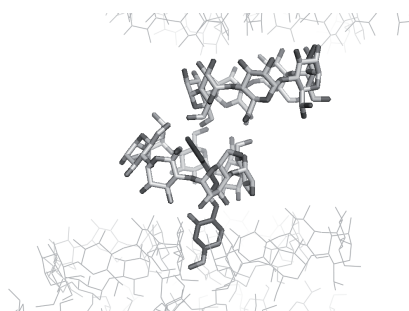
MS24.P76

Acta Cryst. (2011) **A67**, C386-C387

Molecular imprinting effect of the guest in β -cyclodextrin inclusion complexes

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Cyclodextrins (CDs) are well known, water soluble, cyclic oligosaccharides, which are used for micro encapsulation of organic molecules inside their relatively apolar cavity. β CD inclusion complexes of two Schiff bases (anils), derivatives of salicylideneaniline, changed the behaviour of the anils from thermo-chromic (as free crystalline compounds) to photochromic upon encapsulation [1]. Trials to grow single crystals of the β CD/anil complexes from absolute ethanol resulted in isomorphous crystals (P2₁, *a*=15.887(8), *b*=14.784(12), *c*=15.29.680 (14) Å, β =103.19(2)°, *Z*=2) exhibiting a novel packing, observed for the first time, accompanied by dramatic distortions of the β CD conformations. Refinement of both structures did not reveal the guest in a clearly detectable amount, the structures appearing as β CD-ethanol complexes. However, they differ also from any of the three known forms, I – III, of β CD/ethanol complexes [2]. The structures exhibit an open space at the secondary entrance of one of the host monomers, in which the hydrophilic salicylidene moiety of the guests can fit (Figure). It is proposed that the β CD/anil complexes were initially formed by inclusion of the hydrophobic-half of the guests inside the host cavity and the salicylidene part extending outside the entrance of the secondary face. Subsequently, the anils were solvolyzed thereby emptying the cavity and lattice. However due to the low solubility of β CD in ethanol, the formed crystals remained intact bearing the molecular imprint of the guest, whereas its place in the crystals has been taken eventually by ethanol molecules.



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Keywords: anils, cyclodextrin, molecular imprint

MS24.P77

Acta Cryst. (2011) **A67**, C387

Supramolecular study of μ -oxo iron(III) porphyrin malaria pigment model compounds

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Malaria is an infectious disease caused by the parasite *Plasmodium falciparum* invading red blood cells. Toxic free heme released by the parasitic destruction of hemoglobin is detoxified by conversion to malaria pigment. The μ -oxo TPP and OEP heme complexes have been studied as malaria pigment model systems [1]. The current study focuses on structure correlation of these and $[\text{Fe}(\text{PPIX})]_2(\mu\text{-O})$ in an effort to better understand the relationship between the spectra of malaria pigment and the μ -oxo heme complexes. The supramolecular interactions between propionate chains, C–H \cdots O and interplanar interactions, C–H $\cdots\pi$ in $[\text{Fe}(\text{PPIX}^*)]_2(\mu\text{-O})$ are observed. The tight H \cdots O interaction distances are 2.62(4) Å while the H $\cdots\pi$ distances are 2.84(5)–2.93(5) Å.

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Keywords: structure modeling, supramolecular structure, malaria pigment models

MS24.P78

Acta Cryst. (2011) **A67**, C387

Crystal structures of a series of bisazomethine dyes derived from 4-(Dimethylamino)-2-alkoxybenzaldehydes

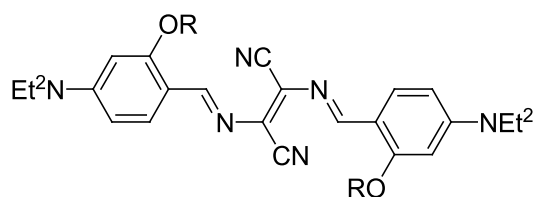
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Bisazomethine dyes derived from diaminomaleonitrile with aminobenzaldehydes are known as a potential dye forming J-aggregates in a solid state like vapour-deposited films [1–3]. We have synthesized a series of bisazomethine dyes based on alkoxy-substituted aminobenzaldehydes shown in the figure in order to investigate the effect of alkoxy-substitution (OR) of the phenyl rings in vapour-deposited films [4]. Here we report crystal structures of the eight bisazomethine dyes focusing on the effect of the substitution on their molecular arrangement in a crystalline state.

All the dyes were found to have their molecules π – π stacked in the two-dimensional (D) staircase molecular arrangements. Within the staircase stacking layer, molecules are stacked along the long

molecular axis with smaller slip angles than the critical angle of dipole-dipole interactions. This 2-D stacking layer is aligned along the short molecular axis to form 3-D crystal structure with spacing related to the length of the substituent R. The effect of R on their molecular arrangement in a crystalline state showed that the interlayer distance between adjacent 2-D stacking layers changed from 8.51 Å to 14.52 Å, when the length of the substituent is less than C10. These structural characteristics were interpreted by lattice energy calculations on the basis of the intermolecular interactions and crystal energies. The first and second energetic contributions to the lattice energy were given from a stacking molecular pair characterized by a large slip angle. In addition, stacking pairs having small slip angles were the third and fourth contributors. In **8**, however, the molecules are no longer stacked in the same manner as in the other dyes in which the specific molecular pair between their long alkyl chains of the alkoxy substituents gave the third and fourth energetic contributions.

In this dye system, the substituents on the phenyl rings can be used as practical parameters for spatial control between the 2-D stacking layers without significant changes in the stacking layer itself, when the length of R is less than C10.



1 R = C₆H₅CH₂, **2** R = C₆H₅, **3** R = C₂H₅, **4** R = C₃H₇,
5 R = C₅H₁₁, **6** R = C₇H₁₅, **7** R = C₈H₁₇, **8** R = C₁₀H₂₁

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Keywords: crystal engineering, organic dye, molecular aggregate

MS24.P79

Acta Cryst. (2011) **A67**, C387–C388

Crystallization of mixed ligand complexes of $M(\text{SO}_4)$ with picolinic acid and carboxylic acids ($M = \text{Mn}, \text{Zn}$)

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A variety of related metal complexes can be prepared from multifunctional ligands which are capable of monodentate and bidentate coordination. The ligands used in this study can also bridge metal atoms or form chelate rings leading to synthesis of new metal-picolinate-carboxylate compounds utilizing the several metal-picolinate binding modes [1]. The mixed ligand complexes prepared from $M(\text{II})$ sulfate ($M = \text{Mn}, \text{Zn}$) reacted sequentially with picolinic acid as a primary ligand (L1) and carboxylic acids (salicylic acid, phthalic acid and succinic acid) as a secondary ligand (L2). XRD of the crystalline products obtained from room temperature reaction of 1:1:1 (M :L1:L2) mole ratio showed that new compounds were formed. Composition of the crystals was characterized by elemental analysis, SEM/EDS microscopy, and