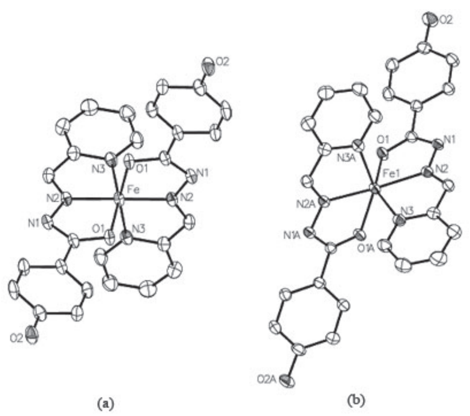
also carried out a detailed analysis of the crystal structures at different temperatures, where we found trapped HS and LS complexes or spin-crossover materials.

Additionally, this kind of complexes also shows a light induced excited spin state trapping (LIESST). The structural features of these excited states were also studied in the solid state by light irradiation at very low temperatures.



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Keywords: spin-crossover, Iron(II) complexes, LIESST

MS66.P22

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Extending the concept of half antiperovskites

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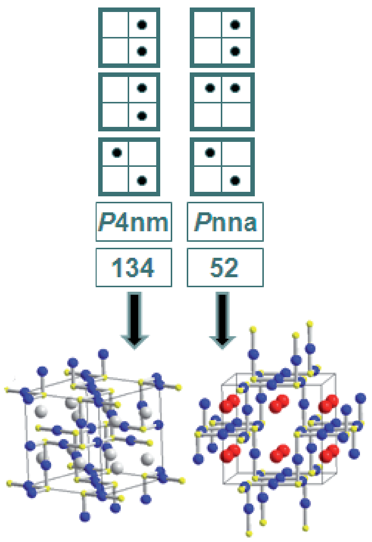
The concept of ordered half antiperovskites (*HAP*) $A_2M_3X_2$ was developed to describe crystal structures of thiometallates related to trigonal shandite ($Pb_2Ni_3S_2$), monoclinic parkerite ($Bi_2Ni_3S_2$), and cubic $Bi_2Pd_3S_2$ [1-4]. Furthermore, type-antitype relations to oxostannates(II) were found [1, 2]. The impact of *M* site ordering is found in structure-property relations of low dimensional magnetic $Sn_2Co_3S_2$ [3]. The highly anisotropic bonding was analysed for the isotypic Rh compounds and $Tl_2Ni_3S_2$ [5]. Recently, the appearance of superconductivity in parkerites could be related to the low dimensional crystal and electronic structures that is absent for cubic $Bi_2Pd_3S_2$ [6, 7]. From new investigations, novel structures are now presented that also fit the *HAP* scheme (see Fig. 1) including group-subgroup relations. In addition, the impact of *A* site ordering is addressed. The systematical approach is used to predict and identify stable and metastable ordering variants.



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Keywords: structure, ordering, subgroup

MS66.P23

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Phase and spin transition in the spin crossover compound $[Fe(dpp)_2(NCS)_2]$·py.

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Iron(II) spin crossover complexes [1, 2] show a transition between the $^5T_2$ (S=2) high-spin (HS) state and the $^1A_1$ (S=0) low-spin (LS) state on change of temperature, light irradiation, application of pressure or magnetic field. These compounds are interesting because of their potential for applications in molecular switching, memory storage and display devices.

The temperature dependence of the effective magnetic moment of the spin crossover complex $[Fe(dpp)_2(NCS)_2]$·py (dpp=dipyrido[3,2-a:2′,3′-c]phenazine, py=pyridine] shows abrupt transition from HS to LS state around 103 K on slow cooling and from LS to HS state around 163 K on heating [3, 4]. By rapid cooling, however, the HS state remains frozen in metastable state below 100 K.

The complex crystallises in the monoclinic P2/n space group with one guest pyridine molecule per iron complex and undergoes an isostructural phase transition near 100 K on cooling and around 155 K on heating. The space group does not change upon spin transition despite the occurrence of hysteresis with ca. 55 K width, which is clearly seen in the temperature dependence of the lattice parameters. Unfortunately, the X-ray single crystal measurements could be performed only down to 140 K, because the crystals cracked into many pieces during the spin transition. From the synchrotron powder measurements we see that the lattice parameters in the HS state differ drastically from those in the LS state. A significant decrease of the lattice parameters *a* (3.5%) and *c* (8.2%) and an increase of the lattice parameters *b* (13.9%) and *β* (4.3%) were observed between the two spin states when the sample was cooled down to 100 K and kept at this temperature. At the same time, however, the unit cell volume decreases only by 0.1%. The observation that the unit cell volume does not change despite the drastic changes of lattice parameters is not unusual for example in ferro-elasticity, but rather unusual in spin transition phenomena. A characteristic feature of spin transition is the change of the bond distance between iron and the donor atom of the ligands; the iron-to-donor atom distance is longer by ca. 20 pm in HS than in LS state. These different bond lengths induce changes of the HS and LS molecular volumes and usually the unit cell volumes. In the spin crossover compound under study only the volume of the octahedral ($Fe\text{-}N_6$) chromophor drastically decreases on HS to LS state transition. The strong intermolecular π-π interactions rather cause changes of molecular packing, but do not affect the unit cell volume. The thermal hysteresis is connected with changes of weak hydrogen bonds in HS and LS state [5].

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Keywords: iron(II), spin transition, phase transition

MS66.P24

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Novel Compounds Based on Malonate Derivatives and 4,4'-Azobispyridine.

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The assembly of inorganic coordination polymers, or metal-organic frameworks (MOFs), have been remarkably developed in recent years due to the combination of the efficience of their synthesis from relatively simple subunits and their potential applications in a wide variety of research fields. Moreover, this kind of complexes exhibits a vast range of supramolecular architectures with different dimensionalities – 1D, 2D and 3D.

The conformational flexibility of the aliphatic dicarboxylate type ligands is reflected in the diversity of their connecting modes and it is essential for the self-assembly processes. For the other hand, rigid rod-like spacer molecules like 4,4'-azopyridine (azpy) can be used to control topologically the resultant architectures because it can act as pillars between metallic ions to connect one-dimensional or two-dimensional networks, leading to robust structures of bigger dimensionality.

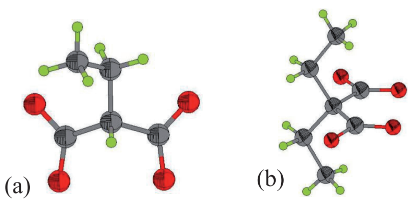

Figure 1. Aliphatic dicarboxylic acids used as bridging ligands in the different syntheses: (a) Ethylmalonic acid. (b) Diethylmalonic acid.

Here we present the synthesis, structural characterization and magnetic properties of a series of novel transition metal compounds based on dicarboxylic acids derived from the malonic acid (such as the ethylmalonic or diethylmalonic acids) and the 4,4'-azobispyridine as bridging ligands.

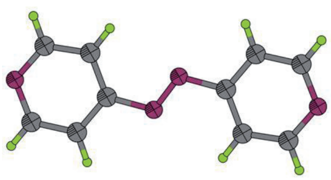

Figure 2. 4,4'-azobispyridine.

Keywords: Crystal Structure, Carboxylic acids, Metal-Organic Frameworks.

MS66.P25

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Influence of the substituent in the coordination chemistry of R-Malonates.

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Metal-organics frameworks (MOFs) exhibit fascinating structural topologies and potential applications as multifunctional materials, and this is the cause of the rapidly and increasing development of this kind of complexes in recent years.[1] The rational design of MOFs lies in an appropriate choice of the kind of metal ions and the number of coordination modes provided by the organic ligand, such as the rigidity or flexibility of the ligands used.

Polycarboxylic acids are well known due to their flexibility, which gives rise to a great variety of their connecting modes that lead from discrete entities to 3D networks,[2] so they constitute an important family of mutidentate-donor ligands. Specifically, malonic acid is widely used due to its excellent coordination ability. This ligand ocuppies one or two coordination positions of the coordination sphere, neutralizing positive charges of the metal ion. Moreover, modifying this acid, we can increase the degree of control over the intermolecular interactions and improve the structural and physic properties of these compounds.

In the context of molecular magnetism, on the other hand, the study of the magneto-structural correlations allow us to understand the structural and chemical factors that govern the exchange coupling between paramagnetic centres through multiatomic bridges.

We present herein the synthesis, structural characterization and magnetic properties of a series of new copper(II) compounds based on substituted malonate ligands, such as ethylmalonic or dimethylmalonic acid, emphasizing the role of the different intermolecular interactions present in the structures.

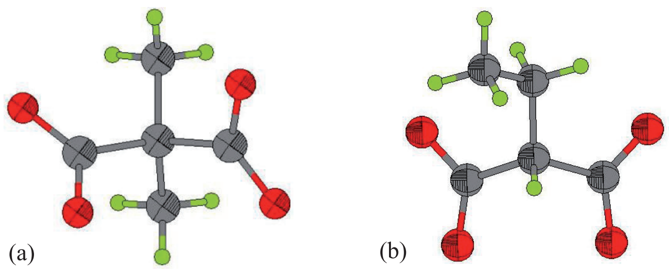

Figure 1. Some aliphatic dicarboxylic acids used as bridging ligands in the syntheses: (a) Dimethylmalonic acid. (b) Ethylmalonic acid.

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Keywords: copper, magnetism, dicarboxylic acids, intermolecular interactions, weak interactions, crystal packing.