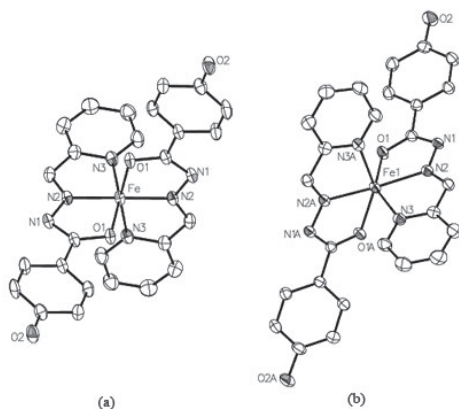


also carried out a detailed analysis of the crystal structures at different temperatures, where we found trapped HS and LS complexes or spin-crossover materials.

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

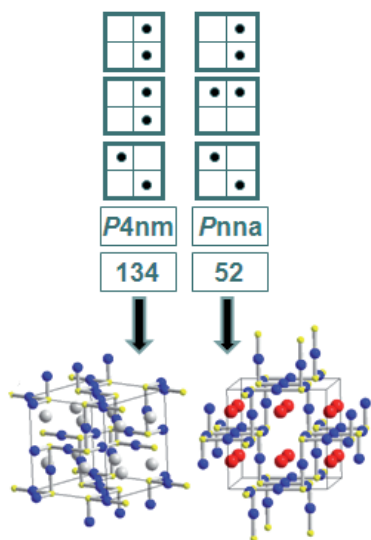
### MS66.P22

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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)<sub>2</sub>(NCS)<sub>2</sub>]<sub>2</sub>·py.

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Iron(II) spin crossover complexes [1, 2] show a transition between the <sup>5</sup>T<sub>2</sub> (S=2) high-spin (HS) state and the <sup>1</sup>A<sub>1</sub> (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)<sub>2</sub>(NCS)<sub>2</sub>]<sub>2</sub>·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-N<sub>6</sub>) chromophore drastically decreases on HS to LS state transition. The strong intermolecular  $\pi$ - $\pi$  interactions rather cause