

Poster Sessions

molecule. Each 2,2'-iminobenzoate unit is linking two Cu(II) ions in a bis-bidentate mode, and the phenantroline unit is acting as a blocking ligand. The unit cell parameters are: $a = 31.7600(5)$, $b = 9.8517(2)$, $c = 14.4899(3)$ Å, $\alpha = 90$, $\beta = 113.204(1)$, $\gamma = 90^\circ$, $V = 4167.00(14)$ Å³, space group C 2/c.

The magnetic properties of both compounds, namely the magnetization in function of the applied magnetic field and the susceptibility in function of the temperature will be presented and discussed.

Keywords: coordination compound, molecular magnetism, Cu(II) chain

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Effect of low Sr-Ba on the transport and magnetic behaviour of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

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The optimally doped composition ($x=0.33$) of the intermediate bandwidth manganite system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has been studied extensively since the observation of large negative magneto resistance and strong ferromagnetism [Jin.S et al 1994]. In this compound, the double-exchange mechanism (DE) and electron-lattice coupling are believed to play major role in the occurrence of phenomena such as Ferromagnetism (FM), insulator-metal transition and colossal magneto resistance [Millis.A.J et al1995]. It is known that the substitution of cations of different size for A-site ions (La^{3+} and Ca^{2+}) affects the unit cell structure and the corresponding changes in the distortion or rotation of MnO_6 octahedrons give rise to wide variety of electronic properties [Hwang.H.Y et al 1995]. The conduction bandwidth of e_g electrons of Mn ions for instance is known to be strongly affected by the average size of A-site cations. By increasing the value of the latter by substitution method, both the conductivity and the paramagnetic to ferromagnetic transition temperature (T_C) may be increased. In this context the electronic transport and the magnetic susceptibility properties of optimally doped compounds $\text{La}_{0.67}\text{Ca}_{0.25}\text{Sr}_{0.04}\text{Ba}_{0.04}\text{MnO}_3$ (LCSBMO) and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) synthesized under identical conditions are studied and compared. In the former composition, the average size of A-site ions has been increased lightly by simultaneous substitution of small percentage of large size ions such as Sr^{2+} and Ba^{2+} for Ca^{2+} ions. The focus of this work has been to study the effect of this low level substitution on the structural, microstructure, electronic transport and magnetic susceptibility properties of this widely studied LCMO. The electrical parameters which arise out of the fitting of standard models with resistivity data for $T < T_{\text{MI}}$ and $T > T_{\text{MI}}$ are compared and discussed in the above context apart from the paramagnetic to ferromagnetic transition temperatures (T_C)

Keywords: electronic transport, magnetic measurements, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

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Classification of stacking interaction geometries of terpyridyl complexes

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Stacking interactions of terpyridyl square-planar complexes in crystal structures were studied analyzing data from the Cambridge Structural Database. In most of the crystal structures, two terpyridyl complexes were oriented “head-to-tail” or “head-to-head”, with “head-to-tail orientation” being most prevalent. The number of structures with other orientations was very small. Based on the analysis of interacting geometries, we classified overlaps of terpyridyl complexes into six types. The types were defined by values of several geometrical parameters and all interactions of the same type had very similar overlap patterns. Stacking interactions of aromatic nitrogen-containing ligands were geometrically analyzed in crystal structures of metal complexes. The results show that nitrogen-containing aromatic rings usually form an offset (or parallel-displaced) stacking interactions. A terpyridine (2,2';6',2''-terpyridine) molecule coordinating to a metal ion forms a large planar system of five rings, three pyridine fragments and two chelate rings. This planar system has propensity to form stacking interactions. Stacking interactions between terpyridyl complexes were observed in crystal structures and in solution. Recent review papers present interesting properties of terpyridyl complexes from luminescence to biological activity. Propensity for stacking interactions is important for using these complexes in biochemistry, supramolecular and medicinal chemistry [1].

[1] G. Janjic, J. Andric, A. Kapor, Z.D. Bugarčić, S.D. Zarić, *CrystEngComm*, **2010**, *12*, 3773-3777.

Keywords: stacking, CSD, terpyridine

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Structural Studies of N_4O_2 Iron(II) Spin Crossover Complexes

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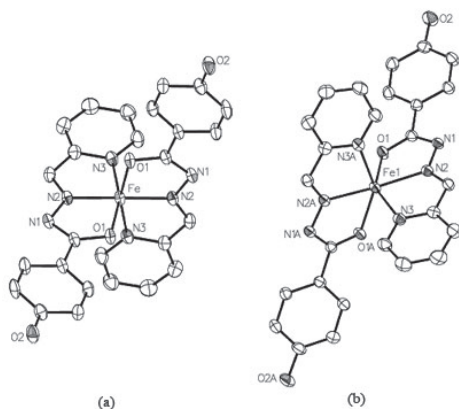
Spin crossover (SCO) materials are molecular compounds switchable between a diamagnetic low-spin state (LS), which is stable at low temperatures and a paramagnetic high-spin state (HS), which is stable at higher temperatures. In general, the switching process in solid-state systems is controlled by cooperative intermolecular interactions. The correlation of structure with physical properties is crucial to the identification of these interactions and ultimately the understanding of the complex processes that control the SCO phenomenon.

We have carried out the syntheses and crystal structure analyses of iron(II) complexes with N_4O_2 coordination spheres using the tridentate Schiff base ligand, 4-hydroxy-N'-((pyridin-2-yl)-methylene)-benzohydrazide (HL) previously reported by Zhang *et al.* [1] In the mononuclear complex FeL_2 the average bond lengths Fe-N and Fe-O are 0.25 and 0.14 Å shorter in the low-spin state compared with the high spin state. These variations allowed us to characterise the spin states of other N_4O_2 iron(II) complexes under different environmental conditions.

We have synthesised the mononuclear complexes FeL_2 in methanol, ethanol, isopropanol and butanol to obtain different solvates. The crystals obtained from these reactions exhibit different spin states at room temperature indicating the importance of the crystal packing for the SCO phenomena. The figure shows the differences between (a) the structure of $\text{FeL}_2 \cdot \text{EtOH}$ (LS) and (b) $\text{FeL}_2 \cdot 2\text{H}_2\text{O} \cdot \text{PrOH}$ (HS). We have

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.



[1] L. Zhang, G.-C. Xu, H.-B. Xu, T. Zhang, Z.-M. Wang, M. Yuan, S. Gao, *Chemical communications* **2010**, 46, 2554-6.

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

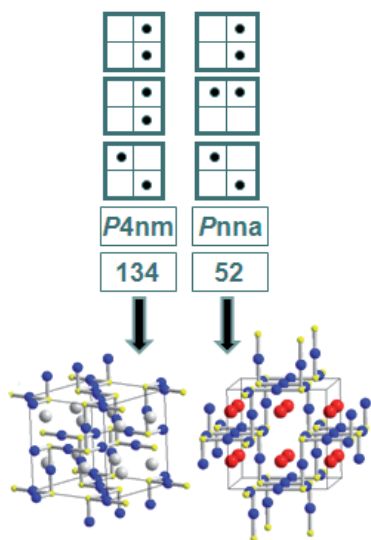
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Extending the concept of half antiperovskites

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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.

[1] R. Wehrich, I. Anusca, M. Zabel, *Zeitschrift für Anorganische und Allgemeine Chemie* **2005**, 631, 1463-1470. [2] R. Wehrich, I. Anusca, *Zeitschrift für Anorganische und Allgemeine Chemie* **2006**, 632, 335-342. [3] R. Wehrich, I. Anusca, *Zeitschrift für Anorganische und Allgemeine Chemie* **2006**, 632, 1531-1537. [4] R. Wehrich et al., *Progress in Solid State Chemistry* **2007**, 35, 309-327. [5] F. Bachhuber, I. Anusca, J. Rothbaler, F. Pielnhöfer, P. Peter, R. Wehrich, *Solid State Science* **2011**, 13, 337-343. [6] S. Seidlmeier, F. Bachhuber, I. Anusca, J. Rothbaler, M. Bräu, P. Peter, *Zeitschrift für Kristallographie* **2010**, 225, 371-381. [7] R. Wehrich, S.F. Matar, I. Anusca, F. Pielnhöfer, P. Peter, F. Bachhuber, V. Eyert, *Journal of Solid State Chemistry* **2011**, 184, 797-804.

Keywords: structure, ordering, subgroup

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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 ⁵T₂ (S=2) high-spin (HS) state and the ¹A₁ (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-N₆) chromophore drastically decreases on HS to LS state transition. The strong intermolecular π-π interactions rather cause