of natural bond orbitals (NBO). This method can only be applied to the wavefunction obtained by either HF or Kohn-Sham DFT methods.

However, it has been shown that R.F.W. Bader's quantum theory of atoms in molecules (QTAIM) can be also used for such analysis. The computational works by R. Mosquera [3] have shown that the SEIs lead to changes in integrated QTAIM charges and energies of participating atoms. We have rationalized these data and developed a universal approach to analysis of SEIs by QTAIM methods: we have shown that the lp-X-C-Y interaction leads to decrease of charge and energy for X and Y atoms and to increase of both for carbon atom [2]. As our method is based on QTAIM, it can be applied to both experimental and calculated charge density.

We have shown the applicability of our approach for interpretation of SEI in organic compounds of different classes including saturated thioorganic heterocycles containing N—C—S fragment, glucose anhydrides (O—C—O), organic cyanides, azides and triazoles (N—C—FG, where FG is a multi-atom group) and tight ionic pairs N=C^+…I^- (as an extreme case of SEI). We have managed to separate the effects of SEI and lp repulsion on the conformational preferences of the thioheterocycles, systematically investigated by high-resolution XRD experiments and a number of quantum-chemistry calculations. Furthermore, the results obtained for N—C—FG allow for a deep insight into the nature of SEI, showing that the complex groups participate in such interactions as a whole, rather than by their terminal atom, as the results of NBO analysis suggest. For the N=C^+…I^- system we have studied the strength of residual C…I binding and demonstrated the inconsistency of the NBO data [4]. Overall, our approach has been shown to complement traditional NBO analysis in all cases and for some compounds it has produced additional information about the presence and nature of intramolecular interactions.

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Keywords: charge, density, energy

MS34.P05

Electron density topology and interaction energy in hydrogen bonded systems

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The existence of empirical dependencies between electron density properties at the hydrogen bond critical point (HBCP) and bonding distance in H⋯O hydrogen bonds was demonstrated from a large compilation of HB topological data in experimental charge density studies [1]. These dependencies agree with those derived from theoretical calculations on a large set of hydrogen bonded complexes in gas phase [2]. Moreover, calculations show that H⋯A interactions can be classified into families according to the acceptor A, each family being characterized by a set of these dependencies with the bonding distance.

An in depth theoretical study of one of these families (A = F) is being undertaken in order to understand the dependency of the electron density properties with the interaction energy E_i, such as the

phenomenological relationships observed between E_i and the potential energy density at HBCP, which was established from a combination of theoretical and experimental data [3]. Hydrogen bonded dimers under an external electric field that emulates a polarizing environment (for example a crystal environment) are being used as case examples [4].

In the picture of the HB arising from this study, performed in the framework of the Quantum Theory of Atoms in Molecules (QTAIM) [5], interaction energy and equilibrium distance are given by the balance between a stabilizing contribution, mostly related to the mutual polarization of donor and acceptor, and a destabilizing contribution associated to the early steps of the transformation of the HB into a chemical bond. The environment of the interaction, represented by the substituents and the external electric field, tunes the interaction energy as well as the properties at HBCP, giving rise to the aforementioned dependencies between these quantities [6]. The scattering of values around the average dependencies can be explained by the complexity of the environment effects. As this scattering is smaller, the property is better suited for the estimation of the HB energy from the electron density.

From this analysis, the curvature along the HB at the HBCP is better estimator of the HB energy than the potential energy density. The exponential dependency of this curvature with the HB energy spans from very weak to very strong interactions and presents small scattering of values in the theoretical case. In the experimental case, this property presents smaller experimental error than the laplacian, which is in principle an excellent estimator for medium and strong HB.

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TOPAZ – neutrons going smaller

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Supramolecular chemistry is the foundation for the design and development of materials with potential applications reaching from catalysis to gas storage. Understanding intermolecular interaction is crucial for these systems, and hence the precise determination of atomic positions, especially hydrogen, is important. The model compounds for the present studies are hydroquinone host-guest systems, $3C_6H_4(OH)_2 \cdot xS$, with S being the enclathrated solvent.[1]

Single crystal neutron experiments have until recently required a large sample (several cubic millimeters), which for some materials is unattainable. The immense power of the Spallation Neutron Source is utilized at the TOPAZ instrument to study single crystalline samples of sub-millimeter size, and thereby accessing a regime that so far has been unexplored. The goal is to be able to study the exact same crystal using a neutron source as used on the home X-ray source.

The first results from the TOPAZ instrument are promising, as

measurements on a non-deuterated hydroquinone clathrate sample have shown high quality positional and thermal parameters. The obtained atomic displacement parameters are investigated and compared with data from the same compound at the High Flux Isotope Reactor and an X-ray source.

The obtained positional and thermal parameters from the neutron experiment are used in combination with high quality X-ray data for a state-of-the-art charge density refinement. The investigation of these hydroquinone host-guest systems revealed significant charge redistribution of the host structure with the so-called weakly interacting guest solvent molecule.

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Comparative study of the electron distribution in *3d*-orbitals

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In tetrakis(μ_2-Acetato)-diaqua-di-copper(II) complex for the coordinated Cu central atom only Cu-O bonds in the equatorial plane form the coordination bonds [1,2]. Contrary to very small apical Cu-O bond distance of 2.1443(1) Å, this interaction is not a coordination bond. Fully populated d_{z^2} orbital (2.019(5) e) is pointing directly to O(5) atom and accordingly the oxygen O(5) lone electron pair is repelling. The value of the O(5)-Cu-Cu* angle is 173.977(4)°.

Comparing similar crystal structures we have found the crystal structure of Diaqua-bis(2,7-dimethyl-5-oxo-5H-pyrano(4,3-B)pyran-1-ium-4-oxalato-O,O')-copper(II) diperchlorate (YUSNIK) [3] in which the axial Cu-O(5) distance is also very short (2.160 Å), but the O(5)-Cu-O(5)* angle is exactly 180° according to the symmetry. Preliminary B3LYP/G311G* quantum-chemical calcul-ations show highly unusual order of *d*-orbitals on the hexacoordinated central Cu atom.

In order to explain the electronic structure in YUSNIK the electronic structure study was undertaken.

The GEMINI R diffraction data at 100K will be used for electronic structure study. As the space group is a monoclinic (P 2_1/n) and the whole diffraction sphere was measured, a high redundancy was established. The multipole refinement and the results of both experimental and theoretical topological analysis will be discussed.

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MS34.P08

Electron density studies of magnetic di-nuclear complexes,

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In the aim to rationalise the conception of single molecular magnets the first step is to explore the interactions in molecular magnetic complexes and to understand their role. To this end we modeled the experimental electron density distributions in di-nuclear complexes. For example, we studied a cobalt(II) compound ($[Co2(sym-hmp)_2](BPh_4)_2$) which was theoretically studied by Tone *et al.* in 2007[1]. When decreasing the temperature, the magnetic susceptibility of this complex deviates from the Curie law (Fig. 1) because of the anti-ferromagnetic exchange interaction, but the susceptibility increases sharply at low temperature (< 20K). The theoretical analysis of Tone *et al.* showed that this behavior is explained by a tilt of local distortion axes around cobalt atoms and not by a paramagnetic impurity. A polarized neutron diffraction experiment was carried out in order to model the spin density and verify this hypothesis (Borta *et al.* (2011), accepted in Phys. Rev. B.)

To support this electronical approach and to better describe the metal-ligand interactions, we determined the charge density of this complex using high resolution X-ray diffraction at 100 K. We will present our multipolar model[2] and its description using various tools (Fig. 2). The different interactions will be described and comparison will be made with spin density results from polarized neutron diffraction experiments. We will finally introduce our project of a new program for joint refinements of a unique electronic model based on X-rays and polarized neutrons diffraction data.
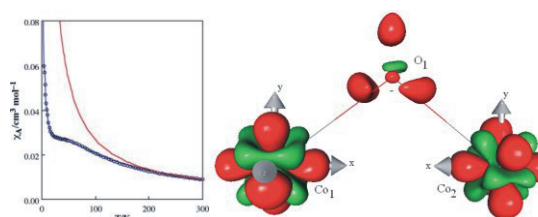

Fig.1. (left) Temperature dependencies of χ_A (O) at 100K.
Fig.2. Electron deformation density around each Co atom.

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MS34.P09

Charge density analysis of K_2SO_4

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