

MS23-O5 Charge density of the semiquinone radical anionKrešimir Molčanov¹, Christian Jelsch², Emmanuel Wenger², Vladimir Stilinović³, Biserka Kojić-Prodić¹

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Semiquinones are a class of stable organic radical anions; especially stable are ones with four electronegative substituents such as halogens, which enhance delocalisation of the unpaired electron. Therefore, they are potential candidates for design of functional materials with fine-tuned magnetic properties.

Here we present a detailed study of electron density and delocalisation in two polymorphs of N-methylpyridinium (N-MePy) salt of tetrachlorosemiquinone (CA) radical anion (N-MePy·CA), which are especially interesting due to their stability and semiconductivity [1]. In the diamagnetic polymorph closely bound radical dimers occur, similar to previously known K·CA·Me₂CO [2] and similar alkali salts of 5,6-dichloro-2,3-dicyanosemiquinone (DDQ) [3], and the crystals are diamagnetic due to spin pairing. In the orthorhombic polymorph radicals are equidistant, leading to 1D antiferromagnetic coupling between the spins.

Electronic delocalisation in the semiquinones is particularly interesting because it is somewhere between aromatic (fully delocalised π electrons) and quinoid (distinguishable single and double bonds), as confirmed by previous crystallographic [2,3] and computational studies. However, exact bond orders of C-C and C-O bonds have not yet been experimentally determined. Also, study of charge density reveals subtle differences between diamagnetic (triclinic) and antiferromagnetic (orthorhombic) phases, which will enable more insight into the phenomenon of magnetic exchange between organic molecules.

This is the first experimental study of electronic structure of ionic semiquinones and is complemented by periodic DFT studies.

[1] K. Molčanov, V. Stilinović, N. Maltar-Strmečki, A. Šantić, B. Kojić-Prodić, D. Pajić, L. Androš Dubraja, presentation on the ECM29 (Rovinj, Croatia, 2015), *Acta Crystallogr. A*, **A71**, s136.

[2] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Žilić, B. Rakvin, *CrystEngComm*, **13** (2011), 5170.

[3] K. Molčanov, D. Babić, B. Kojić-Prodić, J. Stare, N. Maltar-Strmečki, L. Androš, *Acta Crystallogr. B*, **70** (2014), 181.

Keywords: semiquinone radical, charge density, spin coupling, electron delocalisation

MS24 Inorganic and metal-organic magnetic structures

Chairs: Georg Eickerling, Dominik Schaniel

MS24-O1 Elucidating the magnetic behaviour of a unique linear Fe(I)-complex using the electron densityJacob Overgaard¹, Maja K. Thomsen¹, Phil Bunting², James P.S. Walsh^{1,3}, Jeffrey R. Long²

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Single-molecule magnets (SMM) are able to preserve an induced magnetization after external magnetic field, but in contrast to the domains that explain magnetism in bulk ferromagnets, in SMMs this has a purely molecular origin. Such tiny magnets are naturally in high demand as they have potential technological applications in e.g. spin-based electronics. Lanthanide-based SMMs offer promising candidates for this purpose.¹ However, cheap and earth-abundant metals such as iron are obviously desirable alternatives to lanthanide-based materials. The SMM behaviour is due to a bi-stable magnetic ground state ($\pm M_{J_{\text{eff}}}$) in which the two levels are separated by an energy barrier, thus a barrier hindering magnetic relaxation. The presence of such a barrier is due to molecular magnetic anisotropy, which for a transition metal complex can be tuned through variation of the ligand field. The premier mononuclear transition metal-based SMM so far discovered took combines two unusual features of an iron complex, namely two-coordinate Fe(I),² $[\text{Fe}(\text{C}(\text{SiMe}_3)_2)]^+$ (Figure 1). This complex has a record high effective relaxation barrier ($U = 226(4) \text{ cm}^{-1}$). Based on *ab initio* calculations the authors found that the low coordination number and the low oxidation state result in a very weak ligand field and also find that the d_{z^2} -orbital is lower in energy than the other d -orbitals. This is unexpected from a basic crystal field theory viewpoint. We have therefore derived the experimental electron density of this compound, as well as its di-valent analogue, and in this presentation we use these densities to discuss and assess the molecular magnetic properties.

[1] See, for example: Meihaus, K. R. and Long, J. R., *J. Amer. Chem. Soc.*, **2013**, *135*, 17952–17957.

[2] Zadrozny, J. M., Xiao, D. J., Atanasov, M., Long, G. J., Grandjean, F., Neese, F., Long, J. R., *Nature Chem.*, **2013**, *5*, 577–581.

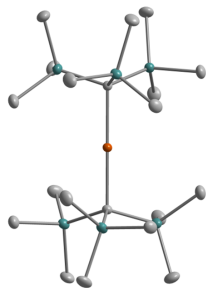


Figure 1. ORTEP drawing of the $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)]^-$ anion at 100 K. Atoms are depicted as 50 % probability ellipsoids. Orange, petrol blue and grey refer to iron, silicon and carbon, respectively. Hydrogen atoms have been omitted for clarity.

Keywords: Electron density, single molecule magnet, synchrotron radiation, topological analysis

MS24-O2 Spin, charge and momentum densities of YTiO_3 perovskite

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High resolution X-ray (XRD) and polarized neutron diffractions (PND) are routinely used to model charge and spin densities of localized electrons, while inelastic Compton scattering (ICS) is a valuable mean for determining delocalized electrons. Our objective is to construct a unique electron density model common to these three experimental data sets. We have demonstrated that a joint refinement of a multipolar model based on polarized neutron and X-ray diffraction data is possible and brings more insight in the electron distribution [1]. The inclusion of ICS data implies to go beyond the atom centered model to take into account bicentric terms. As the multipolar model is thus no more adapted, a new model based on atomic orbitals under development will be discussed and applied to a YTiO_3 perovskite crystal. This compound is ferromagnetic at low temperature (below 29K), suggesting that a single d electron (0.84mB/mol) mainly localized on the Ti atom gives rise to the magnetic interactions.

Reference 1. "First spin-resolved electron distributions in crystals from combined polarized neutron and X-ray diffraction experiments". Maxime Deutsch, Béatrice Gillon, Nicolas Claiser, Jean-Michel Gillet, Claude Lecomte, and Mohamed Souhassou, *IUCrJ*. 2014 May 1; 1(Pt 3): 194–199.

Keywords: charge spin densities , xray diffraction, polarised neutron diffraction, magnetic compton scattering, joint refinement, magnetic materials