[MS34-P04] Crystal engineering of molecular magnets based on dichlorodicyanosemiquinone radical.

Biserka Kojić-Prodić, Krešimir Molčanov, Nadica Maltar-Strmečki and Lidija Androš

Rudjer Bošković Institute, POB-180, HR-10002 Zagreb, Croatia
E-mail: kojic@irb.hr

Due to their unique magnetic and conducting properties, organic radicals have recently become interesting in design of functional materials [1]. Semiquinones are an especially promising class of radicals, both due to their stability and similarity with biologically active molecules [2-5]. Quinones with four electronegative substituents are known to form stable semiquinone anion radicals. Tetrachloro- and tetrabromosemiquinone radicals are especially stable; their alkali salts can be crystallised and their crystal structure were determined by X-ray structure analysis [4,5]. Due to a close contact between the radical rings, electron spins may be coupled. Thus, crystal engineering can be used to control the separation distance between the radical anions changing their magnetic properties. Critical distance for spin coupling is about 3.30 Å. We have already prepared diamagnetic [4] and antiferromagnetic [5] compounds, and a salt which undergoes a temperature-dependent magnetic phase transition: the low-temperature phase (100 K) is diamagnetic, while the high-temperature phase (200 K) is paramagnetic-like [5]. Nitrile substituents are more electronegative than halogens, so they influence electron density of the (semi)quinoid ring much more, rendering the semiquinone radical more stable. They are also sterically larger and better proton acceptors. Three novel alkali salts of 5,6-dichloro-2,3-dicyanosemiquinone radical ($DDQ^{\cdot}$) were prepared and characterised. They crystallise as hydrates: $LiDDQ \cdot 2H_2O \cdot (CH_3)_2CO$, $RbDDQ \cdot 2H_2O$ i $CsDDQ \cdot 2H_2O$. In their crystal structures closely interacting radical dimers are observed, with interplanar separation shorter than 2.9 Å. These dimers are stacked by weak π-interactions with interplanar distances longer than 3.5 Å. EPR spectroscopic study of single crystals and polycrystalline samples revealed diamagnetic coupling of the dimers. To get more insight into a nature of electron interactions and charge redistribution the research has been extended to IR spectroscopy method. An assignment of the spectra was assisted by by quantum chemical calculations. The three novel semiquinoid salts are unexpectedly stable in air, allowing X-ray measurements at 150 K and room temperature. Thermal decomposition using TG/DTA method revealed degradation in air at temperatures above 473 K.

[1] I. Ratera, J. Veciana, *Chem. Soc. Rev.*, **41** (2012), 303-349.
[2] S. V. Rosokha, J. Lu , T. Y. Rosokha and J. K. Kochi, Phys. Chem. Chem. Phys., 2009, 11, 324–332.
[3] K. Molčanov, B. Kojić-Prodić, M. Roboz, *Acta Cryst. B*, **B62** (2006), 1051-1060.
[4] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Žilić, B. Rakvin, *CrystEngComm*, **13** (2011), 5170-5178.
[5] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Pajić, N. Novosel, K. Zadro, *CrystEngComm*, **14** (2012), 79587964.

Keywords: radical anion salts, magnetic properties, spin coupling, FTIR spectroscopy, electron paramagnetic resonance, magnetic exchange, molecular magnetism