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Study of electronic structure of tetrakis(μ_2 -Acetato)-diaqua-di-copper(II) complex

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The nature of Cu-Cu interaction in tetrakis(μ_2 -Acetato)-diaqua-di-copper(ii) complex has been studied by both experimental and theoretical treatments. A large experimental data set (CCD GEMINI R diffractometer, 387268 diffractions at 100 K, resolution of 0.39 Å, an average redundancy of 30.6) was measured. The data reduction (*CrysAlis* [1]) gives a unique 12674 diffractions ($R_{int} = 0.026$, $R(\sigma) = 0.006$). Refinement with the XD package [2] gives $R\{F\} = 0.0187$. In order to identify the systematic errors in the experimental data sets of structure factors, the new procedure for obtaining the theoretical structure factors at 100 K from the theoretical grid electron density has been developed. The electron density at grid points is evaluated by CRYSTAL06 software for periodic quantum-chemical calculations at B3LYP level of theory [3]. The distance between the discrete grid point and the closest particular atom is used as a criterion for assigning the temperature factor to each grid point. The procedure developed might enable us to obtain spin density distribution, too.

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Keywords: charge density, spin density, magnetic properties

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Estimation of optical properties from wavefunction fitting of X-ray diffraction data

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In general, the crystallography of important nonlinear optical (NLO) materials is not well described and much remains to be done to characterize their relevant properties (electric and optical) in the solid state. This encouraged us to perform the detailed charge density studies on a series of organic molecular crystals with known

NLO properties. The materials of interest are 2-(N-prolinol)-5-nitropyridine (PNP), N-(4-nitrophenyl)-L-prolinol (NPP) and 3-methyl 4-nitropyridine N-oxide (POM), which have very high second order NLO coefficients. Charge density analyses have already been reported for NPP [1] and POM [2], but we are revisiting these materials, along with PNP, to critically test a number of novel approaches to the estimation of linear and nonlinear optical properties using constrained wavefunctions fitted to the X-ray diffraction data [3]. Charge density analyses are based on X-ray diffraction data collected on an Oxford Diffraction Xcalibur S instrument at 100 K. Hydrogen atom ADPs are estimated using a recently described SHADE2 procedure [4]. Results presented will include conventional multipole refinements, details of wavefunction fitting, estimates of the zero-frequency dipole polarisability tensors for the molecules and crystal refractive indices, and molecular first hyperpolarisability tensors. Critical comparison of the estimated results with independent experimental data will be made where possible.

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Magnetic interactions in thiazyl-based magnets: The role of the charge and spin densities

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The crystal structure of the organic radical p-O₂NC₆F₄CN₂SSN was determined at 20 K through a single-crystal neutron-diffraction experiment. It crystallises in the tetragonal space group *P4₁2₁2*, unchanged from a previous single-crystal X-ray diffraction experiment at 220 K although there are some changes in molecular geometry and intermolecular contacts arising from the contraction of the unit cell. Polarized neutron diffraction at 1.5 K revealed that the spin distribution is predominantly localised on the N and S atoms of the heterocyclic ring with a small negative spin density on the heterocyclic C atom. Spin populations determined using a multipolar analysis were -0.06, +0.25 and +0.28 on the C, N and S sites, respectively. These spin populations are in excellent agreement with both ab-initio DFT calculations (spin populations on the C, N and S sites of -0.07, 0.22 and 0.31, respectively) and cw-EPR studies which estimated the spin population on the N site as 0.24. The DFT calculated spin density revealed less than 1% spin delocalisation onto the perfluoroaryl ring, several orders of magnitude lower than the density on the heterocyclic ring. cw-ENDOR studies at both X-band (9 GHz) and Q-band (34 GHz) frequencies probed the spin populations at the two chemically distinct F atoms. These spin populations on the F atoms ortho and meta to the dithiadiazolyl ring are of magnitude 10⁻³ and 10⁻⁴ respectively. Additional high-