

CRYSTAL STRUCTURE OF COBALT-BASED CHAIN MOLECULAR MAGNET CoCu(opba)(DMSO)₃ AT ROOM TEMPERATURE AND 100 K

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Since the discovery in 1986 of the first molecular-based magnets exhibiting a spontaneous magnetization below a critical temperature T_c there has been a rapid development within this field of research. In this work we report a structural study of the Co-based chain molecular magnet CoCu(opba)(DMSO)₃. Here opba stands for orthophenylene-bis-oximate and DMSO stands for dimethyl-sulfoxide. Three consecutive single crystal X-ray experiments (Enraf-Nonius Kappa-CCD) were performed using the same crystal: 1) at room temperature; 2) at 100 K; and 3) at room temperature after the freezing and heating (steps 1 and 2). A same orthorhombic unit cell was obtained for all measurements. Nevertheless, different space groups were found to the low and high temperature structures. The room temperature data 1 and 2 were solved in the space Group *Pnam* (phase A). The low temperature structure was solved in *Pna2*₁ (phase B). In spite of the unit cell being unchanged, this compound surprisingly shows a temperature-dependent reversible phase transition. In both phases, the structure consists of linearly ordered bimetallic chains with the Cu(opba)₂ unit tied by the Co²⁺ forming a one-dimensional system along the b axis. In the phase A the DMSO molecules, which are co-ordinated to either metallic cations Cu and Co, are disordered. On the other hand, no disorder take place in the low temperature phase A. Therefore, our results show that DMSO ordering plays an important role in the low phase transition observed for this compound. Temperature dependent magnetization curves will be performed in order to determinate the phase transition temperature.

Keywords: MOLECULAR MAGNETS COCU(OPBA)(DMSO)₃ PHASE TRANSITION

ELECTRON DELOCALIZATION IN ACYCLIC AND N-HETEROCYCLIC CARBENES AND THEIR COMPLEXES: A COMBINED EXPERIMENTAL AND THEORETICAL CHARGE DENSITY STUDY

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Organometallic carbene complexes play an increasingly important role as intermediates in homogeneous catalysis in reactions such as alkene metathesis, Fischer-Tropsch synthesis, alkene and alkyne polymerization and cyclopropanation. Recently, N-heterocyclic carbenes have been used to complement and extend the capabilities of the ubiquitous phosphane ligands. Much of the interest in N-heterocyclic carbenes derives from the advantages they impute as ligands in organometallic catalysts, where they broaden the scope of applications reached by phosphanes. Combined experimental and theoretical charge-density studies on free and metal-coordinated N-heterocyclic carbenes have been performed to investigate the extent of electron delocalization in these remarkable species. Tracing the orientation of the major axis of the bond ellipticity (the least negative curvature in the electron density distribution) along the complete bond paths distinguishes unambiguously between fully delocalized systems and those with interrupted cyclic electron delocalization. Evaluation of charge density based properties such as atomic quadrupole moments serves as a direct and quantitative measure of the extent of π -electron delocalization, and reveals consistency between theory and experiment. A detailed topological analysis of theoretical charge densities for two benchmark carbene systems, viz. 1,2-dimethylpyrazol-3-ylidene 1a and 1,3-dimethylimidazol-2-ylidene 2a, and their corresponding stable chromium pentacarbonyl complexes 1 and 2 highlights the advantages of charge-density based criteria to analyze such complex electronic situations. We found that 2a should display significant aromaticity, whilst 1a should enjoy no such stabilization; yet nearly identical $p(\pi)$ occupations at the carbene center are computed for 1a and 2a. However, evaluation of atomic quadrupoles Q_{zz} - as the density analog to $p(\pi)$ occupation - reveals faithfully the electronic differences in 1a and 2a and demonstrates the sensitivity of charge density-based properties to the bonding situation. The acyclic aminocarbene (iPr₂N)₂CCr(CO)₄ has also been studied, and the high barrier to rotation about the C-N bond is shown not to arise solely from p-p π -bonding.

Keywords: CHARGE DENSITY, ATOMS IN MOLECULES, X-RAY

CHARACTERISATION OF THE Mn(hapto(2)-SiH) INTERACTION BY ANALYSIS OF EXPERIMENTAL AND THEORETICAL CHARGE DENSITIES
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Metal complexes containing both a hydride and a silyl ligand are known to act as intermediates in metal-catalysed hydrosilylation and related reactions. In the present study we investigated the peculiarities of agostic TM⁻H-Si bonding (TM = transition metal) in a classical silyl complex Cp(OC)₂Mn(H)SiPh₂ [1], Cp=C₅H₅Me, by means of combined experimental and theoretical charge density studies. The experimental charge density of this complex was determined by fitting a multipole model [2] to high resolution X-ray diffraction data ($\sin\theta/\lambda < 1.11$ 1/Å, T = 120 K) and was further compared to theoretical charge densities obtained by DFT methods. Anisotropic thermal parameters of hydrogen atoms obtained by neutron diffraction [1] at the same temperature were included into the least-squares adjusted experimental model and detailed topological analysis of both experimental and theoretical (BPW91/DZVP2) charge densities of the complex was carried out. The approach we have used gives a direct insight into the nature of chemical bonding in the endocyclic Mn⁻H-Si fragment. The bonding situation in this complex is compared to that established for a classical hydride HMn(NO)₂(PMe₃)₂ [3]. The following conclusions can be drawn from this study: 1. The Si-H bond critical point and the ring critical point (Mn⁻H-Si) in the complex are proximal and not very pronounced. The electron densities obtained for the Si-H bond critical point and the ring critical point are nearly identical. The Si-H bond path is strongly curved so that the Si-H bond critical point and the ring critical point nearly merge together. Thus, the bond and ring critical points almost form a singularity in the charge density, a phenomenon characteristic of bond fission. The same is true for the Mn-Si bond critical point. 2. The Mn-H bond path is curved in such a way that the Mn-H bond critical point is displaced towards the ring critical point indicating electron deficiency. On the contrary, the Mn-H bond path found in the benchmark classical hydride HMn(NO)₂(PMe₃)₂ is straight.

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STRUCTURAL, MAGNETIC AND SUPRAMOLECULAR PROPERTIES OF ANIONIC METAL DICYANAMIDE POLYMERS
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The polydentate ligand dicyanamide (dca, N(CN)₂⁻) is being widely used to produce coordination polymers with novel structural and magnetic properties. In this research anionic species M(dca)₃⁻ and M(dca)₂²⁻ have been synthesised using cation and solvent templation methods. Several structures were obtained, displaying octahedral geometry about individual d-block ions (Mn, Fe, Co, Ni) and ligand coordination through the nitrile nitrogens. Complexes of the type (Ph₄E)[M(dca)₃], (E= P, As) show extended anionic M(dca)₃⁻ 2D (4,4) sheets, separated by layers of Ph₄E⁺ cations. The species (Ph₄As)₂[M₂(dca)₆H₂O]·H₂O·xMeOH (M= Ni, Co) are ladder-like 1D polymers, cross-linked by hydrogen bonding into sheets and separated by layers of cations. The complexes (MePh₃P)[M(dca)₃] consist of 3D anionic M(dca)₃⁻ networks of metal atoms, singly and doubly bridged into a (6,3) hexagonal framework, the cations occurring in pairs within hexagonal cavities. Use of the cation PrPh₃P⁺ and different solvents produced either 1D chains of (PrPh₃P)₂[M(dca)₄], or complexes (PrPh₃P)[M(dca)₃]-n-PrOH, again with anionic M(dca)₃⁻ (4,4) sheets, but with cations and solvent between the sheets. Recent use of a non-linear optical cation yielded a (6,3) anionic net of doubly bridged metal atoms. Factors affecting the network topology include subtle cation-cation and cation-anion interactions, charge and size complementarity between cations and the repeat unit of the anionic network, and solvent inclusion. The nickel(II) complex (Ph₄As)[Ni(dca)₃], displayed long-range magnetic order ($T_c = 20.1$ K)¹ while the other complexes showed weak antiferromagnetic coupling.¹

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