**Conference Abstracts**

**s2.m1.p15 Contribution to the Charge Density Studies of Cu⁺-Complexes.**

1. J. Kozisek, H. Fuess and N.K. Hansen, Department of Inorganic Chemistry, Slovak University of Technology, SK-81237 Bratislava, Slovakia.

**Abstract:**

Bonding properties of transition metals in coordination compounds are of great importance for inorganic as well as bioinorganic chemistry. In order to better understand the reactivity of the active sites in enzymes the model structure of 3d-coordination compounds are studied by single crystal diffraction. Inspection of coordination compounds in the Cambridge Structural Data Base shows that with copper as a central atom and coordination number 4, either a square-planar (Cu⁺), or tetragonal (Cu₂⁺, Cu⁺) coordination polyhedron is preferred. Trigonal-pyramidally distorted tetrahedron with one elongated CuDONOR atom bond is predominant for Cu⁺ oxidation state, as trigonal-planar coordination with coordination number 3 is exclusively found in rigid Cu⁺ coordination compounds.

We are interested in [CuN₄] chromophore in phthalocyanine-like complexes and in [CuN₃S₂] chromophore in blue-proteins of type I. The biological activity of active sites in enzymes the model structure of CuN₄ chromophore is +2 with a pseudo-octahedral coordination of Cu⁺ atom in trans-bis(cyanamidinitrato-N,O)bis(imidazole-N') copper(II) complex. In both compounds the oxidation state of copper is +2 with a d⁸ configuration and a hole mostly located in the d₅² orbital.

**References:**


**s2.m1.p16 Comparison of the Charge Density Distribution in Compounds Containing Elements of Group 15 and 16.**

D. Leusser, D. Stalke, Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.

**Abstract:**

The charge density distributions of three compounds containing elements of group 15 and 16, particularly S(N'Bu)₄, CH₂[Si(Bu)₃(PhNH)₂]₂ and Py₂(NSiMe₃)P(NH₂SiMe₃) were investigated by low temperature high resolution X-ray diffraction experiments.

Subsequent to a high-order refinement a multipole refinement using the atom-centred density-normalized multipole formalism of Hansen and Coppens was carried out. The atomic density ρ_{atom}(r) is composed of: ρ_{atom}(r) = ρ_{s}(r) + P_{l} ρ_{l}(r) + ρ_{ρ}(r'), where ρ_{s}(r) is the spherical core-density, ρ_{ν}(r) is the spherical valence-density and ρ_{ρ}(r') = \sum_{l} R_{l}(r') \sum_{v} P_{l} Y_{v}^{l}(r') is the deformation density with the contraction, expansion parameters κ, κ', respectively, the populations Pₜ and Pₐ, related to the spherical harmonics Y_{lm} and the radial functions R_{l} in terms of Slater-type functions. Subsequent to the multipole refinements a topochemical analysis according to Bader’s theory of “Atoms in Molecules” was carried out and κ-refinements were performed to determine atomic net charges.

All compounds show unusual density correlated properties in the S-N and P-N bonds, respectively. The topological analysis by calculating the first and second derivative of the electron density at the critical points of the S,P,N bonds according to the Bader formalism turned out that the bonding interaction has to be interpreted as a mixture of covalent and closed shell interaction. While in both, deformation density and dynamic model density, relatively high accumulations of density are found in the bonding regions which can be interpreted as covalent shared density, all laplacians in the (3,-1) bond critical points are in a range which indicates domination of closed-shell-interactions in the bonding energy. On the other hand no significant charges can be found by carrying out κ-refinements. This features seem even more contradictory when the ellipticity, a reliable indicator for double-bonding due to its relation to the deviation from rotational symmetry of the density at the bond critical point is considered. All formal S,P=N or S,P-N bonds show a relatively high ellipticity in the range of 0.40 to 0.60 which is therefor near to 0.45 the value for a typical C=C bond².

Accurate investigation of the spatial distribution of the deformation density around the bond critical points shows clear π-density contribution in the area above and below the S,P-N bonding vector, which can be seen in the elliptically shaped deformation density in a plane perpendicular to the bonding vector, containing the bond critical point.

**References:**