s2.m1.p15 **Contribution to the charge density studies of Cu^II-complexes. (II)** J. Kozisek, H. Fuess* and N.K. Hansen#, *Department of Inorganic Chemistry, Slovak University of Technology, SK-81237 Bratislava, Slovakia, *Materials Science, Darmstadt U-niversity of Technology, D-64287 Darmstadt, Germa-ny, #Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, CNRS UPRESA 7036, Université Henri Poincaré, BP 239, 54506 Nancy CEDEX, France.
Keywords: charge density, coordination compound, phtalocyanine.

Bonding properties of transition metals in coordina-tion compounds are of great importance for inorganic as well as bioanorganic 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 Database shows that with copper as a central atom and coordination number 4, either a square-planar (Cu^{2+}), or tetragonal (Cu^{2+}, Cu^+) coordination polyhedron is preferred. Trigonally-pyramidally distorted tetrahedron with one elongated Cu-donor 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 $[CuN_4]$ chromophore in phtalo-cyanine-like complexes and in $[CuN_2S_2]$ chromophore in blue-proteins of type I. The biological activity of ac-tive center is connected with Cu^{2+}/Cu^+ electron trans-fer. According the EXAFS study[1] the bond-length changes on reduction are extremely small. More impor-tant changes should by in the shape of coordination polyhedron. In order to examine the distribution of valence electron density on the central atom, the charge density studies on single crystal of Bis{bis(methoxy-carbimido)aminato}copper(II) complex, a structural an-alogue of phtalocyanine coordination compound[2], was undertaken.

Diffraction data were obtained with a Stoe Stadi 4 diffractometer at 120.0(1)K using the Oxford cryo-systems low temperature attachment. All four sym-metrically independent sets in the space group P 2_1/n were measured. The number of low angle reflections ($0 < \theta < 30°$) is 6960, and the high angle reflections ($30 < \theta < 50°$) is 10168 using Mo Kα radiation. The crystal faces were identified on the diffractometer and optimized according to the measurement of the crystal edges under microscope. Absorption was corrected by a Gaussian quadrature method.

The results of the multipole refinement and charge density analysis will be presented, and discussed for pseudo-octahedral coordination of Cu^{2+} atom in *trans*-bis(cyanamidonitrato-N:O)bis(imidazole-N^3) copper(II) complex[3]. In both compounds the oxidation state of copper is +2 with a d^9 configuration and a hole mostly located in the $d_{x^2-y^2}$ orbital.

[1]Bo G. Malmström and P. Wittung-Stafshede; *Coord. Chem.Rev.*, **185-186** 127-140 (1999).
[2] R. Boca, M. Hvastijová, J. Kozisek, and M. Valko; *Inorg. Chem.*, **35** 4794-4797 (1996).
[3] J. Kozisek, N.K. Hansen and H. Fuess; *Inorg. Chem* (in press).

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.*
Keywords: charge spin density.

The charge density distributions of three compounds containing elements of group 15 and 16, particularly $S(N^tBu)_3$, $CH_2\{S(^tBuN)_2(^tBuNH)\}_2$ and $Py_2(NSiMe_3)P(NHSiMe_3)$ 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[1] was carried out. The atomic density $\rho_{atom}(\mathbf{r})$ is composed of:
$$\rho_{atom}(\mathbf{r}) = \rho_c(r) + P_v\rho_v(\kappa r) + \rho_d(\kappa'\mathbf{r}),$$ where $\rho_c(r)$ is the spherical core-density, $\rho_v(\kappa r)$ is the spherical valence-density and $$\rho_d(\kappa'\mathbf{r}) = \sum_l R_l(\kappa'r) \sum_{m=-l}^{l} P_{lm}Y_{lm}\left(\mathbf{r}/r\right)$$ is the deformation density with the contraction, expansion parameters κ, κ', respectively, the populations P_v and P_{lm}, 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"[2] was carried out and κ-refinements were performed to determine atomic net charges[3].

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 at 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 bond[4]. 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.

[1] Hansen N. K., Coppens P., Acta Cryst. (1978), A34, 909.
[2] Bader R. F. W., "Atoms in Molecules: A Quantum Theory", Oxford University Press, (1990).
[3] Coppens P., Leung T. N., Stevens P., Becker E. D. and Yang Y. W., Acta Cryst. (1979), A35, 63-71.
[4] Bader R. F. W., Slee T. S., Cremer D. and Kraka E., J. Am. Chem. Soc., (1983), 105, 5061.