Poster Presentations

[MS29-P02] The QTAIM Approach to Multicentered (CuHB) Bonding: Charge Density Study of [Cu2(*bipy*)2B10H10].
<u>Anna V. Vologzhanina</u>, Alexander A. Korlyukov, Varvara V. Avdeeva

[†]*A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia 119991,*
[†] *Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia 119991.*
E-mail: vologzhanina@mail.ru

A novel binuclear discrete complex of the [Cu2(*bipy*)2B10H10] composition has been characterized by means of X-ray diffraction. Two copper(I) atoms coordinate a bridge boron cage through an apical BB edge and a BBB face situated at its opposite apical vertices to form four 3c2e (CuHB) and one 2c2e Cu-B(H) bonds. The charge density model was obtained by density functional theory calculations of its isolated molecule and crystal to characterize multicentered (BBB) and (CuHB) bonding. The resulting densities were analyzed using the quantum theory of atoms in molecules (QTAIM, [1]) and electron localizability indicator (ELI-D, [2]). The geometry, the $\rho(r)$ values at bcp's and rcp's for pyridine molecules and decaborate dianion as well as their ellipticities remain almost constant for an isolated molecule and crystal, whilst these of copper(I) coordination environment were found to be sensitive to crystal-field effect. When passing from an isolated molecule to a crystal, the dianion changes its coordination mode (from face-face 1-2-5,6-7-10 to edge-face 1-2,6-7-10), Cu-N bond lengths alternate, and copper atoms donate electron density to nitrogen and apical boron atoms. It was found out, that the multicentred bonding is characterized with an annulus of flat electron density $\rho(r)$ and small $\nabla^2\rho(r)$. As a result, some of the expected B-B, Cu-B or Cu-H bond critical points are absent (Figure). ELI-D function and charge distribution give evidence of predominantly electrostatic nature of Cu -borate bonding. Taking into account, that apical BH groups are more electronegative, than equatorial ones (their charges are, respectively, -0.29 and -0.15 e), disposition of the copper(I) atoms above the faces in the region of apical boron atoms seems to be preferable. Besides, electrostatic nature of bonding does not prevent copper atoms from moving. In the case of copper(I) decaboranes, face coordination of the dianion with three expected bcp's corresponded to Cu-B interactions situated very close to each other as well as to three rcp's (which were obtained in the case of virial graph of an isolated molecule) represents a topological catastrophe where atomic motion would be accompanied with the reorganization of atomic bonds. Barriers of copper migration are expected to be very low, thus the reorganization of atomic charges when passing from an isolated molecule to condensed matter and additional packing energy stabilize the change in the coordination mode of the dianion. The packing energy estimated by means of correlation formula proposed by Espinosa, *et al*. [3] as $E_{A-B} \approx 1/2\,\mathbf{V}^e(r)$ was found to be 29 kcal/mol that is in accord with the value of 26 kcal/mol calculated with inter-molecular potentials using the 'UNI' force field [4]. To sum up, description of this class of compounds in terms of individual bond paths is not satisfactory. Additional QTAIM indicators, which do not rely on the presence of a bcp should be
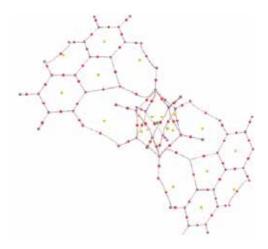

Figure. Molecular graph for the title compound.

[1] Bader, R. F. W. (1991). *Atoms in Molecules. A Quantum Theory*; Cambridge University Press: Oxford U.K.
[2] Kohout, M. (2004). *Int. J. Quantum Chem.* **97**, 651-658.
[3] Espinosa, E., Molins, E. & Lecomte C. (1998). *Chem. Phys. Letters.* **285**, 170-173.
[4] Gavezzotti, A. (2005). *Z. Kristallogr.* **220**, 499-510.

Keywords: copper(I) closo-decaborate; multicentered bonding; the AIM theory