

# QTAIM and ELI-D studies of multicentred bonding in transition metal complexes with boron-containing cages

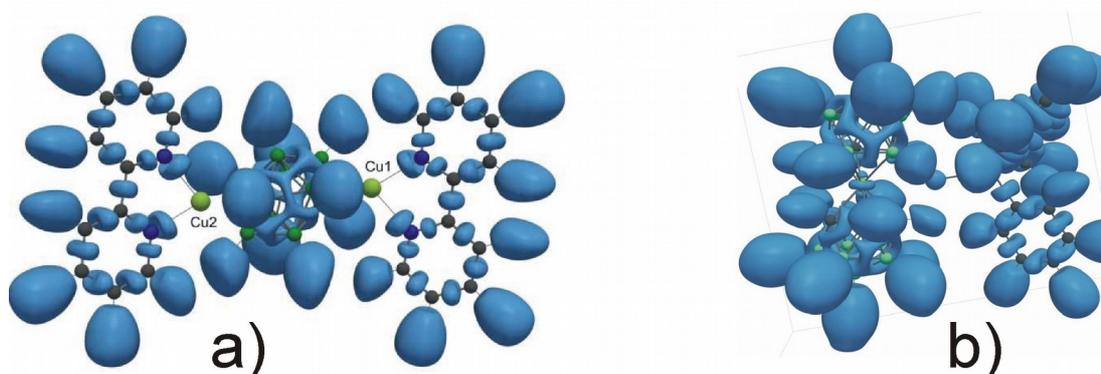
Alexander A. Korlyukov, Alexander F. Smolyakov, *Anna V. Vologzhanina*

A. N. Nesmeyanov Institute of Organoelement Compounds RAS. Vavilova str, 28. 119991 Moscow, Russia. E-mail: vologzhanina@mail.ru

Investigation of chemical bonding in the region of flat electron density is a challenge for the Bader's QTAIM theory. Application of additional techniques such as virial field or electron localizability indicator (ELI-D) topology to  $\pi$ -complexes of transition metals and boron cages allowed overcoming this problem. The QTAIM study of  $[\text{Cu}_2(\text{bipy})_2\text{B}_{10}\text{H}_{10}]$  and  $[\text{Cu}(\text{PPh}_3)\text{Cobdc}]$  (Cobdc = cobalt(III) bis(dicarbollide)) confirmed that electron density  $\rho(r)$  at borate and dicarbollide faces is flat so that the topological instability in the region of multicentered B–H...M bonds is observed. The geometry and the topological parameters of  $[\text{Cu}_2(\text{bipy})_2\text{B}_{10}\text{H}_{10}]$  were found to be sensitive to crystal-field effect. Molecular and virial graphs of both compounds do not coincide. Thus, the nature of chemical Cu...B<sub>10</sub>H<sub>10</sub><sup>2-</sup>, Co...dicarbollide and Cu...Cobdc bonding was also probed with the ELI-D approach. The topological analysis of the ELI-D function (see Figure for ELI-D distribution in both complexes) gives evidence that not only B–H...Cu, but also Co...dicarbollide bonds are multicentered. The B–H...Cu bonds are the 3c2e interactions; and the Co...{*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>} bonding includes 3c2e Co...C–C and Co...C–B interactions and the multicentered Co...BBB bonding. In the latter case not only boron atoms of the C<sub>2</sub>B<sub>3</sub> ring, but also boron atoms of the second B<sub>5</sub> belt of the {*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>}<sup>2-</sup> dianion take part in bonding. Strong localization of charge density on the Cu–PPh<sub>3</sub> bond was associated with delocalization of electron density in the Cobdc<sup>-</sup> anion situated opposite to this bond. Although the ring critical point between Cu and Co atoms was located, there exists a Cu...Co...BBB basin with significant contribution of both metal atoms to the basin population. The B–H...M bonding was found to be presumably electrostatic in nature, that could be the reason of the linkage isomerism for copper(I) decaborates.

Our results indicate that QTAIM study of bonding situation for mono- and polynuclear metallacarboranes and transition metal complexes with boron cages should be accompanied by the ELI-D function analysis. Taking into account presence of an unexpected ELI-D Cu...Co...BBB basin in  $[\text{Cu}(\text{PPh}_3)\text{Cobdc}]$  the latter function could also be helpful in understanding of metal-metal bonding in polynuclear metallacarboranes.

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**Figure.** ELI-D isosurfaces for  $[\text{Cu}_2(\text{bipy})_2\text{B}_{10}\text{H}_{10}]$  (a) and  $[\text{Cu}(\text{PPh}_3)\text{Cobdc}]$  (b) drawn at  $\gamma_D(r) = 1.4$ .