The structure and chemical bonding in the N_2—CuX and N_2···XCu (X= F, Cl, Br) systems studied by means of the molecular orbital and quantum chemical topology methods.

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Streszczenie

Ab initio studies carried out at the MP2(full)/6-311+G(2df) and MP2(full)/aug-cc-pVTZ-PP computational levels reveals that dinitrogen (N_2) and cuprous halides (CuX, X = F, Cl, Br) form three types of systems with the side-on and end-on coordination of N_2: N≡N→CuX ($C_{\infty v}$), N_2→CuX (C_{2v}) stabilized by the donor–acceptor bonds and weak van der Waals complexes N_2···XCu (C_{2v}) with dominant dispersive forces. An electron density transfer between the N_2 and CuX depends on type of the N_2 coordination and a comparison of the NPA charges yields the $[N{\equiv}N]^{\delta+}$-$[CuX]^{\delta-}$ and $[N_2]^{\delta-}$-$[CuX]^{\delta+}$ formula. According to the NBO analysis, the Cu←N coordinate bonds are governed by predominant $LP_{N2} \rightarrow \sigma^*(Cu{-}X)$ “2e-delocalization” in the most stable N≡N→CuX systems, meanwhile back donation $LP_{Cu} \rightarrow \pi^*(N{-}N)$ prevails in less stable N_2←CuX molecules. A topological analysis of the electron density (AIM) presents single BCP between the Cu and N nuclei in the N≡N→CuX, two BCPs corresponding to two donor-acceptor Cu←N bonds in the N_2←CuX and single BCP between electron density maximum of the N≡N bond and halogen nucleus in the van der Waals complexes N_2···XCu. In all systems values of the Laplacian $\nabla^2\rho(r)(r_{BCP})$ are positive and they decrease following a trend of the complex stability i.e. N≡N→CuX ($C_{\infty v}$) > N_2→CuX (C_{2v}) > N_2···XCu (C_{2v}). A topological analysis of the electron localization function (ELF) reveals strongly ionic bond in isolated CuF and a contribution of covalent character in the Cu←Cl and Cu←Br bonds. The donor–acceptor bonds Cu←N are characterized by bonding disynaptic basins V(Cu,N) with attractors localized at positions corresponding to slightly distorted lone pairs V(N) in isolated N_2. In the N≡N→CuX systems, there were no creation of any new bonding attractors in regions where classically the donor–acceptor bonds are expected and there is no sign of typical covalent bond Cu←N with the bonding pair. Calculations carried out for the N≡N→CuX reveal small polarization of the electron density in the N≡N bond, which is reflected by the bond polarity index being in range of 0.14 (F) to 0.11 (Cl).

Słowa kluczowe

electron localization function, NBO, NPA, natural orbitals, electron delocalization, van der Waals complex, topology, SAPT, AIM, Bader

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