Laplacian and bond critical point properties of the electron density distributions of sulfide bonds: A comparison with oxide bonds*

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Abstract

Topological and bond critical point properties of electron density distributions, $\rho(\mathbf{r})$, were calculated for a series of sulfide molecules, containing first- and second-row main group M-cations. Laplacian maps of the distributions, $\nabla^2\rho(\mathbf{r})$, show that the valence shell charge concentration (VSCC) of the sulfide anion is highly polarized and extended into the internuclear region of the M-S bonds, coalescing with the VSCCs of the more electronegative first-row cations. On the other hand, maps for a corresponding set of oxide molecules show that the oxide anion tends to be less polarized and more locally concentrated in the vicinity of its valence shell, particularly when bonded to second-row M-cations. A search for extrema in the $\nabla^2\rho(\mathbf{r})$ distributions reveals maxima in the VSCCs that can be ascribed to bonded and nonbonded electron pairs. The different and distinctive properties of sulfides and oxides are examined in terms of the number and the positions of the electron pairs and the topographic features of the Laplacian maps. The evidence provided by the electron density distributions and its topological properties indicates that the bonded interactions in sulfides are more directional, for a given M-cation, than in oxides. The value of the electron density distribution at the bond critical point and the length of a given M-S bond are reliable measures of a bonded interaction, the greater the accumulation of the electron density and the shorter the bond, the greater its shared (covalent) interaction.