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Nucleophilic and electrophilic influence zones from the electrostatic potential Ignasi Mata^a, Enrique Espinosa^b, Elies Molins^a, ^aICMAB-CSIC Barcelona, Spain, ^bUniversité Henri Poincaré, Nancy, France.

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The topology of the electrostatic potential has been studied for single molecules using geometries and electron distributions determined from high-resolution single-crystal X-ray diffraction experiments. The electrostatic potential gradient, which is the negative of the electric field, has been represented, revealing the position of zero-flux surfaces and critical points [1]. Through the representation of the electric field lines, the relationship between the topology of the electrostatic potential and the reactivity of the molecule is explored.

Local maxima, corresponding to the nuclei, are associated to electrophilic sites, while local minima, which are related to local accumulations of electron density (i.e. in lone pairs) are identified as nucleophilic sites. Both kind of reactive sites present influence zones delimited by zero-flux surfaces. Space can be partitioned in disjoint volumes (*primary bundles*) [2], each of them corresponding to the intersection of the influence zones of at most one nucleophilic and one electrophilic sites, which are both situated on the surface of the primary bundle. As a result of the interaction with the whole molecule, a probe charge inside one primary bundle is directed to, or away from, the reactive sites on the surface of this volume. The bundles can be added to generate two separate partitions in nucleophilic and electrophilic influence zones, the completeness of these last partitions depending on either the neutral or ionic character of the molecule.

Analogous to the bond and ring critical points in the electron density topology, electrostatic potential saddle critical points appear on the zero-flux surfaces. They are related to the limits of the electrophilic and nucleophilic influence zones, which can extend to infinite or present a finite volume. In this last case, a saddle point reveals the limit of the influence zone and the path for preferred attack on the reactive site.

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We are interested in polynuclear complexes that behave as single-molecule magnets (SMMs) [1]. SMMs are molecules that may be magnetized and keep the magnetization after removal of the magnetic field in the way of magnets.

For a polynuclear complex to have such behavior require a large magnetic ground state with a large negative magnetic axial anisotropy ($D < 0$) [1-2]. Indeed, this induces two possible orientations (up and down) between which the magnetization can fluctuate. The time the molecule may be magnetized in zero fields, or the relaxation time, depends on the energy barrier (U) that separates the two orientations. For a ground spin state (S), well separated from the excited states, U is as $-DS^2$. Therefore, the larger the D and S values are, the higher the barrier is and the longer the magnetization is retained.

Thus the aim of our current research is to synthesize polynuclear complexes with a high nuclearity (S) and a strong axial anisotropy ($D < 0$) so that the barrier will be the higher and the relaxation time long. This is crucial if one thinks to applications. This is not an easy task and any progress in the bench work is tightly dependant on the structural information. Indeed, it is the understanding of the magneto-structural relationships that helps to tune the chemical approach.

I will illustrate my paper with some of our recent results [3] and show how polarised neutron diffraction brings information on the nature and mechanism of the intracuster magnetic interactions [4].

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