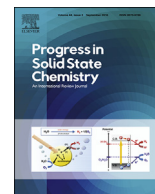




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## Stereochemistry and ab initio topology analyses of electron lone pair triplets and twins in interhalogen compounds and halogen suboxides

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In Memoriam of Prof. Dr. Fawzi ADAIMI, founder and former President of the Lebanese-German University: LGU (Lebanon) and Prof. Bernard DARRIET, University of Bordeaux (France).

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## ABSTRACT

The paper reports a thorough investigation of little inspected two classes of group VIIA based crystals: interhalogen compounds ClF, ClF<sub>3</sub>, BrF<sub>3</sub> and IF<sub>3</sub> on one hand and halogen suboxides F<sub>2</sub>O, Cl<sub>2</sub>O and Br<sub>2</sub>O on the other hand, as well as rare gas fluorides (here exemplarily XeF<sub>4</sub>), all exhibiting peculiar stereochemistry of electron (non-bonding) lone pairs merging in forms of twins and triplets. Particularly with respect to the well known VSEPR (Valence Shell Electron Pair Repulsion) model we present original approach merging crystal chemistry and density functional theory (DFT) electron localization function (ELF) to provide accurate topologic analyses and precise metrics of electron lone pairs geometries. In this context we rewrite the chemical formulae above by adjoining E designing the lone pair (LP) and M\* formulating the LP-bearing element: ClF{E<sub>3</sub>}, M\*<sub>2</sub>OE<sub>2</sub>{E<sub>3</sub>}<sub>2</sub> (M\* = F, Cl, Br), M\*F<sub>3</sub>E<sub>2</sub> (M\* = Cl, Br, I) and XeF<sub>4</sub>E<sub>2</sub>. Then in ClF{E<sub>3</sub>} and M\*<sub>2</sub>OE<sub>2</sub>{E<sub>3</sub>}<sub>2</sub> (M\* = F, Cl, Br) family an original stereochemistry is developed with LP concentration in E triplets which generate electronic torus revolving around Cl and M\* which in the neighborhood of largely electronegative F, exhibit cationic-like behavior. E around Cl in ClF and then around M\* of the series under consideration exhibits an ellipsoidal shape with an equivalent sphere of influence radius (r<sub>E</sub>) increasing along with the atomic number Z, i.e. r<sub>E,F</sub> = 0.52 Å, r<sub>E,Cl</sub> = 0.65 Å and r<sub>E,Br</sub> = 0.70 Å. From selected sections in ELF data we obtained precise topology and metrics details of these tori. For M\*<sub>2</sub>OE<sub>2</sub>{E<sub>3</sub>}<sub>2</sub> family the E twins attached to O have also been localized, their size remaining constant with r<sub>E,O</sub> = 0.68 Å in all studied compounds. The lone pair twins in the series M\*F<sub>3</sub>E<sub>2</sub> (M\* = Cl, Br, I; M\* trivalent oxidation state) as well as in noble gas tetrafluoride XeF<sub>4</sub>E<sub>2</sub> provide remarkable examples: r<sub>E</sub> evolution versus Z, r<sub>E,Cl</sub> = 0.77 Å (Z = 17), r<sub>E,Br</sub> = 0.85 Å (Z = Br) and r<sub>E,I</sub> = 0.90 Å (Z = 53), follow a linear expansion while in the xenon case with a close Z<sub>Xe</sub> = 54 but with tetravalent oxidation state, Xe exhibits a radius r<sub>E,Xe</sub> = 0.95 Å, indicating the important influence of the charge magnitude on E volume. The interaction of cations with E centroid: Ec -defined as the electronic volume attached to the lone pair- of neighboring molecules is plausible in explaining unusually short distances between cations. Even surrounded by E torus the cations obviously exert attractive influence through its vortex axis.

Based on combined stereochemistry and ab initio topology analyses the paper endeavors showing the unavoidable necessity to accurately account for electron lone pairs:

- position of their centroid,
- their shape,
- their size,
- and their deformation (knowing that the electron cloud which accompanies them exhibits a certain plasticity), in order to fully understand their remarkable influence on crystal networks.

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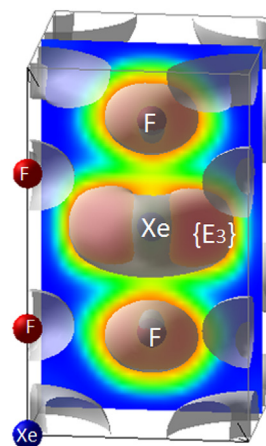
## 1. Introduction

Several atoms exhibit electronic configuration particularity of presenting valence electron pair not involved in the bonding. Cases extend throughout the Periodic table from {He}2s<sup>2</sup> up to {Xe}4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup> (Po<sup>4+</sup>). The lone pair E ns<sup>2</sup> (2 ≤ n ≤ 6) is designated herein by M\*. Models in molecular chemistry are well established as the Valence Shell Electron Pair Repulsion (VSEPR) [1]. The situation is somewhat different when it comes to consider E in the solid state where M\* elements provide a wealth of compounds with crystal structures revealing original characteristics with empty channels, thick layers separated or impenetrable volumes excluding any other atoms thanks to E owing to its peculiar stereochemistry. In recent years we have endeavored exploring this field, for oxides, fluorides and oxyfluorides [2,3] within original approach merging crystal chemistry and accurate position and steric development of E thanks to quantum mechanical approaches leading mainly to explicit electron localization volumes and slices with ELF electron localization function [4] as well a detailed description of the electronic band structure illustrated by the site projected density of states (DOS) and quantum mixing of the valence states of the different chemical constituents pertaining to the chemical bonding. Also when more than one lone pair such as triplets of lone pairs {E<sub>3</sub>} in noble gas fluorides NgF<sub>2</sub> (Ng = Kr, Xe) their whirling around Ng is smeared out into a torus. This is illustrated in Fig. 1 for XeF<sub>2</sub> where Xe is centered within {E<sub>3</sub>} torus. In such Ng compounds torus topology and metrics were examined recently [5]. In continuation of our former investigations [2,3,5] we address in this paper such properties of lone pairs assembling into twins and triplets within an original class of exotic materials

consisting of interhalogen and halogen oxides.

## 2. Theoretical and computational frameworks

In theoretical physics and chemistry studies going beyond the Hartree-Fock approach, exchange and correlation (XC) effects are equally and accurately accounted for within the quantum density functional theory DFT [6,7]. In these DFT founding papers the first



**Fig. 1.** XeF<sub>2</sub> and its {E<sub>3</sub>} torus centered on Xe in 3D ELF electron localization representation (grey volumes). In the ELF 2D slice crossing all atomic species, blue, green and red zones correspond to zero, free electron like and strong electron localization (see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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