

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Novel Li₃X₃ supersalts (X = F, Cl, Br & I) and their alkalide characteristics

Ambrish Kumar Srivastava^a and Neeraj Misra^{a*}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We have theoretically predicted the formation of novel species by interaction of LiX₂ superhalogens with Li₂X superalkalies for X = F, Cl, Br & I. The resulting Li₃X₃ supersalts are found to be more stable than traditional LiX salts. The chemical reactivity of Li₃X₃ is discussed with the help of various electronic parameters and it is shown that they may possess the alkalide characteristics. The present report will pave a way for experimentalists to design such novel species with pronounced properties.

Introduction

The fundamental understanding of the building blocks of materials has been a field of continuous investigations due to design and development of new compounds. The pioneering work of Khanna and Jena proposed the atomic clusters of suitable size and composition as superatoms which are able to mimic the chemistry of atoms in the periodic table¹. These superatoms can be considered as building blocks of novel materials with tailored properties. Gutsev and Boldyrev introduced the terms ‘superhalogen’ and ‘superalkali’ for superatoms possessing higher electron affinities than halogens and lower ionization potentials than alkalies, respectively².

These superatoms are designed, initially, by suitable combination of highly electropositive (such as alkali metal) and highly electronegative atoms (such as halogen). The superhalogen properties of many species belonging to the formula of MX_{k+1}, where *k* is the formal valence of *s* block metal atom (M) and X is halogen or oxygen, have been reported^{3–6}. Further investigations used transition metal instead of *s* block metal and explored the superhalogen behavior of a number of molecular species^{7–10}. In the similar lines, superalkali nature of various molecular species has been investigated^{11–15}.

In the present investigation, we have theoretically designed some novel compounds by interacting LiX₂ superhalogens with Li₂X superalkalies for X = F, Cl, Br and I. We have discussed the structure and stability of resulting Li₃X₃ supersalts and calculated various parameters in order to explore their electronic properties. Recently, the compounds with excess electrons, termed as ‘alkalides’ have attracted considerable attention^{16–19}, owing to their potential applications in chemical synthesis, catalysis, nanodevices and functional materials. Alkalides are compounds containing anionic alkali metals (e.g. Na[–], K[–], Rb[–] or Cs[–])²⁰. The excess electron in the alkali anion is loosely bound in space because of the small electron affinity of alkali atoms. Room-temperature stable alkalides such as K⁺(aza222)Na[–] and K⁺(aza222)K[–] have already been synthesized¹⁹. We have shown that

these Li₃X₃ supersalts may also possess the alkalide characteristics.

Despite of enormous progress in the research of superatoms, a few attempts have been made in their utilization for designing supersalts with unique chemical properties. For instance, BF₄–NLi₄ supersalt has been reported to possess remarkable non-linear optical properties²¹ which are even more pronounced in case of BLi₆–X supersalts for X = LiF₂, BeF₃ and BF₄²². More recently, some new supersalts have been predicted by using superhalogen and superalkalies as building blocks²³. Thus present study is expected to aid constructively in further studies on supersalts.

Computational method

All calculations have been performed by second-order perturbative approach of Moller and Plesset, MP2(FC) method²⁴. This method has already been used in a previous study on supersalts²¹. A double zeta type basis set, SDD is employed for all atoms. Gaussian 09 set of programs²⁵ is used to perform all computations and relevant graphics are generated with the help of Gauss View 5.0 program²⁶.

Results and discussions

Superatomic properties of LiX₂ and Li₂X species

We first discuss the structures of LiX₂ and Li₂X species and their superatomic properties. We have calculated IPs of Li₂X species by difference of energies between neutral Li₂X and their cationic counterpart. Similarly, the EAs of LiX₂ are calculated as the energy difference between neutral species and their anions. Table 1 lists geometrical parameters as well as calculated IPs and EA values.

All LiX₂ and Li₂X species take bent C_{2v} structure in which bond-length, Li–X increases with the substitution of heavier halogen, X. The bond-angle in Li₂X decreases with heavier halogen but increases in case of LiX₂. The calculated IPs of Li₂X species, 3.70–4.26 eV lower than IP of Li, 5.39 eV²⁷, suggest their superalkali behavior and the superhalogen nature of LiX₂ species

are supported by their high EAs, 4.24-5.06 eV as compared to Cl, superatoms.
namely 3.26 eV²⁸. Thus Li₂X and LiX₂ species indeed behave as

Table 1 Ionization potential (IP) of Li₂X and electron affinity (EA) of LiX₂ (in eV) along with their geometrical parameters^a

X	Li ₂ X			LiX ₂		
	Bond-length	Bond-angle	IP	Bond-length	Bond-angle	EA
F	1.72	109	3.70	1.77	68	5.06
Cl	2.28	76	4.00	2.29	75	4.55
Br	2.46	69	4.09	2.44	79	4.59
I	2.70	63	4.26	2.65	84	4.24

^a In Å°, deg.

Interaction between Li₂X and LiX₂ species

In order to study the interaction between Li₂X and LiX₂ species, we place these two units parallel to each other. After optimization, we find a benzene shaped planar ring structure of Li₃X₃ as shown schematically in Fig. 1 for X = F. One can see that the bonding in Li₃F₃ takes place via two Li-F bonds. In Table 2, we have collected bond-length, Li-X and bond-angles for Li₂X and LiX₂ moieties in Li₃X₃. The bond-length, Li-X in Li₃X₃ is found to be average values of those in Li₂X and LiX₂ species (see Table 1). For X = F, the bond-angles are only increased by 6-12° as compared to 120°, those in benzene ring. The distortion from ideal benzene ring increases with the substitution of heavier halogens. The equilibrium structures of Li₃X₃ can be seen in Fig. 2 for X = Cl, Br and I. The changes in bond-angles of Li₂X and LiX₂ moieties follow the same trend as already observed from Table 1. For X = I, the deviation in bond-angle from benzene structure is increased by about 25°.

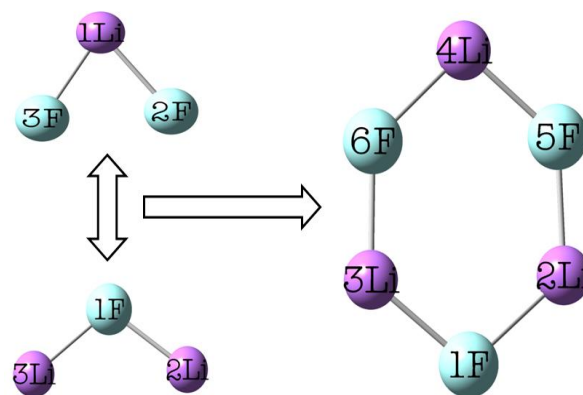


Fig.1 Interaction between LiF₂ superhalogen and Li₂F superalkali leading to the formation of Li₃F₃ ring structure.

Table 2 The binding energy (ΔE) and HOMO-LUMO gap (E_{gap}) of Li₃X₃ (all in eV) along with their geometrical parameters^a

X	Li-X	\angle LiX ₂	\angle Li ₂ X	ΔE	E_{gap}
F	1.74	126.8	132.2	8.76	14.32
Cl	2.28	138.0	107.9	6.18	12.22
Br	2.45	139.6	102.3	5.50	11.20
I	2.67	145.8	95.3	4.75	10.20

^a In Å°, deg.

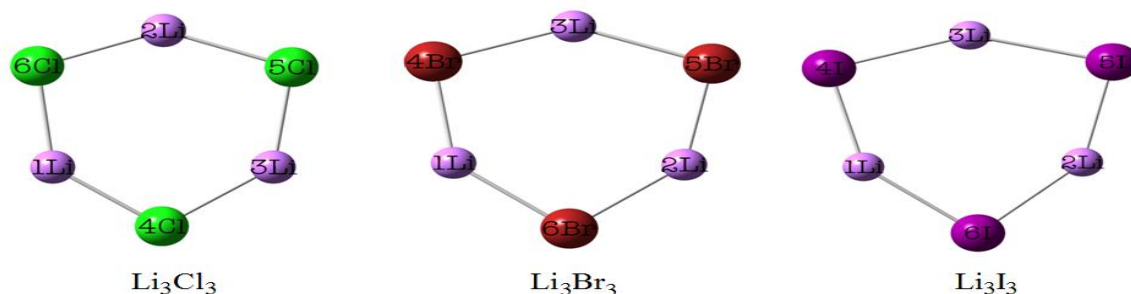


Fig.2 Equilibrium geometries of Li_3X_3 supersalts predicted at MP2/SDD method for $\text{X} = \text{Cl}$, Br and I .

Normal mode calculations performed on Li_3X_3 provide all real frequencies. Thus they correspond to at least a local minimum in the potential energy surface, implying they are all kinetically stable. In order to further analyze the thermodynamic stabilities of Li_3X_3 , we have calculated the energy gap (E_{gap}) between highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). This energy can be used to compare relative chemical stability of Li_3X_3 as well. The calculated E_{gap} values are given in Table 2. The energy gap of Li_3X_3 lies between 10.2–14.3 eV which is very large as compared to that of fullerene cage, namely 1.6 eV. These larger gaps may offer the enormous thermodynamic stability to Li_3X_3 , thereby, indicating the possibility of existence of Li_3X_3 at a wide range of temperatures.

The energy gap of Li_3F_3 , 14.3 eV is slightly smaller than 15.9 eV in LiF_2 but very large as compared to 4.3 eV in Li_2F . This implies that Li_2F moiety is significantly stabilized by interaction with LiF_2 . The same calculation returns the energy gap value of 12.2 eV in LiF , a traditional salt which is smaller than that of non-traditional Li_3F_3 . Thus, Li_3X_3 species are expected to be thermodynamically more stable as compared to traditional LiX salts. With the substitution of heavier halogens, however, this stability tends to decrease and Li_3X_3 species become chemically more reactive.

The interaction energies (ΔE) between LiX_2 and Li_2X moieties of Li_3X_3 are calculated at the MP2/SDD level. We have used the counterpoise (CP) procedure^{29,30} to eliminate the basis set superposition error (BSSE) effect as given below

$$\Delta E = E_{\text{AB}}(X_{\text{AB}}) - E_{\text{A}}(X_{\text{AB}}) - E_{\text{B}}(X_{\text{AB}})$$

where the same basis set, X_{AB} , has been employed for the calculations of energies of the complex (E_{AB}) as well as its constituting units (E_{A} and E_{B}).

Table 2 also lists BSSE corrected ΔE values of Li_3X_3 species for $\text{X} = \text{F}$, Cl , Br and I . The interaction energies follow the same trend as that of the energy gap, that is, decrease as we move down in the halogen group. This is consistent with fact that the electronegative nature of elements decreases on moving down in a group in the periodic table. The interaction energy of Li_3F_3 , 8.76 eV is larger than the binding energy of LiF , namely 5.20 eV calculated at the same level of theory. This may suggest that the interaction between LiF_2 and Li_2F superatoms is stronger than that between Li and F atoms which is a consequence of low IP and high EA of Li_2F and LiF_2 as compared to Li and F , respectively.

In order to discuss the nature of interaction between LiX_2 and Li_2X moieties in Li_3X_3 , we have performed natural population

analysis (NPA) on Li_3F_3 . The calculated partial charge on Li_2F moiety is found to be +0.89 e which is close to unity. This not only suggests that the interaction between Li_2F and LiF_2 is ionic but also the fact that Li_3F_3 can be regarded as a supersalt.

Electronic properties and alkali characteristics of Li_3X_3 supersalts

The electronic parameters of Li_3X_3 supersalts are calculated by orbital vertical method (OVM). Note that the validity of Koopmans' approximation, upon which OVM rests, is limited to unrelaxed orbitals. It considers neither orbital relaxation effects nor electron correlation effectively. These effects cause to shift HOMO eigen-values up and LUMO eigen-values down from negative ionization potentials and negative electron affinities respectively^{31–34}. Thus our calculated ionization potentials (I) and electron affinities (A) by OVM are unlikely to be exact. Other parameters viz. absolute electronegativity (χ), chemical hardness (η) and electrophilicity (ω) are calculated by finite difference approximations^{35–38}.

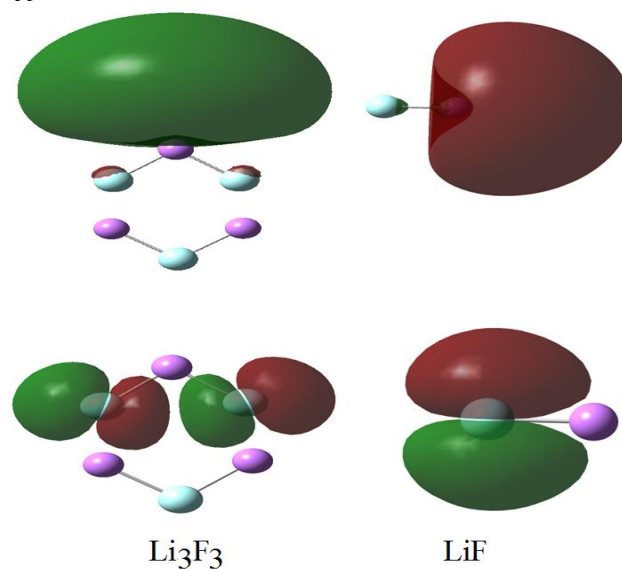


Fig.3 HOMO (lower row) and LUMO (upper row) surfaces of Li_3F_3 and LiF with an isovalue of 0.002. The red represents electron poor region and green corresponds to the region of excess electron.

Table 3 Various electronic parameters^a of Li₃X₃ calculated at MP2/SDD level.

X	$I = -E_{\text{HOMO}}$	$A = -E_{\text{LUMO}}$	$\chi = \frac{1}{2}(I + A)$	$\eta = \frac{1}{2}(I - A)$	$\omega = \chi^2/\eta$
F	13.64	-0.68	6.48	7.16	5.86
Cl	11.53	-0.70	5.42	6.12	4.80
Br	10.69	-0.51	5.09	5.60	4.62
I	9.75	0.45	5.10	4.65	5.60

^a In eV.

Notes and references

^a Department of Physics, University of Lucknow, Lucknow, Uttar Pradesh-226007, India

* Author for correspondence, E-mail: neerajmisra11@gmail.com

1. S. N. Khanna and P. Jena, *Phys. Rev. B* 1995, **51**, 13705.
2. G. L. Gutsev and A. I. Boldyrev, *Chem. Phys.* 1981, **56**, 277.
3. X. B. Wang, C. F. Ding, L. S. Wang, A. I. Boldyrev and J. Simons, *J. Chem. Phys.* 1999, **110**, 4763.
4. C. Ashman, S. N. Khanna, M. R. Pederson and J. Kortus, *Phys. Rev. B* 2000, **62**, 16956.
5. B. K. Rao, P. Jena, S. Burkart, G. Gantefor and G. Seifert, *Phys. Rev. Lett.* 2001, **86**, 692.
6. W. Xu, G. Li, G. Yu, Y. Zhao, Q. Li, Y. Xie and H. F. Schaefer III, *J. Phys. Chem. A* 2003, **107**, 258.
7. R. N. Compton and P. W. Reinhardt, *J. Chem. Phys.* 1980, **72**, 4655.
8. O. Graudejus, S. H. Elder, G. M. Lucier, C. Shen and N. Bartlett, *Inorg. Chem.* 1999, **38**, 2503.
9. G. M. Lucier, C. Shen, S. H. Elder and N. Bartlett, *Inorg. Chem.* 1998, **37**, 3829.
10. P. Koirala, M. Willis, B. Kiran, A. K. Kandalam and P. Jena, *J. Phys. Chem. C* 2010, **114**, 16018.
11. G. L. Gutsev and A. I. Boldyrev, *Chem. Phys. Lett.* 1982, **92**, 262.
12. G. L. Gutsev and A. I. Boldyrev, *Adv. Chem. Phys.* 1985, **61**, 169.
13. E. Rehm, A. I. Boldyrev and P. v. R. Schleyer, *Inorg. Chem.* 1992, **31**, 4834.
14. V. G. Zakrzewski, W. von Niessen, A. I. Boldyrev and P. v. R. Schleyer, *Chem. Phys.* 1993, **174**, 167.
15. A. N. Alexandrova and A. I. Boldyrev, *J. Phys. Chem. A* 2003, **107**, 554.
16. J. L. Dye, J. M. Ceraso, M. T. Lok, B. L. Barnett and F. J. Tehan, *J. Am. Chem. Soc.* 1974, **96**, 608.
17. F. J. Tehan, B. L. Barnett and J. L. Dye, *J. Am. Chem. Soc.* 1974, **96**, 7203.
18. J. L. Dye, *Chemtracts: Inorg. Chem.* 1993, **5**, 243.
19. J. Kim, A. S. Ichimura, R. H. Huang, M. Redko, M. Phillips, J. E. Jackson and J. L. Dye, *J. Am. Chem. Soc.* 1999, **121**, 10666.
20. J. L. Dye, *Inorg. Chem.* 1997, **36**, 3816.
21. H. Yang, Y. Li, D. Wu and Z.-R. Li, *Int. J. Quantum Chem.* 2012, **112**, 770.
22. Y. Li, D. Wu and Z.-R. Li, *Inorg. Chem.* 2008, **47**, 9773.
23. S. Giri, S. Behera and P. Jena, *J. Phys. Chem. A* 2014, **118**, 638.
24. C. Moller and M. S. Plesset, *Phys. Rev.* 1934, **46**, 618.
25. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J.

Table 3 lists various electronic parameters for Li₃X₃ supersalts calculated at MP2/SDD level. The large *I* and low *A* values of Li₃X₃ supersalts may further suggest their stabilities against subtraction and addition of an extra electron, respectively. Note the higher ionization potential of Li₃X₃ as compared to that of LiX which is, for instance, 9.57 eV and 8.7 eV for X = Cl and Br, respectively³⁹. The chemical reactivity of Li₃X₃ supersalts increases with the heavier halogens as reflected by decrease in their energy gap (see Table 2). In case of protonation reaction, absolute electronegativity inversely correlates with the proton affinity. Thus decrease in χ values may indicate the corresponding increase in their proton affinities. The increase in reactivity of Li₃X₃ is further established by the decrease in the chemical hardness with the substitution of heavier halogen.

The frontier molecular orbitals, HOMO and LUMO, are mainly responsible for chemical reactions or interactions with other species. In Fig. 3, we plot HOMO and LUMO surfaces of Li₃F₃ supersalt. For comparison, the same for LiF molecule are also plotted. In present color grading scheme, the red represents positively charged region and green corresponds to negatively charged surface with an isovalue of 0.02. From Fig. 3, it is evident that the HOMO of Li₃F₃ consists of 2p orbitals of two F atoms just as the HOMO of LiF which is formed by 2p atomic orbital of F. The transition HOMO→LUMO in LiF represents a complete electron transfer from Li to F atom. On the other hand, the same in Li₃F₃ shows an electron transfer to Li, allowing it to possess an excess electron. This excess electron is loosely bound in space due to small EA of Li atom. This implies that Li₃F₃ supersalt possesses alkalide characteristics. Thus it may be possible to design new types of alkalides considering Li in Li₃X₃ supersalts as a source of excess electrons.

Conclusions

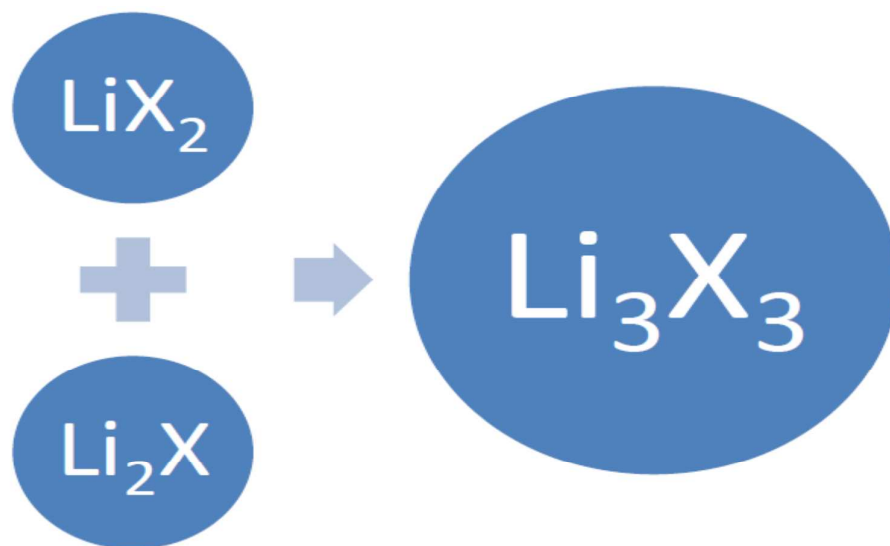
We have shown that the interaction between Li₂X superalkalies and LiX₂ superhalogens leads to the formation of Li₃X₃ supersalts for X = F, Cl, Br and I. The binding energy and HOMO-LUMO energy gap of these supersalts suggest their enhanced stability. The chemical reactivity of Li₃X₃ increases with the substitution of heavier X. Finally, we have proposed that these Li₃X₃ supersalts may possess alkalide characteristics due to excess electron on Li.

Acknowledgement

A.K. Srivastava acknowledges Council of Scientific and Industrial Research, India for providing a research fellowship [Grant No. 09/107(0359)/2012-EMR-I].

- Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford CT, 2010.
26. R. Dennington, T. Keith and J. Millam. GaussView 5.0, Semichem Inc. KS, 2003.
27. W. C. Martin and W. L. Wiese, in *Atomic, Molecular, and Optical Physics Handbook*, Drake, G.W. F., Ed., AIP Press, New York, 1996.
28. H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* 1985, **14**, 731.
29. S. F. Boys and F. Bernardi, *Mol. Phys.* 1970, **19**, 553.
30. P. Hobza and Z. Havlas, *Theor. Chem. Acc.* 1998, **99**, 372.
31. M. J. Allen and D. J. Tozer. *Mol. Phys.* 2002, **100**, 433.
32. D. J. Tozer, *J. Chem. Phys.* 2003, **119**, 12697.
33. D. J. Tozer and F. D. Profit, *J. Phys. Chem. A* 2005, **109**, 8923.
34. C. G. Zhan, J. A. Nichols and D. A. Dixon, *J. Phys. Chem. A* 2003, **107**, 4184.
35. R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, *J. Chem. Phys.* 1978, **68**, 3801.
36. P.W. Ayers, R.G. Parr and R.G. Pearson, *J. Chem. Phys.* 2006, **124**, 194107.
37. R.G. Pearson, *Inorg. Chim. Acta* 1995, **240**, 93.
38. P.W. Ayers and R.G. Parr, *J. Am. Chem. Soc.* 2000, **122**, 2010.
39. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* 1988, **17**, Suppl.1.

Graphical Table of Contents



The picture depicts the formation of Li_3X_3 by interaction between LiX_2 and Li_2X for $\text{X} = \text{F}$, Cl , Br and I .