



# Theoretical Study on New Types of Noble-Gas Containing Anions and $\text{ClLiClNgO}^-$ ( $\text{Ng} = \text{Ar, Kr and Xe}$ )

Yu-Ting Lin, Chin-Mei Liao and Wei-Ping Hu \*

Department of Chemistry and Biochemistry, National Chung Cheng University, Chiayi, Taiwan

## Abstract

We study a new type of noble-gas containing anions  $\text{ClLiClNgO}^-$  ( $\text{Ng} = \text{Ar, Kr, Xe}$ ), which are complexes between the superhalogen  $\text{ClLiCl}^-$  and  $\text{NgO}$ . We expect that  $\text{ClLiClNgO}^-$  to be ion-dipole complexes ( $\text{ClLiCl}^- \dots \text{NgO}$ ) and discussing the impact of superhalogen  $\text{ClLiCl}^-$  on  $\text{NgO}$ . The structures, energies, and electron density are calculated by a high-level theoretical method.

## Introduction

In recent studies, superhalogen-stabilized noble gas compounds predicted<sup>1</sup> and the noble-gas prefer to form anions  $\text{FNgO}^{2-}$ ,  $\text{F}^-(\text{NgO})_n^{3-}$ , the result shows fluoride ion can induce  $\text{Ng-O}$  bonds. Thus, we design a new type of noble-gas containing anions and including superhalogen  $\text{ClLiCl}^-$ , which haven't been studied. The structures, stability, electron density distribution of the noble-gas containing anions  $\text{ClLiClNgO}^-$  will be investigated.

## Methods

MP2 and CCSD(T) electronic structure theory are used, and the basis sets are used Dunning-type aug-cc-pVnZ (abbreviated as apnZ)<sup>4</sup>. The electronic structure calculations were performed using the Gaussian 16 program, revision C01 and electron density profiles using Multiwfn.<sup>5</sup>

## Results and Discussion

### Structures

In figure 1, the structures of  $\text{ClLiClNgO}^-$  ( $\text{Ng} = \text{Ar, Kr, Xe}$ ) are linear and nonlinear, depending on the different theoretical methods we use. The bond length of  $\text{Cl-Ng}$  are 2.994~3.077 Å,  $\text{Ng-O}$  are 1.719~1.929 Å. We know that the  $\text{Cl-Ng}$  and  $\text{Ng-O}$  bond length of  $\text{ClLiClNgO}^-$  increases with the increase of noble gas atomic number. For  $\text{XNgO}^-$  ( $\text{X} = \text{ClLiCl, F and Cl, Ng} = \text{Ar, Kr, Xe}$ ) when increasing of noble gas atomic number, if we compare  $\text{ClLiClNgO}^-$  with  $\text{FNgO}^-$ : (a)  $\text{X-NgO}^-$  increase 0.753, 0.754 and 0.784 Å, respectively; compare  $\text{ClLiClNgO}^-$  with  $\text{ClNgO}^-$  (a)  $\text{X-NgO}^-$  slightly increase 0.158, 0.165 and 0.172 Å. (b)  $\text{XNgO}^-$  increase 0.009 Å, decrease 0.013 and 0.029 Å when compare with  $\text{FNgO}^-$  and compare with  $\text{ClNgO}^-$  (b)  $\text{XNgO}^-$  increase 0.003 Å, decrease 0.008 and 0.017 Å. They have not changed significantly.

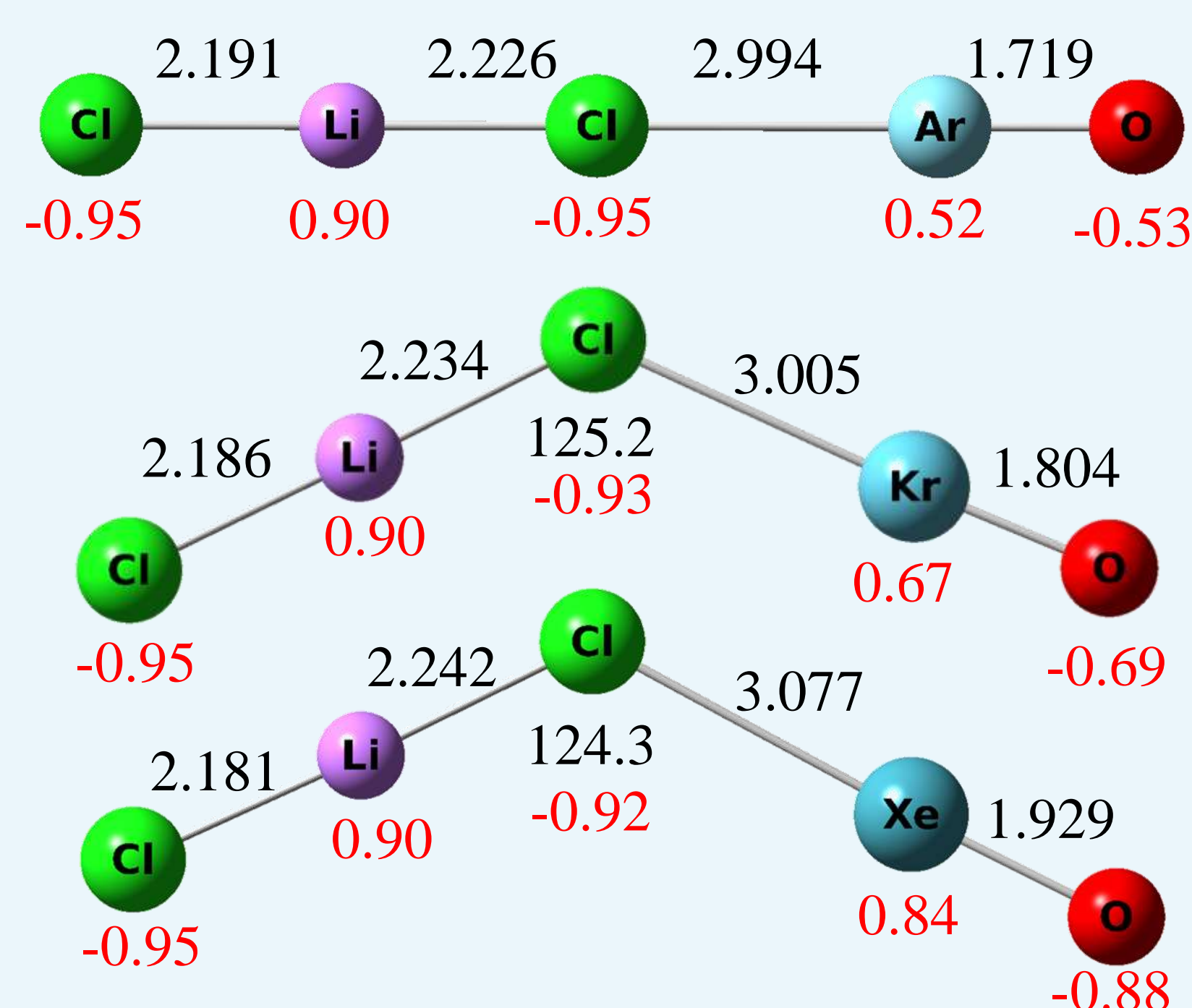


Figure 1. The structures of  $\text{ClLiClNgO}^-$ , unit: Å and °. NBO charge (in red).

### Stability

In Figure 2, we consider all the most plausible dissociation pathways.

(P1)  $\text{ClLiClNgO}^- \rightarrow \text{ClLiCl}^- + \text{NgO}$

(P1-1)  $\text{ClLiClNgO}^- \rightarrow \text{ClLiCl}^- + \text{Ng} + \text{O(S)}$

(P2)  $\text{ClLiClNgO}^- \rightarrow \text{ClLiCl}^- + \text{Ng} + \text{O}^-(\text{D})$

(P3)  $\text{ClLiClNgO}^- \rightarrow \text{ClLiCl}^- + \text{Ng} + \text{O(T)}$

(P4)  $\text{ClLiClNgO}^- \rightarrow \text{ClLiOCl}^- + \text{Ng}$

For  $\text{ClLiClNgO}^-$ , the  $\text{Ng-O}$  bond energies (P1-1) is nearly equal to  $\text{Ng-O}$  of  $\text{ONg}$

(P0:  $\text{ONg} \rightarrow \text{O} + \text{Ng}$ ). This implies that  $\text{ClLiClNgO}^-$  does not affect bond energies of  $\text{Ng-O}$ .

The results show that the stability of  $\text{ClLiClNgO}^-$  are determined by two decomposition pathways: the (P1) pathway is endoergic by 11.9 kcal/mol for  $\text{Ng} = \text{Ar}$ . The barrier of the (P4) pathway is 7.9 kcal/mol for  $\text{Ng} = \text{Ar}$ .

Moreover, for (P3) pathway, the rates of intersystem crossing would be limited by the thermal activation to the crossing points. The triplet state now crosses at much larger  $\text{Ar-O}$  distance (0.150 Å longer than equilibrium bond distance) where the energy is ~3 kcal/mol higher.

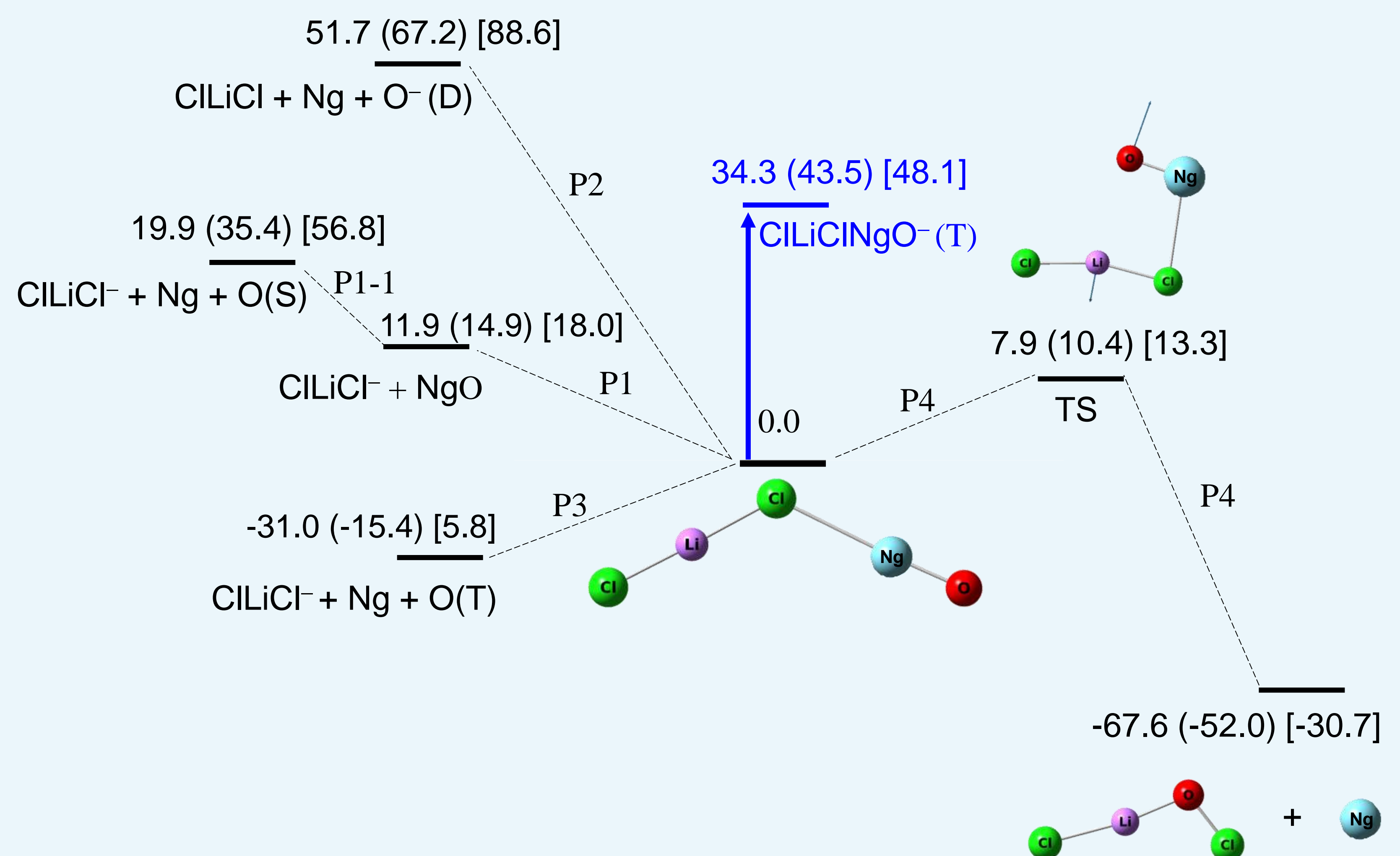


Figure 2. The calculated potential energy (in kcal/mol) profile of  $\text{ClLiClNgO}^-$ .

### Electron density distribution

From electron density profile (figure 3) and NBO charge distribution (Figure 1),  $\text{ClLiCl}^-$  can induce  $\text{Ng-O}$  bonds:  $\text{ClLiCl}^- \dots \text{Ng=O}$ , like  $\text{FNgO}^-$  are ion-dipole interaction:  $\text{F}^- \dots \text{Ng=O}$ .

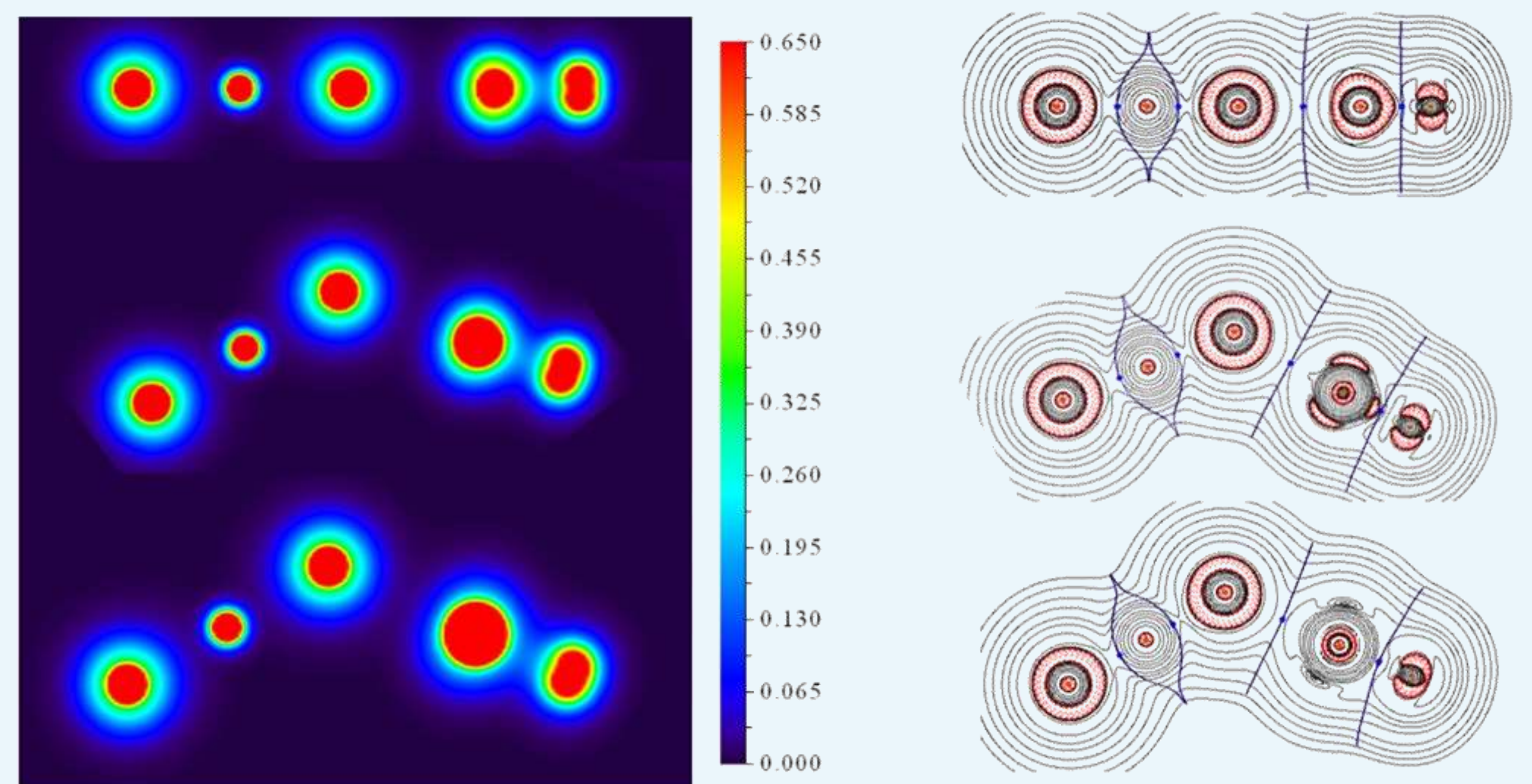


Figure 3. Contour plots of the calculated electron density of  $\text{ClLiClNgO}^-$ .

## Conclusions

This study investigated the structures and stability of  $\text{ClLiClNgO}^-$ . When noble gas atoms are Ar, Kr and Xe, the anion molecules are found to be stable at low temperature.

Importantly, a new type of noble-gas containing anions and including superhalogen  $\text{ClLiCl}^-$ .  $\text{ClLiClNgO}^-$  were stable by ion-dipole interaction ( $\text{ClLiCl}^- \dots \text{Ng=O}$ ). In the future, it will be possible to design types of noble-gas containing anions on different types of superhalogen molecules.

## References

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