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Molecular structure calculations of monomeric and dimeric of rare earth chlorides

S. DALGIC*, M. CALISKAN
Department of Physics, Trakya University, 22100, Edirne, Turkey

In this work, the molecular geometries and vibrational frequencies of selected rare-earth trichlorides (YCl_3 , $CeCl_3$, $DyCl_3$) and their dimerics were computed using the interionic force model. In order to the determine of the model parameters, we have fitted the measurement value of the breathing mode of molecular dimerics in molecular structure calculations. It has been indicated that the ground state structures of monomeric rare-earth thrichlorides have D_{3h} symmetry and their dimerics have D_{2h} symmetry. The results for the equilibrium bond lengths, bond angles and vibrational frequencies are compared with the measured values obtained from electron diffraction and with the results of other theoretical calculations. The agreement can be considered as very reasonable.

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1. Introduction

A number of industrial and technical applications of the rare-earth halides have motivated interest to the study of the chemical and physical properties of these materials. The extraction and processing of rare-earth metals are based on molten salt technologies, motivating an intense effort at determining the thermodynamic and structural properties of these liquids by both experimental and simulation method [1]. Intensive studies have also been made for a number of years of their vapours and of the volatile complexes that they form with alkali or aluminium halides, in view of potential applications related to new energy sources, energy conservation and recycling or separation processes [2,3].

Presently, quantum chemical computations can provide the most detailed structural and vibrational information about rare-earth halides and their dimers. Though the calculated absolute values of the molecular parameters suffer from different errors of the computational methods, computed differences between a monomeric and its dimeric are much more reliable. Using this advantage, a combination of experimental and computational information makes both the identification of dimers and the determination of reliable structural an vibrational data possible [4].

In attempting to develop a refined model for the ionic interaction in rare-earth halides, we have followed the approach developed by Akdeniz et.al. for the simplest MX_3 monomers [5-7]. Recently, it has been applied to chalcogenide clusters for the investigation of their molecular, static and dynamic structure [8-10]. As it has evidenced in the work of Molnar and Hargittai [11], the shape of these molecules has been a matter of controversy for a number of years.

The experimental investigation of metal halide molecular structures started with the beginning of elektron diffraction (ED) technique, in the 1930s [12-15]. A second wave of their investigation came in the mid-1950s. The emerging Moscow ED group, mostly Akishin, Spiridonov, Rambidi, and associates, investigated practically all metal Halide molecules as they marked their may through the periodic table [16-18]. It was also at that time that a relatively new technique microwave spectroscopy (MW) was applied to the alkali halides, one of the few groups of metal halides that could be targeted by MW [19]. Thus gas-phase ED has been the principal tool for their investigation. The Moscow ED studies were truly pioneering in learning about the behaviour and geometries of these high temperature species.

During the past 20 years, computations have become feasible for metal halides. Before that very few and relatively low-level studies appeared. Even today, the quality of the results is not always on a par with that of computational data on small organic molecules. The increasing number of computational studies and the enhanced role of computations in getting geometrical information about metal halides lends special importance to the difference in the physical meaning of geometrical parameters originating from different techniques. A number of subsequent quantum-chemical (QC) calculations, as listed in the review of Hargittai [20], have shown that especially for the heavier members of the rare-earth series the results is sensitive to the theoretical approach: Hartree-Fock (HF) calculations tend to yield a planar structure, whereas computations including correlation effects lead to pyramidal geometries.

In this work, we present a theoretical calculations based on the interionic force model which is successfully used to describe the inter-ionic interactions in rare-earth trichlorides. The goal of the present study is to provide a model of the computational studies on the structural and vibrational frequencies of selected rare-earth trichlorides and their dimerics.

2. Theory

The microscopic model proposed for MCl_3 incorporates (a) the Born model of cohesion in the crystalline state, which attributes binding to electrostatic interactions between ions and ascribes the equilibrium state to a balance between that the net coulombic attractions and quantal closed-shell overlap repulsions [21]. (b) The shell model for vibrational motions and crystal defect, which accounts for ion core polarizability via both dipol induction by the internal electric field and changes in the state of closed-shell overlap due to relative displacements of first neighbours [22]. Electron-shell deformability is described through (a) effective valances z_i subject to overall charge compensation and (b) electrical and overlap polarizabilities of the halogens.

It has been reported that the form of the potential energy $U(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})$ of a molecular cluster in an arbitrary configuration as a function of the bond vector $\mathbf{r}_{ij}$ and of the electric dipol moments $\mathbf{p}_i$ carried by the ions. This is

$$U(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\}) = \sum_{i\neq j}\left[\frac{1}{2}\frac{z_i z_j e^2}{r_{ij}} + \Phi_{ij}(r_{ij}) - \frac{1}{2}\frac{C_i C_j}{r_{ij}^6} + U_{pol}^{cl}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\}) + U_{shell}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})\right]. \quad (1)$$

The successive terms are Coulombic energy of the ionic point charges , the overlap repulsive and van der Waals energies , clasical polarization energy U_{pol}^{cl} associated with the induced dipoles and the shell deformation energy U_{shell}. The overlap repulsive energy in Eq. (1) is taken in the Busing form [23]

$$\Phi_{ij}(r_{ij}) = f(\rho_i + \rho_j)\exp\left[\frac{R_i + R_j - r_{ij}}{\rho_i + \rho_j}\right] \quad (2)$$

where *f* has the standard value $f = 0.05$ $e^2/Å^2$. R_i and ρ_i are characteristic radii and hardness parameters for individual ions. Simple proportionality between R_i and ρ_i holds for polyvalent metal ions [24]. Finally, the classical polarization energy is

$$U_{pol}^{cl}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\}) = \sum_{i\neq j}\left[-z_i e\frac{\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^3} + \frac{1}{2}\frac{\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ij}^3} - \frac{3}{2}\frac{(\mathbf{p}_i\cdot\mathbf{r}_{ij})(\mathbf{p}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} + \frac{1}{2\alpha_h}\sum_j p_j^2\right] \quad (3)$$

and the shell deformation energy can be written as

$$U_{shell}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\}) = \frac{\alpha_s}{\alpha_h}\sum_{i_j,j}\mathbf{p}_j\cdot\hat{\mathbf{r}}_{ij}\left|\frac{d\Phi_{ij}(r_{ij})}{dr_{ij}}\right| \quad (4)$$

where α_h is the electrical polarizability of the halogen and α_s is a short-range polarizability. The sum is in restricted to run over i_j = metal ions which are first neighbours of the *j*-th halogen . Minimization of (1) with respect to the dipoles yields the dipole p_h on a halogen as

$$\mathbf{p}_h = \alpha_h\mathbf{E}_h(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\}) + \alpha_s\sum_{i_j}\hat{\mathbf{r}}_{ih}\left|\frac{d\Phi_{ih}(r_{ih})}{dr_{ih}}\right| \quad (5)$$

where E_h is the self-consistent electric field on the halogen .

3. Results and discussion

The presentation of the results is divided into two parts. The first one concerns with molecular structure for which the experimental data are available. The second one deals with vibrational frequencies in rare-earth trichlorides. The equilibrium of MCl_3 and M_2Cl_6 molecules are described as follows: (a) This is for the optimization of the molecule by minimization of its energy towards states of static (stable and unstable) equilibrium. (b) This is for the evaluation of its vibrational frequencies and of its dynamic evaluation constant energy.

The parameters which enter the short-range overlap interactions involving Cl ion can be taken from earlier studies of alkali halides [7] , while a simple proportionality holds between R_i and ρ_i for the metal ions (R_M / ρ_M = 18.6 ; Li-Tosi [24]). With the above simplifications our model for MCl_3 involves three disposable parameters. These are (a) the ionic radius of the metal ions R_M (b) the effective valance of the metal ions

Z_M and (c) the electrical polarizability of the chloride ion α_X. We take $Z_M = -3 Z_X$ and $R_X / \rho_X = 7.18$. The proposed values for the model parameters of the presented systems are given in Table1 together with the others which are taken in Refs.[7,25,26].

Table 1. Input parameters for Y, Ce and Dy-chlorides (the subscrips M and X denote the trivalent-metal ion and the halogen ion). The meaning of the parameters is discussed in the main text.

	Z_M	Z_X	R_M [b] (Å)	ρ_M (Å)	R_X [a] (Å)	ρ_X [a] (Å)	C_X [a] (eÅ$^{5/2}$)	α_X [a, c] (Å^3)	α_S [a, c] (Å^3/e)
YCl_3	2.259	-0.753	1.20	0.0645	1.71	0.238	5.50	3.00	0.83
$CeCl_3$	2.418	-0.806	1.41	0.0758	1.71	0.238	5.50	2.05	0.46
$DyCl_3$	2.328	-0.776	1.22	0.0656	1.71	0.238	5.50	3.00	0.83

[a] Ref.[7] , [b] Ref.[25] , [c] Ref.[26].

3.1. Yttrium Chlorides

We report our results for the geometrical structure of monomeric and dimeric of yttrium chloride in Table 2 (distances in Å, angles in deg.). Our result for the shape of this molecule can be compared with these obtained from second-order Moller-Plesset perturbation theory (MP2) calculations as reported in the review of Hargittai [20]. It can be seen that our results for the bond lengths and bond angles of YCl_3 and Y_2Cl_6 agree well with the values calculated by the previous work reported in Ref.[20]. There are no experimental and theoretical results for the bond angles of YCl_3 to compare with our results.

Table 2. Calculated geometrical parameters of the monomeric (YCl_3) and dimeric (Y_2Cl_6).

Parameters	Present work	MP2 [a]
Monomeric		
r (Y_1-Cl_2)	2.438	2.437
r (Y_1-Cl_3)	2.438	-
r (Y_1-Cl_4)	2.438	-
r ($Cl_2 \cdots Cl_3$)	4.223	-
r ($Cl_2 \cdots Cl_4$)	4.223	-
r ($Cl_3 \cdots Cl_4$)	4.223	-
$\angle$ (Cl_2-Y_1-Cl_4)	120.00	-
$\angle$ (Cl_3-Y_1-Cl_4)	120.00	-
$\angle$ (Cl_2-Y_1-Cl_3)	119.99	-
Dimeric		
r (Y_1-Y_2)	3.722	-
r (Y_1-$Cl_{3,4}$)= r (Y_2-$Cl_{7,8}$)	2.420	2.420
r (Y_1-$Cl_{5,6}$)= r (Y_2-$Cl_{5,6}$)	2.611	2.616
r (Y_1-$Cl_{7,8}$)= r (Y_2-$Cl_{3,4}$)	5.332	-
r (Cl_3-Cl_4)= r (Cl_7-Cl_8)	4.235	-
r (Cl_3-$Cl_{5,6}$)= r (Cl_5-$Cl_{7,8}$)	4.127	-
r (Cl_4-$Cl_{5,6}$)= r (Cl_6-$Cl_{7,8}$)	4.127	-
r (Cl_3-Cl_7)= r (Cl_4-Cl_8)	6.064	-
r (Cl_3-Cl_8)= r (Cl_4-Cl_7)	7.397	-
r (Cl_5-Cl_6)	3.663	-
$\angle$ (Cl_3-Y_1-Cl_4)= $\angle$ (Cl_7-Y_2-Cl_8)	122.03	118.10
$\angle$ (Cl_5-Y_1-Cl_6)= $\angle$ (Cl_5-Y_2-Cl_6)	88.97	84.10
$\angle$ (Y_1-Cl_6-Y_2)= $\angle$ (Y_1-Cl_5-Y_2)	91.02	-

[a] Ref.[20].

The calculated molecular structures for monomeric and dimeric of yttrium chloride with interionic force model are shown in Figs 1.a and 1.b. It is clear in Fig.1 that YCl_3 has D_{3h} symmetry and Y_2Cl_6 has D_{2h} symmetry [27].

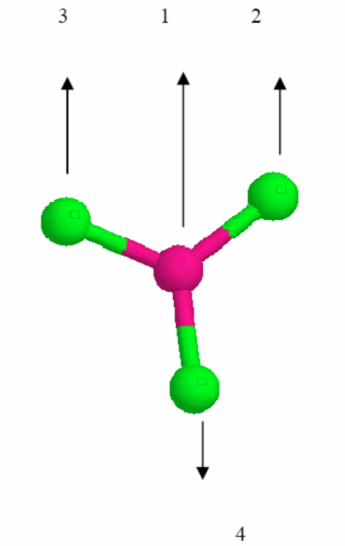

Fig. 1.a.The molecular structure of YCl_3 monomeric. Equilibrium geometries D_{3h}.

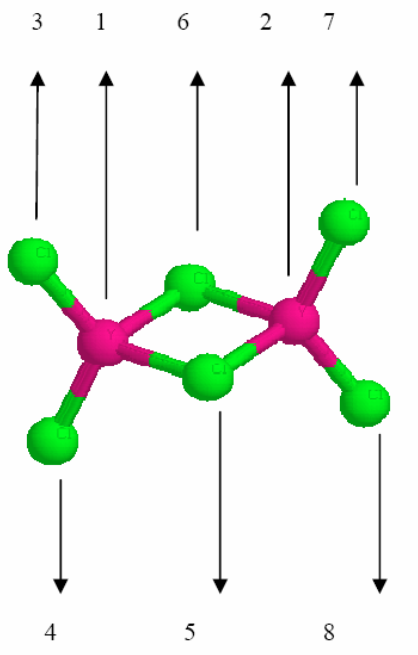

Fig. b.The molecular structure of Y_2Cl_6 dimeric. Equilibrium geometries D_{2h}.

Table 3 : Calculated geometrical parameters of the monomeric ($CeCl_3$) and dimeric (Ce_2Cl_6).

Parameters	Present work	QC [b]	MP2 [a]
Monomeric			
r (Ce_1-Cl_2)	2.625	2.644	2.640
r (Ce_1-Cl_3)	2.625	-	-
r (Ce_1-Cl_4)	2.625	-	-
r ($Cl_2 \cdots Cl_3$)	4.547	-	-
r ($Cl_2 \cdots Cl_4$)	4.546	-	-
r ($Cl_3 \cdots Cl_4$)	4.546	-	-
$\angle$ (Cl_2-Ce_1-Cl_4)	120.07	120.00	-
$\angle$ (Cl_3-Ce_1-Cl_4)	120.07	-	-
$\angle$ (Cl_2-Ce_1-Cl_3)	119.85	-	-
Dimeric			
r (Ce_1-Ce_2)	4.353	-	-
r (Ce_1-$Cl_{3,4}$)= r (Ce_2-$Cl_{7,8}$)	2.624	-	-
r (Ce_1-$Cl_{5,6}$)= r (Ce_2-$Cl_{5,6}$)	2.841	-	-
r (Ce_1-$Cl_{7,8}$)= r (Ce_2-$Cl_{3,4}$)	6.025	-	-
r (Cl_3-Cl_4)= r (Cl_7-Cl_8)	4.666	-	-
r (Cl_3-$Cl_{5,6}$)= r (Cl_5-$Cl_{7,8}$)	4.493	-	-
r (Cl_4-$Cl_{5,6}$)= r (Cl_6-$Cl_{7,8}$)	4.493	-	-
r (Cl_3-Cl_7)= r (Cl_4-Cl_8)	6.757	-	-
r (Cl_3-Cl_8)= r (Cl_4-Cl_7)	8.211	-	-
r (Cl_5-Cl_6)	3.652	-	-
$\angle$ (Cl_3-Ce_1-Cl_4)= $\angle$ (Cl_7-Ce_2-Cl_8)	125.51	-	-
$\angle$ (Cl_5-Ce_1-Cl_6)= $\angle$ (Cl_5-Ce_2-Cl_6)	79.86	-	-
$\angle$ (Ce_1-Cl_6-Ce_2)= $\angle$ (Ce_1-Cl_5-Ce_2)	100.13	-	-

[a] Ref.[20] , [b]Ref.[29].

3.2. Cerium Chlorides

Table 3 reports the calculated bond lengths and bond angles in $CeCl_3$ and Ce_2Cl_6 at ground state equilibrium and compares than with the data of QC calculations and MP2 method taken from Refs.[20,29]. There are no experimental and theoretical results for bond lengths and bond angles of Ce_2Cl_6 to compare with our results.

We have also illustrated the molecular structure of $CeCl_3$ and Ce_2Cl_6 in Figs.2.a and 2.b. In these figures the D_{3h} symmetry for $CeCl_3$ and D_{2h} symmetry for Ce_2Cl_6 are obtained, respectively

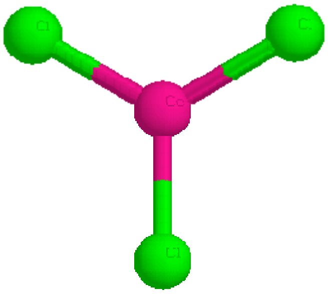

Fig2.a.The molecular structure of $CeCl_3$ monomeric. Equilibrium geometries D_{3h}.

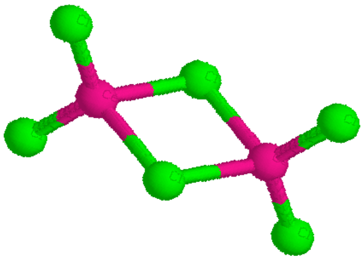

Fig2.b.The molecular structure of Ce_2Cl_6 dimeric. Equilibrium geometries D_{2h}.

3.3. Dysprosium Chlorides

We have also studied bond lengths and bond angles of $DyCl_3$ and their dimers. We report our results compared with the QC, MP2 and Becke's three parameter hybrid method using the Lee-Yang-Parr (B3LYP) correlation functional, where available, in Table 4 [20,29]. It appears in Table 4 that the calculated bond lengths of $DyCl_3$ using the interionic force model are the same value compared with those obtained by QC and MP2 models, but yield longer (by about 0.014 Å) than B3LYP model.

Table 4. Calculated geometrical parameters of the monomeric ($DyCl_3$) and dimeric (Dy_2Cl_6).

Parameters	Present work	QC [b]	B3LYP [a]	MP2 [a]
Monomeric				
r (Dy_1-Cl_2)	2.511	2.511	2.497	2.506
r (Dy_1-Cl_3)	2.511	-	-	-
r (Dy_1-Cl_4)	2.511	-	-	-
r ($Cl_2 \cdots Cl_3$)	4.350	-	-	-
r ($Cl_2 \cdots Cl_4$)	4.350	-	-	-
r ($Cl_3 \cdots Cl_4$)	4.350	-	-	-
∠ (Cl_2-Dy_1-Cl_4)	120.00	120.00	-	120.00
∠ (Cl_3-Dy_1-Cl_4)	120.00	-	-	-
∠ (Cl_2-Dy_1-Cl_3)	119.98	-	119.00	-
Dimeric				
r (Dy_1-Dy_2)	3.806	-	-	-
r (Dy_1-$Cl_{3,4}$)= r (Dy_2-$Cl_{7,8}$)	2.452	2.452	2.449	-
r (Dy_1-$Cl_{5,6}$)= r (Dy_2-$Cl_{5,6}$)	2.643	2.664	2.680	-
r (Dy_1-$Cl_{7,8}$)= r (Dy_2-$Cl_{3,4}$)	5.429	-	-	-
r (Cl_3-Cl_4)= r (Cl_7-Cl_8)	4.300	-	-	-
r (Cl_3-$Cl_{5,6}$)= r (Cl_5-$Cl_{7,8}$)	4.182	-	-	-
r (Cl_4-$Cl_{5,6}$)= r (Cl_6-$Cl_{7,8}$)	4.182	-	-	-
r (Cl_3-Cl_7)= r (Cl_4-Cl_8)	6.164	-	-	-
r (Cl_3-Cl_8)= r (Cl_4-Cl_7)	7.516	-	-	-
r (Cl_5-Cl_6)	3.669	-	-	-
∠ (Cl_3-Dy_1-Cl_4)= ∠ (Cl_7-Dy_2-Cl_8)	122.47	116.7	116.1	-
∠ (Cl_5-Dy_1-Cl_6)= ∠ (Cl_5-Dy_2-Cl_6)	87.93	83.6	84.1	-
∠ (Dy_1-Cl_6-Dy_2)= ∠ (Dy_1-Cl_5-Dy_2)	92.06	96.4	-	-

[a] Ref.[20] , [b] Ref.[29].

The molecular structure of $DyCl_3$ and Dy_2Cl_6 calculated with the presented model are shown in Figs.3.a and 3.b. As it can be seen there, $DyCl_3$ and Dy_2Cl_6 have D_{3h} and D_{2h} symmetries, respectively.

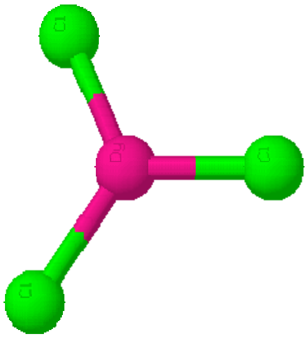

Fig3.a.The molecular structure of $DyCl_3$ monomeric. Equilibrium geometries D_{3h}.

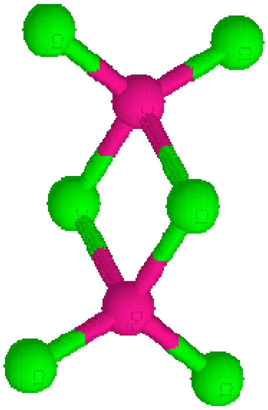

Fig3.b.The molecular structure of Dy_2Cl_6 dimeric. Equilibrium geometries D_{2h}.

3.4. Vibrational Frequencies

The accuracy of the vibrational frequencies is an important consideration for thermodynamic calculations. Computations tend to overestimate frequencies, except for the very modes in the case of floppy molecules, whose values are too small and unreliable. The experimental frequencies, originating from matrix isolation spectroscopy, are usually affected by the matrix and tend to be smaller than the gas-phase values. Therefore, it is desirable to have experimental gas-phase frequencies, even if their determination may be difficult due to the usually high temperatures and the highly populated excited vibrational and rotational levels [20].

The vibrational frequencies are listed in Table 5. We have calculated the values for the vibrational frequencies of each monomeric: the ν_1 symmetric stretch, the ν_2 out-of-plane bending, the ν_3 anti symmetric stretch and the ν_4 in-plane bending mode. The Table also includes the mode frequencies as reported by Kovács and Konings [28] for $CeCl_3$ and $DyCl_3$ and as reported by Hargittai [20].

Table 5. Vibrational frequencies (in cm^{-1}) of rare-earth chlorides from experiment and computation.

		ν_1	ν_2	ν_3	ν_4
YCl_3	Present work	349	24	370	75
	gas-IR [a]	-	-	370	-
$CeCl_3$	Present work	307	18	317	61
	QC [b]	292	26	317	61
$DyCl_3$	Present work	324	23	335	69
	QC [b]	311	38	335	70

[a] Ref.[20] , [b] Ref.[29].

For the computational details of the presented model, the contributions of the ground state energy expressed in Eq. (1) have been listed in Table 6. According to the our knowledge that the experimental and theoretical values for the energy contributions of these molecules have not been reported yet. The first column as U_c+U_r in Table 6 represent the sum of coulombic and the overlap repulsive energies. The contribution of Van der Waals interaction to the potential energy has shown in second column. The U^{cl}_{pol} represents the values for the classical polarization energy. The results for the shell deformation energy are given as U_b. As it is mentioned that all these contributions are negative values, except U_b , to the potential energy. It has noted that the largest contribution comes from the coulombic and repulsive interactions of the ionic point charges. The polarization energy is also still dominant in which can describe the equilibrium structure of the presented molecules.

Table 6. Various contributions to energy (in eV) of rare-earth chlorides.

	U_c+U_r	Uvw	U^{cl}_{pol}	U_b	U_T
YCl_3	-1.4607	-0.0159	-0.3547	0.1254	-1.7061
Y_2Cl_6	-3.1686	-0.0735	-0.7855	0.2528	-3.7748
$CeCl_3$	-1.5637	-0.0102	-0.2210	0.0712	-1.7237
Ce_2Cl_6	-3.2056	-0.0488	-0.4121	0.1224	-3.5441
$DyCl_3$	-1.5160	-0.0133	-0.3376	0.1210	-1.7459
Dy_2Cl_6	-3.7640	-0.0686	-0.8787	0.2989	-4.4124

4. Conclusions

In this work, we present a simple ionic model for equilibrium structure of monomeric and dimeric of rare-earth chlorides. Our main attention has been on the model parameters as effective valance, ionic radius and electronic polarizability of the rare-earth ions, for which we proposed same simple and reasonable trends across the whole systems of chlorides. Our results are in good agreement with the available experimental values and other theoretical calculations.

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*Corresponding author: dseyfe@yahoo.co.uk