

Bonding in the Extended Metal Chain Compound $\text{La}_4\text{Cl}_5\text{C}_2$

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The rare-earth metal halides form a variety of highly reduced phases that contain metal clusters. The basic framework in most of these compounds consists of either discrete or condensed edge-sharing M_6X_{12} -type octahedral cluster units that are interstitially centered by an endohedral entity ranging from main group atoms to transition metals. The halogen atoms are located over free edges of the metal octahedra. Over the past 30 years the structures of a large number of new cluster compounds of rare-earth metal halides have been described in the literature.¹⁻⁶ These rare-earth cluster units may be understood as anti-Werner complexes with the endohedral atom surrounded by a first coordination sphere of rare earth metal atoms and a second coordination sphere of halogen atoms.⁶

The C_2 interstitials are found endohedrally in octahedral M_6 clusters, not only in isolated clusters as in $\text{Sc}_6\text{I}_{11}\text{C}_2$ but also in condensed cluster halides as in $\text{Sc}_4\text{I}_6\text{C}_2$.⁷ The former contains isolated Sc_6C_2 clusters and might be viewed as $(\text{Sc}^{3+})_6(\Gamma)_{11}(\text{C}_2^{6-})(e^-)$ with scandium in the oxidation state of +2.83. In $\text{Sc}_4\text{I}_6\text{C}_2$, scandium has an oxidation state of +3. The excess electrons may not only be delocalized, as in metallic $\text{Sc}_{0.9}\text{I}_2$,⁸ but may also be localized at the atoms (Sc^{2+}) or in Sc-Sc bonding, as evidenced by the short Sc-Sc distance in NaSc_2I_6 .⁹

We give here a detailed analysis of the electronic and bonding aspects for the $\text{La}_4\text{Cl}_5\text{C}_2$ phase with 1-D metal cluster chain structures. This compound occurs in the orthorhombic space group $Immm$: $a = 3.921 \text{ \AA}$, $b = 7.945 \text{ \AA}$, $c = 17.297 \text{ \AA}$.¹⁰ In $\text{La}_4\text{Cl}_5\text{C}_2$ (with C_2^{5-} and Cl^-), lanthanum has an oxidation state of +2.5, if a purely ionic model is considered. Hence, there are two excess electrons per formula unit, according to $(\text{La}^{3+})_4(\text{Cl}^-)_5(\text{C}_2^{5-})\cdot 2e^-$. The focus of the present work is on where these electrons reside and what role they play in chemical bonding of this compound. These electrons are likely to reside in the shortened La-La bonds of shared edges between the La_6 octahedra running parallel to the a -axis. In other words, the La_6 octahedron is held together in chains by stronger La-La bonding forming the common *trans* edges. Computational analysis of the La-La, La-C, and La-Cl interactions reveals that the dominant bonding contributions in this compound come from the La-C and La-Cl components, in contrast to the La-La cluster interactions. The molecular orbital energy levels, the density of states (DOS) and the crystal orbital overlap population (COOP) curves were computed using the extended Hückel tight-binding (EHTB) method^{11,12}; atomic parameters are given in

Table 1. Parameters for EH calculations

atom	orbital	H_{ii} , eV	ζ_1^b	ζ_2^b	c_1^a	c_2^a
La	5d	-8.21	3.780	1.381	0.7765	0.4586
	6s	-7.67	2.14			
	6p	-5.01	2.08			
Cl	3s	-26.3	2.183			
	3p	-14.2	1.733			
C	2s	-21.4	1.625			
	2p	-11.4	1.625			

^aCoefficients used in double- ζ expansion. ^bSlater-type orbital exponents.

Table 1.

Figure 1 views the structure of $\text{La}_4\text{Cl}_5\text{C}_2$ down the short (3.921 Å) a axis. The La_4Cl_6 chains run down the crystallographic a axis, whose length (3.921 Å) is identical with that of the La1-La1 edge of the rectangular face that is bridged by Cl1. The La_4Cl_6 chains are surrounded by edge-bridging Cl atoms, which also connect them. The arrangement of lanthanum atoms is seen to generate nominal metal octahedra that share *trans* edges to form infinite chains, while

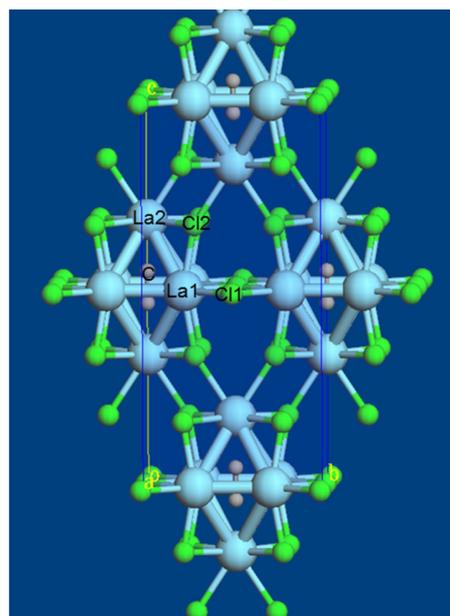


Figure 1. Projection of the crystal structure of $\text{La}_4\text{Cl}_5\text{C}_2$ along the a -axis with unit cell outlined. The infinite chains are comprised of the octahedral metal clusters running parallel to the a -axis and are interconnected by edge-bridging chlorine atoms. The C_2 units are centered within these clusters.

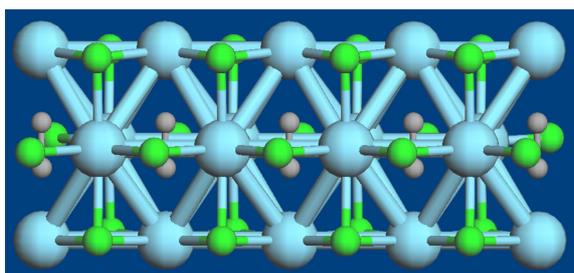


Figure 2. Portion of the infinite chain of edge-sharing La_6 octahedra in $\text{La}_4\text{Cl}_5\text{C}_2$ (La, Cl, and C atoms, respectively, drawn with decreasing size).

chlorine atoms bridge all exposed edges of these octahedra. The octahedra contain C_2 units as an interstitial, where the C_2 unit is parallel to the c axis. The octahedral base is distorted to a rectangle with edges of 3.399 and 3.921 Å. The three-dimensional structure can be generated easily if the cluster chains are linked by four-coordinate chlorine (Cl2) in a planar array ($\text{La2-Cl2} = 2.951$ Å) and edge-bridging chlorine (Cl1) atoms at the waist of the metal octahedra ($\text{La1-Cl1} = 3.001$ Å). A view of a portion of an individual chain (Figure 2) illustrates the result of condensation of M_6X_{12} -type clusters with chloride ligands capping the edges of the metal octahedron.

The $\text{La}_4\text{Cl}_5\text{C}_2$ structure exhibits some of the characteristic features of condensed clusters. The shared La1-La1 edges are in the shortest La-La distance at 3.399 Å. The other La1-La1 edges (3.921 Å) are elongated along the chain. A longer separation between these La1 and the apical La2 atoms of the octahedron is 3.983 Å. The C_2 unit is side-on and end-on bound to the four waist metal atoms ($\text{La1-C} = 2.692$ Å) and the two vertices ($\text{La2-C} = 2.303$ Å), respectively. The short La2-C value, 2.303 Å, is much less than the sum of single-bond radii for lanthanum and carbon atoms (2.46 Å).¹³ Although lines have not been included in Figure 1 to represent La-C bonding interactions, these contacts are certainly strong (see below). The C-C distance, 1.44 Å, is in between the values of a C-C single bond (1.54 Å) and a C=C double bond (1.34 Å). In an approximate manner, we can therefore assign the charge as $(\text{C}_2)^{5-}$ for this C_2 unit.

Results and Discussion

An understanding of the chemical bonding in $\text{La}_4\text{Cl}_5\text{C}_2$ needs simpler structure. Let us focus on a $\text{La}_6\text{Cl}_{14}\text{C}_2$ cluster taken out from the $\text{La}_4\text{Cl}_5\text{C}_2$ lattice. Molecular orbital calculations are performed on the C_2 -centered La_6 octahedral cluster system as well as the C_2 -free structure in order to judge the effect of the interstitial C_2 on the stabilization of clusters. The C_2 interstitial exists as C_2^{5-} , similar to other compounds such as $\text{Gd}_{12}(\text{C}_2)_3\text{I}_{17}$ [14] and $\text{Dy}_{12}(\text{C}_2)_3\text{I}_{17}$,¹⁵ with the C-C distance (1.44 Å) comparable with those in these compounds. This bond distance corresponds to the shortened C-C single bonds, thus suggesting the simple electron partitioning of $(\text{La}^{3+})_4(\text{Cl}^-)_5(\text{C}_2^{5-})_2e^-$ with two excess electrons per formula unit. With Cl^- and $(\text{C}_2)^{5-}$

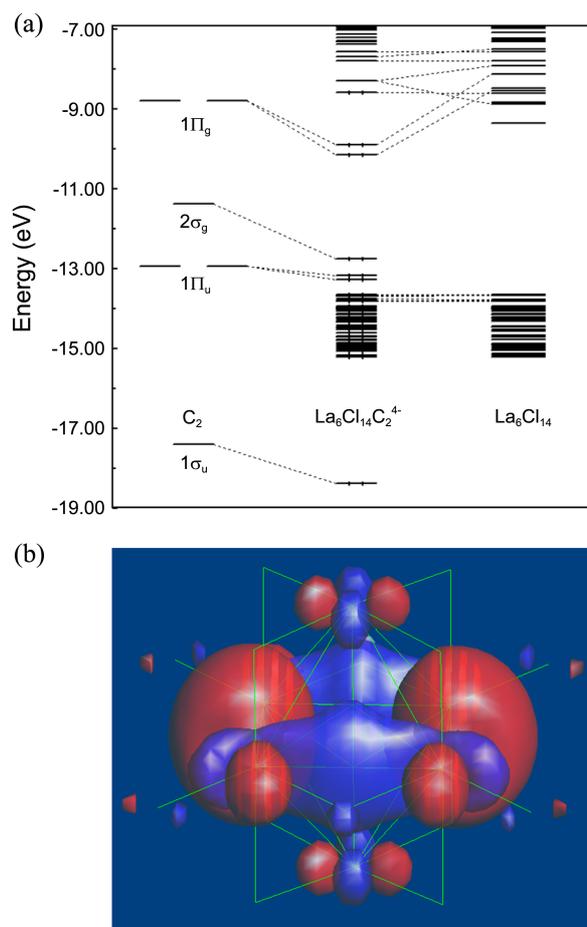


Figure 3. (a) Orbital interaction diagram of the $\text{La}_6\text{Cl}_{14}\text{C}_2^{4-}$ cluster observed in $\text{La}_4\text{Cl}_5\text{C}_2$. (b) Plot of the highest occupied x^2-y^2 orbitals of $\text{La}_6\text{Cl}_{14}\text{C}_2^{4-}$.

lanthanum has the oxidation state of +2.5. This leaves three excess electrons per $\text{La}_6\text{Cl}_{14}\text{C}_2$ cluster, *i.e.*, $(\text{La}_6\text{Cl}_{14}\text{C}_2)^{4-}$. These electrons are responsible for La-La bonding interactions which are covalent in character.

In order to clarify more localized bonding interactions, fragment molecular orbital (FMO) analysis is made of the distinct $\text{La}_6\text{Cl}_{14}\text{C}_2^{4-}$ cluster. Figure 3(a) shows an interaction diagram between $\text{La}_6\text{Cl}_{14}$ states and C_2 orbitals. The resulting molecular orbital levels are shown schematically in Figure 3(a). These levels will correlate directly with the states in the infinite chains. A closer inspection of the frontier orbitals of this cluster reveals that the highest occupied (HO) La-La $\sigma(x^2-y^2)$ bonding orbital (Figure 3(b)) exists right above the C_2 $1\pi_g$ orbitals. Just above the HOMO level three t_{2g} (xy , xz , and yz orbitals) bonding levels are found, with the shared La-La edges. All these levels are also of weakly La-Cl antibonding character. Thus the filling of these levels with some additional electrons will stabilize the structure slightly. This may be achieved by intercalation of cations into the structure.

Once C_2 (C-C distance: 1.44 Å) is present as an interstitial in the $\text{La}_6\text{Cl}_{14}\text{C}_2^{4-}$ cluster, its molecular orbital levels will become different from the isolated one. The order of

increasing energies of the molecular orbitals for an isolated C_2 is $1\sigma_g$, $1\sigma_u$, $1\pi_u$, $2\sigma_g$, and $1\pi_g$. This is shown at left in Figure 3(a). All the metal-metal bonding “acceptor” orbitals, except for the x^2-y^2 , can interact with the lower lying C_2 “donor” orbitals to form metal-carbon bonding (occupied) and antibonding (unoccupied) combinations. Orbital interactions of filled $1\pi_g$ with the empty La $d\pi$ states yield La-C($1\pi_g$) bonding combinations around -10.1 eV. Backbonding from filled $1\pi_g$ orbitals of the C_2 unit into empty d states of the La atoms obviously leads to a certain degree of electron delocalization. The $1\pi_g$ orbitals are stabilized greatly in the C_2 -to-metal π backbonding process. This type of bonding removes electron density from the C_2 . Therefore, C_2 is formally present as C_2^{5-} and enhanced La-La bonding always occurs together with La-C bonding in $La_4Cl_5C_2$. It may be noted that the bonding La-C($1\pi_g$) combination contains more carbon contribution than lanthanum. The $1\sigma_u$ and $2\sigma_g$ orbitals interact with z^2 orbitals of the two axial La neighbors to form La-C bonding combinations (near -18.4 and -12.8 eV). One can see that they have been considerably stabilized by mixing with the lanthanum orbitals. A stabilization of the $La_6Cl_{14}C_2$ cluster structure on inclusion of C_2 is evident.

A better theoretical picture can be extracted from band structure calculations. These calculations were performed for $La_4Cl_6C_2^-$ chains. Figure 4(a) shows the DOS plot calculated for the chain system. The density of states can be divided into several distinctive regions. Contributions of chloride p-block states to the total DOS are shown in the energy region between -13.5 and -15.5 eV, followed by three main peaks stemming predominantly from C_2 molecular orbitals. At higher energies the lanthanum d bands are only partially occupied. These valence bands are made up predominantly of lanthanum x^2-y^2 states. Contributions of most La d states to the total DOS are found, with dominant portions above the Fermi level.

A graphical interpretation of the COOP (Figure 4(b)) reveals that there are rather strong La-La bonding states right below the Fermi level. The vacant La $d\pi$ bonding states are also involved in bonding with C_2 $1\pi_g$. The $1\pi_g$ states (*ca.* -9.5 to -10.8 eV) are La-C bonding and C-C antibonding. The $2\sigma_g$ and $1\pi_u$ states fall just above the energy block of the chloride p states. The $2\sigma_g$ and $1\pi_u$ states (*ca.* -12.5 to -13.5 eV) are not only C-C bonding but also La-C bonding. Finally, the $1\sigma_u$ state (*ca.* -18.5 eV) is much less antibonding through the mixing with the $2\sigma_u$ orbital, but clearly La-C bonding. These may be compared with the interaction diagram in Figure 3(a). It is interesting to note in Figure 4(a) that the C_2 states have five peaks below the Fermi level which are derived from the $1\sigma_g$, $1\sigma_u$, $1\pi_u$, $2\sigma_g$, and $1\pi_g$ orbitals. This implies that the number of C_2 occupied states is close to that for a C-C single bond, giving a bond order of one. The integrated overlap population (OP) of 0.81 for the C-C bonds in $La_4Cl_5C_2$ is closer to the value of a C-C single bond than that of a C=C double bond (0.74 and 1.30 for ethane and ethylene calculated by EH method, respectively).

Figure 4(b) shows the COOP curves for some selected La-La, La-Cl, and La-C bonds as well as the C-C bond in the

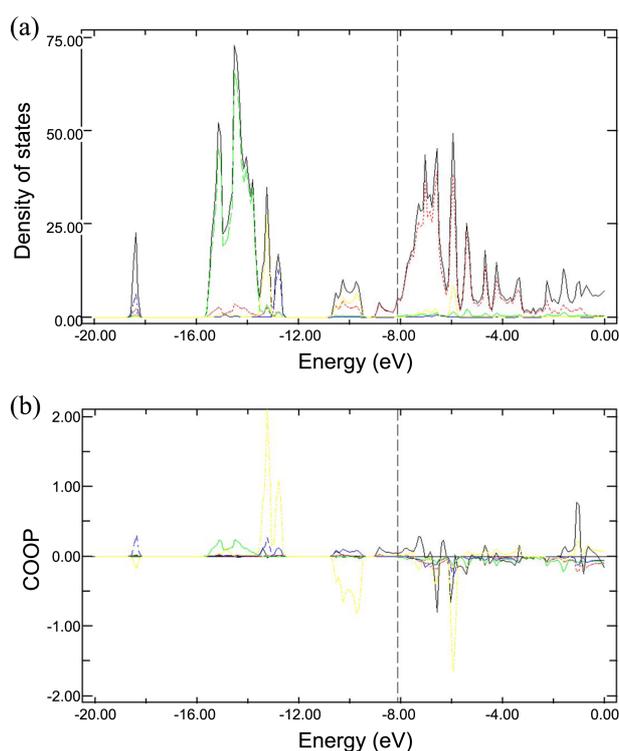


Figure 4. (a) Total DOS (black line) and the contributions of La d (red), Cl p (green), C p_z (σ , blue), and C p_{xy} (π , yellow) orbitals to it in $La_4Cl_6C_2^-$ chains. (b) Crystal orbital overlap populations for La-La (3.399 Å, black), La-La (~ 3.95 Å, red), La-Cl (green), La-C (blue), and C-C (yellow) bonds in $La_4Cl_6C_2^-$ chains. The Fermi level is indicated by the vertical dashed line.

$La_4Cl_6C_2^-$ chain structure. The COOP curves emphasize the major bonding roles of La-C and La-Cl and the lesser La-La contributions. The La-C interactions are distributed over the entire energy region, in contrast to the polar La-Cl interactions. The axial La2-C bond is remarkably short, 2.303 Å, and evidently very strong (OP = 0.62). Note the highly bonding OP value of the La2-C bond. The shortest La-C contact distance observed can be understood from bonding effects from occupied C_2 $2\sigma_g$ and $1\pi_g$ orbitals into the vacant La d orbitals of appropriate symmetry. The La-Cl contacts ranging between 2.951 and 3.001 Å have average overlap populations of 0.29. These La-Cl interactions are responsible for the broad DOS peaks around -14.5 eV (Figure 4(a)). These La-Cl distances are within the normal range as in many other reduced rare earth chlorides. Thus, La-Cl bonding must be covalent.

A substantial difference appears in the OP values for La-La contacts. Comparisons of the refined distances with the OP values for each bond are listed in Table 2. The largest contrasts lie between the three independent La-La distances, which vary from 3.399 to 3.983 Å, their overlap populations vary from 0.02 to 0.10. The small overlap populations pertain to La1-La1 and La1-La2 contacts, 3.921 and 3.983 Å, in distinct contrast to the large overlap populations for the 3.399 Å separations of the shared edges, La1-La1. The La-La separations of shared edges within the La_6 octahedron are unusually short. This short La-La separation may be the

Table 2. Overlap populations (OP) for a pair of atoms in $\text{La}_4\text{Cl}_5\text{C}_2$

bond	bond length (Å)	OP
La1-La1	3.399	0.10
La1-La1	3.921	0.02
La2-La1	3.983	0.04
La2-C	2.302	0.62
La1-C	2.692	0.16
La-Cl	2.951-3.001	0.29
C-C	1.439	0.81

result of relatively strong La-La bonding. Indeed, nearly all states just below the Fermi level have strong La-La σ bonding character and are clearly derived from x^2-y^2 . A substantial fraction of the La 5d bonding states fall above the Fermi level, confirming the above FMO analysis. With an oxidation state of +2.5 for lanthanum, one electron can be allocated to each of the two short La-La bonds in the octahedron. The OP values reflect the strength of La-C, La-Cl, and La-La bonding interactions. The above arguments are consistent with the formal electron partition of $(\text{La}^{3+})_4(\text{Cl}^-)_5(\text{C}_2^{5-})\cdot 2e^-$ for this compound, with the assumption that the excess electrons reside mainly in strong localized La-La bonds within the shared edges between the La_6 octahedra which are considerably shorter than the remaining ones. On the other hand, little is known about the physical properties of this compound.

Conclusion

In summary, the bonding in $\text{La}_4\text{Cl}_5\text{C}_2$ is dominated by strong covalent La-C with lesser La-Cl and La-La interactions. Interstitial C_2 units are essential to the stability of the compound; formally, they provide electrons to the La_6 cage and engage in strong La-C bonding that is much stronger than the La-La bonding. The band structure calcu-

lations for a $\text{La}_4\text{Cl}_5\text{C}_2^-$ chain reveal that $2\sigma_g$ and $1\pi_g$ levels of C_2 are substantially stabilized. All La-C and La-Cl bonding states are occupied and La x^2-y^2 orbitals combine to form the highest occupied x^2-y^2 bonding band. The shortened C-C single bond may be understood by π^* -backbonding from the occupied C_2 $1\pi_g$ orbitals into the empty La $d\pi$ states, in agreement with the formal charge distribution of $(\text{La}^{3+})_4(\text{Cl}^-)_5(\text{C}_2^{5-})\cdot 2e^-$. The two excess electrons are available for intra-cluster bonding and are likely to be localized in the shortened La-La bonds forming the shared edges between the La_6C_2 octahedra within the chain.

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