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# Symmetry and magnetism in $\text{Ni}_9\text{Te}_6$ clusters ligated by CO or phosphine ligands

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The removal of a single ligand from the magnetic  $\text{Ni}_9\text{Te}_6(\text{L})_8$  ( $\text{L} = \text{P}(\text{CH}_3)_3$ , CO) clusters is found to quench the magnetic moment. The reduction in magnetic moment is caused by a geometric deformation of the  $\text{Ni}_9\text{Te}_6$  core that breaks the octahedral symmetry of the cluster. This effect is observed in both the CO and phosphine based ligands. The octahedral symmetry bare cluster is also found to have a large magnetic moment. These results highlight the dilemma faced by magnetic ligand protected clusters whose symmetry has been broken: whether to break the spin symmetry as in Hund's rules or to break the spatial symmetry as in the Jahn-Teller effect. The spatial symmetry breaking is found to be an oblate distortion that forms additional Ni-Te bonds resulting in the enhanced stability of the cluster. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4973609>]

## I. INTRODUCTION

One of the fundamental problems in physics is the appearance of magnetic order. Starting from the atoms, partially filled degenerate electronic levels lead to higher multiplicity ground states in accordance with Hund's multiplicity rule.<sup>1</sup> According to this rule, the filling of the states with parallel spin reduces the electron-electron repulsive interaction although more recent studies have suggested that Hund's rule results from the Fermi correlation between the electrons with parallel spin which leads to a reduced screening of the nucleus in a higher spin state.<sup>2,3</sup> Irrespective of the mechanism, a single atom breaks the spin symmetry to lower its energy by having electrons with parallel spin. This lowering of the energy by breaking of the spin symmetry takes a new dimension as one extends from atoms to form molecules or small cluster of atoms.<sup>4-6</sup> The electronic states in small compact clusters are grouped into shells much in the same manner as in atoms except that the electronic states are spread over multiple atoms.<sup>7</sup> Partially filled states in a degenerate shell then face a dilemma in mechanisms to lower their energy. The cluster can lower its energy by maintaining the spatial symmetry but breaking the spin symmetry and increasing its spin multiplicity in a manner similar to Hund's coupling in atoms resulting in high multiplicity. However, in clusters, any distortion of the cluster that breaks the spatial symmetry can act as a perturbation to remove the degeneracy of the electronic states generally resulting in lowering the energy of some states and raising the energy of others.<sup>8-12</sup> The cluster can therefore lower its energy by breaking the spatial symmetry and filling states with paired electrons through Jahn-Teller distortions. Depending on the magnitude of exchange coupling, one of the two processes dominates and one either ends up with a distorted cluster of low spin multiplicity or a symmetric cluster of higher multiplicity. This competition between

breaking the symmetries of the spatial and spin manifold is central to magnetic order in finite systems.

The purpose of this paper is to demonstrate this intriguing interplay between the geometrical distortion and the stability of magnetic order by considering the ligated chalcogenide cluster  $\text{Ni}_9\text{Te}_6\text{L}_n$  with various ligands ( $\text{L}$ ).<sup>13,14</sup> These clusters belong to a new class of superatoms<sup>15,16</sup> obtained by capping metal-chalcogenide cores with ligands. Recent studies by Nuckolls and co-workers indicate that these superatoms are highly stable, can be prepared in solutions, can have either donor or acceptor characteristics, and can form ionic solids when combined with complementary counterions maintaining their core structure.<sup>17-22</sup> In their initial studies, Nuckolls and co-workers reported  $\text{Co}_6\text{Se}_8(\text{PET}_3)_6$ ,  $\text{Cr}_6\text{Te}_8(\text{PET}_3)_6$ , and  $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$  superatoms where metal-chalcogenide cores were decorated with tri-ethylphosphine ( $\text{PET}_3$ ) ligands attached to metal sites.<sup>17</sup> These clusters are electron donors and form ionic compounds when combined with  $\text{C}_{60}$  with  $\text{C}_{60}$  having a high electron affinity and acting as an acceptor. More recent studies have focused on manipulating metal-ligand bonds to create motifs offering newer features.<sup>23,24</sup> This includes replacing electron donor  $\text{PET}_3$  ligands by electron acceptor CO ligands or isonitriles to form superatomic dimers.<sup>19</sup>

Our interest in  $\text{Ni}_9\text{Te}_6\text{L}_x$  clusters,  $x = 0-8$ , is motivated by the observed magnetic properties of  $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$ . The  $\text{Ni}_9\text{Te}_6$  core with a central Ni and 8 Ni sites occupying the cubic positions is decorated with 8 tri-ethylphosphine ( $\text{PET}_3$ ) ligands attached to Ni sites and 6 Te atoms decorating the 6 cubic faces. The cluster forms a rock-salt (NaCl) solid when combined with  $\text{C}_{60}$ . Experiments indicate that the ionic solid is magnetic and undergoes a ferromagnetic phase transition at low temperatures (4 K) while it exhibits a Curie-Weiss behavior at higher temperatures (above 10 K).<sup>22</sup> SQUID measurements also indicate that the individual clusters behave as isolated localized magnets with a magnetic moment of around  $5.4 \mu_B$  per functional unit. Theoretical studies have examined

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the effect of ligands on the electronic and magnetic properties of the  $\text{Ni}_9\text{Te}_6$  core and bring out several interesting effects.<sup>23–25</sup> First, the electron donor/acceptor characteristics of the metal-chalcogenide cores are controlled by the ligands. In fact, an isolated  $\text{Ni}_9\text{Te}_6$  cluster has a high spin magnetic moment of  $6.0 \mu_B$  and a high ionization potential of 5.88 eV. The addition of 8  $\text{PET}_3$  ligands reduces the ionization potential to 3.33 eV making  $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$  a superalkali and a strong donor. Our studies also showed that the  $\text{PET}_3$  ligands form charge transfer complexes where the metal core gains charge from ligands. The primary effect of charge donation by ligands can be modeled as a quantum well that lifts the electronic spectrum of the cluster making it an electron donor. What is interesting is that the magnetic moment of the cluster is unchanged during the ligation. The studies also show that if the 8  $\text{PET}_3$  ligands are exchanged by an electron withdrawing 8 CO or  $\text{PCl}_3$  ligands, the cluster becomes an electron acceptor with an electron affinity of 3.23 eV for 8 CO ligands and 3.77 eV for 8  $\text{PCl}_3$  ligands.<sup>24</sup> Here, the principal effect is the charge flow from cluster to that lowers the spectrum increasing the electron affinity. Again the addition of ligands leaves the magnetic moment unchanged.

Since the bare  $\text{Ni}_9\text{Te}_6$  and ligated  $\text{Ni}_9\text{Te}_6\text{L}_8$  clusters both have octahedral symmetry, it is important to enquire if the identical magnetic moment for a bare or fully ligated system is driven by the symmetry of the cluster. How are the magnetic moments changed if the cluster has uneven distribution of ligands that allow geometrical (Jahn-Teller) distortions and that can allow the stabilization of the less magnetic/non-magnetic ground state by lifting the degeneracy of the electronic orbitals? We have carried out theoretical first principles studies on  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$  and  $\text{Ni}_9\text{Te}_6(\text{CO})_x$  clusters to investigate the progression of magnetic moment as the ligands are successively added. The studies provide insight into how the symmetry stabilizes the magnetic state at these small sizes providing a unique illustration of spin and symmetry at these nanoscale superatomic clusters.

## II. COMPUTATIONAL DETAILS

First principles theoretical studies of the electronic structure and magnetic moments were carried out using Amsterdam

Density Functional (ADF) set of codes using density functional theory (DFT).<sup>26</sup> A generalized gradient approximation (GGA) functional proposed by Perdew, Burke, and Ernzerhof (PBE) was used to incorporate the exchange and correlation effect.<sup>27</sup> Slater-type orbitals (STOs) located at the atomic sites are used to express the atomic wave function, and the cluster wave functions are formed via a linear combination of these atomic orbitals. The studies used a TZ2P basis set and a large frozen electron core, and relativistic effects were incorporated using the zero-order regular approximation (ZORA).<sup>28</sup> This basis has been found to accurately describe the spin magnetic moment and structure of the  $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$  cluster and has proven to be a reliable method for many cluster studies.<sup>23</sup> For ligated systems, structures corresponding to various positions of ligands were examined and the spin multiplicity was optimized for each case. The total energies and the forces at the atomic sites are computed and a quasi-Newton method was used to optimize the structures without any symmetry restriction. The charge density was considered to be converged once the error, the commutator of the Fock matrix and the P matrix, is less than  $1 \times 10^{-6}$ . The structure was considered to be converged once the change in energy and nuclear gradients was less than  $1 \times 10^{-3}$  hartree and  $1 \times 10^{-3}$  hartree/Å. All arrangements of the ligands were considered, and both symmetric and multiple deformed  $\text{Ni}_9\text{Te}_6$  cores were tested to identify the lowest energy structure.

## III. RESULTS AND DISCUSSION

We start by considering the case of  $\text{Ni}_9\text{Te}_6(\text{CO})_x$  clusters. Figure 1 shows the ground state structures of the clusters along with the spin magnetic moment. In Fig. 2, we have plotted the magnetic moment for various clusters to provide a better view of the variation of the moment with number of ligands. Table S1 of the [supplementary material](#) shows the average magnetic moments on the Ni atoms, depending on the location of the atom and whether the atom is bound by a ligand. The bare  $\text{Ni}_9\text{Te}_6$  and the fully ligated cluster  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  both have the highest spin magnetic moment of  $6.0 \mu_B$ . In the case of  $\text{Ni}_9\text{Te}_6$  and  $\text{Ni}_9\text{Te}_6(\text{CO})_8$ , the magnetic structure is 0.69 eV and 0.55 eV more stable than the non-magnetic structure. However, the addition of a single CO to the bare cluster or the removal of a single CO from the fully

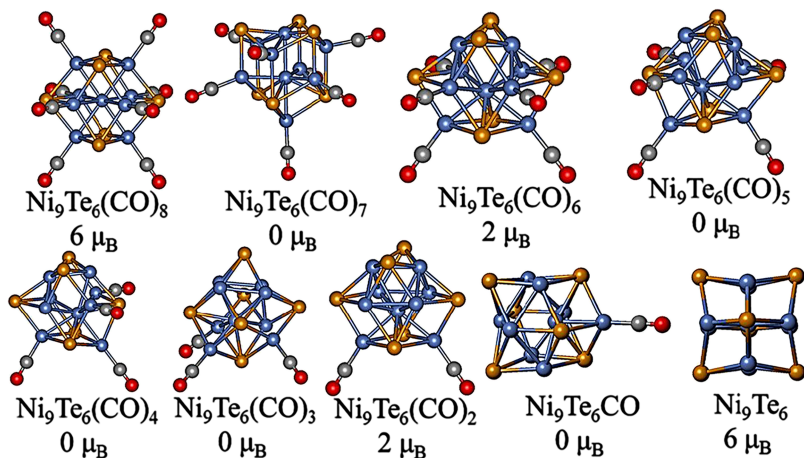


FIG. 1. The optimized ground state structures and spin magnetic moments of  $\text{Ni}_9\text{Te}_6(\text{CO})_x$ ,  $x=0-8$ . The Ni, Te, C, and O atoms are dark blue, orange, gray, and red, respectively.

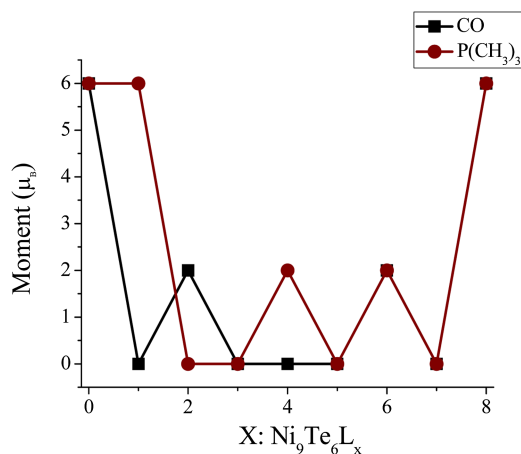


FIG. 2. The spin magnetic moment of  $\text{Ni}_9\text{Te}_6(\text{CO})_x$  and  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$ ,  $x = 0-8$ .

ligated cluster quenches the magnetic moment leading to a singlet ground state. In  $\text{Ni}_9\text{Te}_6(\text{CO})_7$ , the nonmagnetic structure is 0.26 eV more stable than the structure with unpaired electrons. DFT typically stabilizes states with unpaired electrons over singlet states, so the energy difference between the magnetic and nonmagnetic states is substantial. Removal of two CO molecules from the fully ligated cluster or addition of two CO's to the bare cluster partially restores the moment to  $2.0 \mu_B$ . The remaining clusters have singlet ground states. Examining the atomic moments indicates that the ligated Ni atoms have lower spin moments than bare Ni in 3 of the cases: in one case the opposite is true, and in one case the moments are the same. This tells us that the bonding is not causing a local interaction that uniformly lowers the spin state. This can also be inferred from the fact that the fully ligated system has the largest magnetic moment. An inspection of the geometrical structure shows that the addition of single CO to bare cluster or the removal of a CO from a fully ligated cluster does result in a distorted geometry suggesting that the quenching of the magnetic moment is related to the

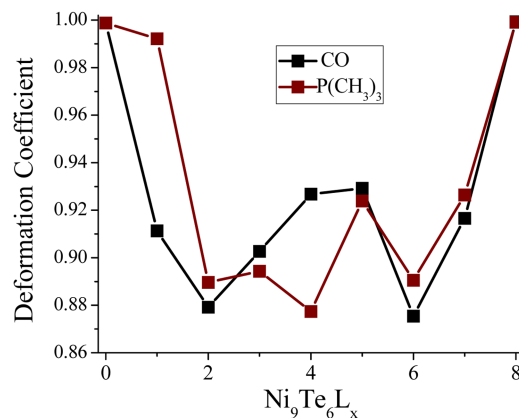


FIG. 3. The deformation coefficient ( $D_f$  from Eq. (1)) for  $\text{Ni}_9\text{Te}_6(\text{CO})_x$  and  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$ .

geometrical distortion of the cluster.  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  and bare  $\text{Ni}_9\text{Te}_6$  have  $O_h$  symmetry, while  $\text{Ni}_9\text{Te}_6(\text{CO})_7$  and  $\text{Ni}_9\text{Te}_6\text{CO}$  belong to the point group  $C_{3v}$ . This reduction in symmetry is further supported by the case of two CO's that partially restore a symmetric structure. To further investigate this relationship, we considered a deformation coefficient ( $D_f$ ) defined by

$$D_f = \frac{2Q_x}{Q_y + Q_z} \quad (1)$$

in which the  $Q_x$ ,  $Q_y$ , and  $Q_z$  are the eigenvalues of the deformation tensor

$$Q_{ij} = \sum_I R_{Ii}R_{Ij} \quad (2)$$

in which I runs over every Ni and Te ion,  $R_{Ii}$  is the  $i$ -th coordinate of ion I, and  $R_{Ij}$  is the  $j$ -th coordinate of ion I relative to the center of mass.<sup>10</sup> Note that we are only examining the deformation of the  $\text{Ni}_9\text{Te}_6$  core; the ligand atoms are not considered in this analysis. A spherical cluster will have a  $D_f$  of 1.0 while a number less than 1 corresponds to an oblate spheroidal deformation, and a value of 0 corresponds

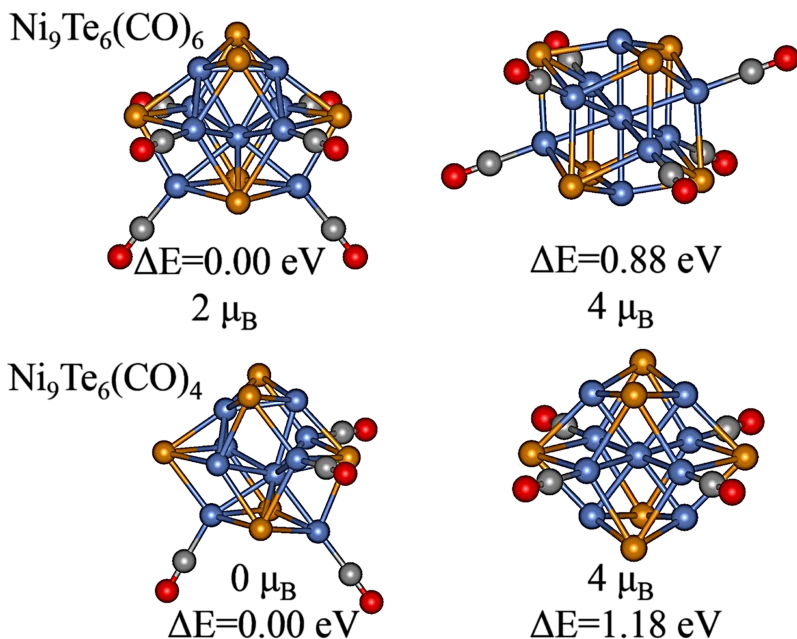


FIG. 4. The relative energy of the ground state and  $C_{3v}$  structures of  $\text{Ni}_9\text{Te}_6(\text{CO})_6$ , and the ground and  $C_{2v}$  structures of  $\text{Ni}_9\text{Te}_6(\text{CO})_4$ .

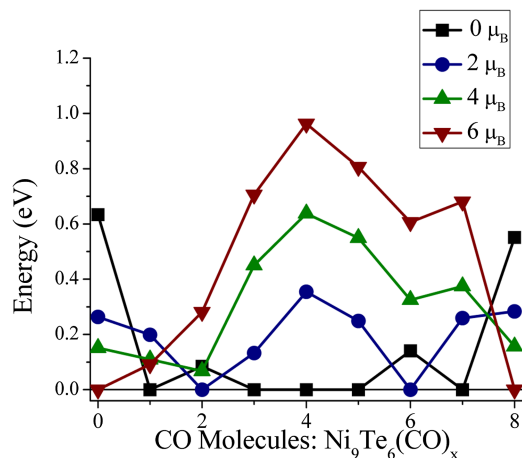


FIG. 5. The relative energy of the different spin states of  $\text{Ni}_9\text{Te}_6(\text{CO})_x$ ,  $x = 0-8$ .

to a planar structure. In Fig. 3 we have plotted  $D_f$  for all the sizes for both CO and phosphine ligands. The bare and the fully ligated cluster correspond to a  $D_f$  of 1.0 while other sizes have  $D_f$  between 0.87 and 0.92. To further illustrate the role of symmetry in stabilizing the magnetic state, we considered the case of  $\text{Ni}_9\text{Te}_6(\text{CO})_6$  that has a spin moment of  $2.0 \mu_B$ . We examined the change in multiplicity if the ligands were placed in a more symmetrical configuration. Fig. 4 shows that a more symmetrical placement of ligands enhances the magnetic moment to  $4.0 \mu_B$ . A similar enhancement is also seen in  $\text{Ni}_9\text{Te}_6(\text{CO})_4$  that has a singlet ground state. A more symmetrical placement of ligands (see Fig. 4) increases the moment to  $4.0 \mu_B$  confirming that more symmetrical structures stabilize the magnetic state. This is intriguing, as in most ligand protected clusters, a more symmetrical arrangement of ligands typically leads to enhanced stability.<sup>29-31</sup> To examine more closely how the geometrical distortions affect the relative stability of various spin states, we show in Fig. 5 the relative energies of the various spin states. It is interesting to note that the spin state with a moment of  $6.0 \mu_B$  is only stable for the no or fully ligated system and becomes less stable as the ligands are added to partially surround the metallic core. In fact the nonmagnetic state becomes more stable towards the case of 4 CO compared to all other states starting from either end. We would

like to add that  $D_f$  is only one measure of the deformation. If we examine the symmetry group of the clusters, we come to a similar conclusion as the point group of  $\text{Ni}_9\text{Te}_6(\text{CO})_x$  progresses from  $O_h$ ,  $C_{3v}$ ,  $C_{2v}$ ,  $C_1$ ,  $C_s$ ,  $C_s$ ,  $C_{2v}$ ,  $C_{3v}$ ,  $O_h$ , as  $x$  goes from 8 to 0. The high spin clusters have  $O_h$  symmetry and the  $2 \mu_B$  clusters have  $C_{2v}$  symmetry. We note that the  $C_{3v}$  clusters have spin moments of  $0 \mu_B$ , so the changes in C type symmetry are not directly related to the magnetic moment as only  $C_{3v}$  has the intrinsic degeneracies. Thus there is a clear connection between the spin magnetic moment and the deformation from the  $O_h$  clusters to lower symmetry clusters.

To examine if the above results are specific to CO ligands, we also carried out calculations on  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$  ligands. As opposed to CO that it is an electron acceptor, the trimethylphosphine ligands are electron donors and therefore could be expected to lead to different distortions of the cluster. Fig. 6 shows the structure of the clusters and the associated magnetic moments and Fig. 2 shows the variation of the moment as a function of the number of ligands. As in the case of CO, the bare and the fully ligated clusters have a spin magnetic moment of  $6.0 \mu_B$ . However, while the removal of a single  $\text{P}(\text{CH}_3)_3$  ligand quenches the magnetic moment of the fully ligated cluster, the addition of a single ligand to the bare cluster results in the magnetic and nonmagnetic states having essentially the same energy, with the  $6 \mu_B$  state being more stable by a negligible 1.5 meV. This means that a mixture of nonmagnetic and magnetic states is likely to occur for this species. This is different from the case of CO where the addition of a single CO quenched the moment of the bare cluster. The reason for this difference is most likely due to the larger binding energy of CO versus  $\text{P}(\text{CH}_3)_3$ . Adding a ligand to the bare cluster results in the Ni atom extending out from the center of the cluster to enhance the bonding with the ligand. This deformation has a slight energy penalty that is overcome by the CO binding energy, but in the case of phosphine the energy of the high spin low deformation, and low spin high deformation structures are essentially the same. The remaining trends are the same as in the case of CO except that  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_4$  has a spin magnetic moment of  $2.0 \mu_B$  while the cluster is nonmagnetic for CO ligands. To examine the deviation in behavior, we have also plotted the  $D_f$  for  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$  clusters in Fig. 3. Note that unlike the case of CO, the addition of a single

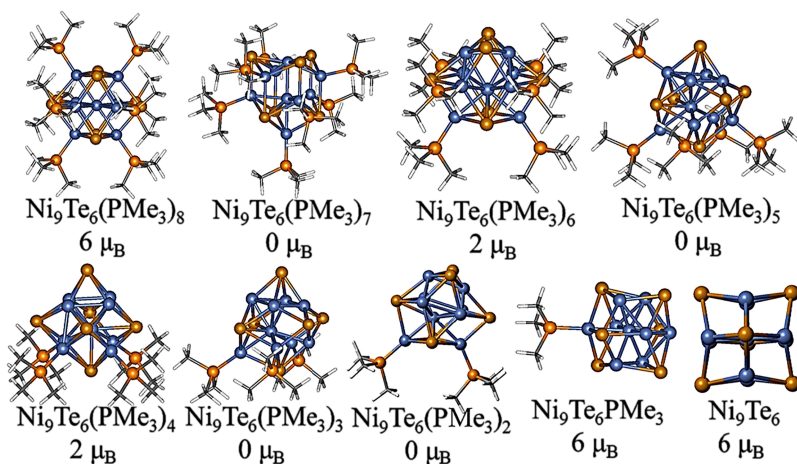


FIG. 6. The optimized ground state structures and spin magnetic moments of  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$ ,  $x = 1-8$ . The Ni, Te, and P atoms are dark blue, dark orange, and orange, respectively.

$\text{P}(\text{CH}_3)_3$  ligand does not significantly deform the cluster with it having a  $D_f$  greater than 0.99 and a spin moment of  $6 \mu_B$ . This further supports that the change in magnetic moments is largely driven by the geometry of the cluster. We also show the relative stability of various spin states as a function of ligands in Fig. 7. The case of 4  $\text{P}(\text{CH}_3)_3$  ligands is particularly interesting since the states with  $6.0 \mu_B$ ,  $4.0 \mu_B$ , and non-magnetic moment are almost degenerate while the ground state has a spin moment of  $2.0 \mu_B$ . This is different from the case of 4 CO ligands where the non-magnetic state is far more stable than other states of increasing spins. An examination of Figs. 1 and 6 shows that this could be attributed to the symmetry of the ground state. For  $\text{P}(\text{CH}_3)_3$  ligands, the  $\text{Ni}_9\text{Te}_6$  core has a  $D_{4h}$  symmetry which is likely to stabilize the magnetic states.

In the above, we have focused on the magnetic state of the clusters. We also examined the change in the binding energy of the ligands as successive ligands are added. This was investigated by calculating the removal energy (R.E.) using the expression

$$\text{R.E.} = E(\text{Ni}_9\text{Te}_6(\text{L})_{x-1}) + E(\text{L}) - E(\text{Ni}_9\text{Te}_6(\text{L})_x) \quad (3)$$

and represents the energy required to remove a single ligand from the cluster. Fig. 8 shows the variation of R.E. with size for both ligand types. Note that in both cases, the R.E. initially increases and then drops as one approaches the fully ligated systems. It is conceivable that this is related to ligand-ligand interaction as the cluster is fully ligated. The fact that the addition of a single CO and  $\text{P}(\text{CH}_3)_3$  results in a similar binding energy of 1.47 and 1.37 eV when in one case the spatial symmetry is broken while in the other case the spin symmetry is broken suggests that the binding energies and spin magnetic moment are not directly correlated. The reduction in the  $\text{P}(\text{CH}_3)_3$  binding energy is most likely driven by the fact that the phosphine ligand is an electron donor, so adding a large number of electron donors to a species will eventually destabilize the cluster as it would prefer to have donor-acceptor pairs.<sup>32,33</sup> In the case of CO, the binding energy drops precipitously from seven ligands to eight and when the spin magnetic moment jumps from 0 to  $6 \mu_B$ . In this case, the Jahn-Teller deformation enhances the stability of the  $\text{Ni}_9\text{Te}_6(\text{CO})_7$  cluster; however, the high spin  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  cluster is forced to be

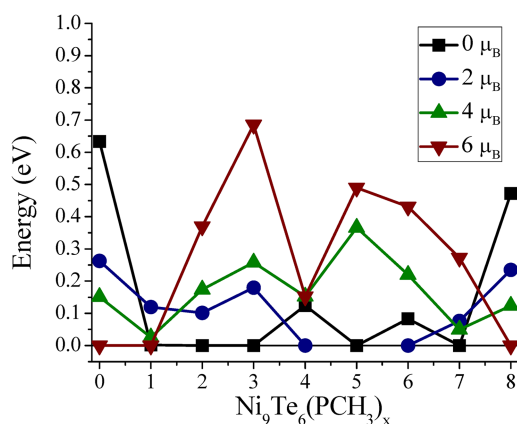


FIG. 7. The relative energy of the different spin states of  $\text{Ni}_9\text{Te}_6(\text{P}(\text{CH}_3)_3)_x$ ,  $x = 0-8$ .

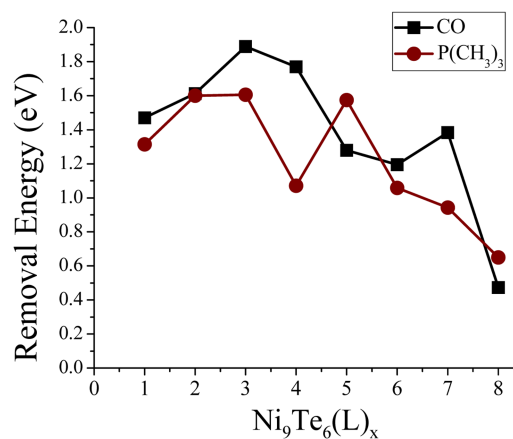


FIG. 8. The removal/dissociation energy of the CO and  $\text{P}(\text{CH}_3)_3$  ligands from  $\text{Ni}_9\text{Te}_6(\text{L})_x$ .

$\text{O}_h$  due to the number of ligands so the binding enhancement is lost.

We had previously shown that the ligands form charge transfer complexes.<sup>24</sup> We had also shown that while the electron donor ligands lower the ionization potential of the ligated cluster, electron withdrawing ligands increase the electron affinity of the metallic cluster. These conclusions were based on the studies of fully ligated clusters. It is then interesting to ask how the geometrical distortions for partially ligated species affect these conclusions. To this end, we show in Fig. 9 the variation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as the  $\text{P}(\text{CH}_3)_3$  and CO ligands are successively added. Note that the addition of  $\text{P}(\text{CH}_3)_3$  ligands leads to a rise of HOMO and LUMO leading to only small variations in the HOMO-LUMO gap while the addition of CO ligands leads to a stabilization of the HOMO and LUMO. One thing that stands out is that the stabilization afforded by CO is less than the rise in HOMO or LUMO for  $\text{P}(\text{CH}_3)_3$  ligands. This analysis confirms that the  $\text{P}(\text{CH}_3)_3$  is acting as a donor, as a donor will increase the absolute value of the HOMO, while an acceptor will lower the HOMO as seen with the addition of CO.

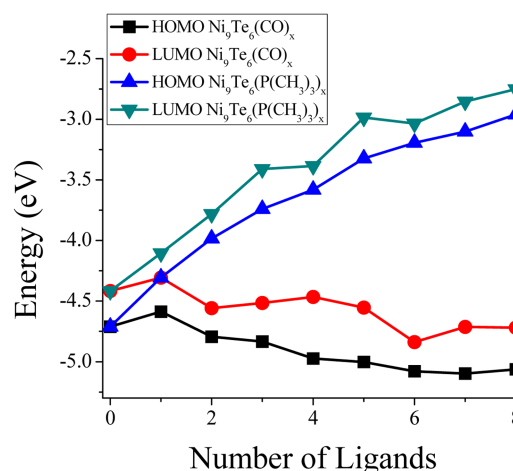


FIG. 9. The HOMO and LUMO of  $\text{Ni}_9\text{Te}_6(\text{L})_x$ , as a function of the number of ligands,  $x = 0-8$ ,  $\text{L} = \text{CO}, \text{P}(\text{CH}_3)_3$ .

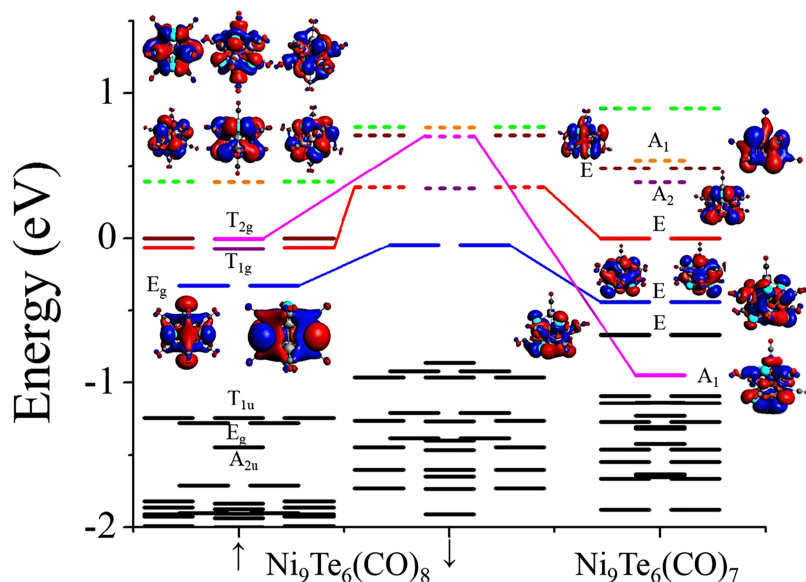


FIG. 10. A molecular orbital analysis of  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  and  $\text{Ni}_9\text{Te}_6(\text{CO})_7$ . The HOMO corresponds to an energy of 0 eV.

We finally examine the microscopic mechanism by which the ligands change the magnetic state of the clusters, by considering the electronic structure of the  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  and  $\text{Ni}_9\text{Te}_6(\text{CO})_7$  clusters. As stated previously, the removal of a single CO quenches the magnetic moment from  $6.0 \mu_B$  for the fully ligated cluster to non-magnetic case for a cluster with 7 CO ligands. Fig. 10 shows the majority and minority one electron levels for  $\text{Ni}_9\text{Te}_6(\text{CO})_8$  and the one electron levels for the non-magnetic  $\text{Ni}_9\text{Te}_6(\text{CO})_7$  cluster. Note that the fully ligated cluster is marked by 6 majority spin states close to HOMO which result in a cluster with a moment of  $6.0 \mu_B$ . The octahedral structure leads to two sets of triply degenerate  $T_{1g}$  and  $T_{2g}$  orbitals. These states are stabilized by Hund's rule that places 6 parallel spins in the states close to HOMO. The removal of a single CO allows the cluster to undergo a geometrical distortion that stabilizes the energy of the three states, marked magenta and red while destabilizing the states marked in maroon and purple. The stabilized magenta orbital converts from a Ni-CO bonding orbital to a Ni-CO and Ni-Te bonding orbital. The red orbitals are  $T_{1g}$  and converted to  $E$  with the removal of the CO ligand. In comparison, the  $T_{2g}$  maroon orbitals that have more nodes along the primary  $C_3$  axis are more destabilized and are emptied. This purple orbital whose nodes are also located along the circumference of the primary  $C_3$  axis is also destabilized and emptied. Thus, this oblate deformation helped to stabilize orbitals whose nodes were evenly distributed around the cluster, while the orbitals whose nodes were localized along the primary axis were destabilized. The gain in energy due to this Jahn-Teller distortion is larger than the 0.55 eV exchange coupling in the system leading to the non-magnetic state.

#### IV. CONCLUSION

To summarize, our studies have examined the evolution of the magnetic character as a bare  $\text{Ni}_9\text{Te}_6$  cluster with a spin magnetic moment of  $6.0 \mu_B$  is ligated with CO or  $\text{P}(\text{CH}_3)_3$  ligands. Our results show that the stabilization of the

magnetic state is governed by the geometrical structure of the cluster. For symmetric clusters, the presence of degenerate states close to HOMO and the lack of distortions stabilize the magnetic state. In fact, the magnetic moment of some of the clusters can be enhanced by placing the ligands in a symmetrical position. On the other hand, for partially ligated clusters, geometrical distortions can break the degeneracy of the states near HOMO leading to a partial or complete quenching of the moment through Jahn-Teller like distortions. We note that these deformations could play a role in the magnetic properties of cluster assembled materials constructed from these clusters. While the existing synthesized cluster assembled material exhibits magnetic behaviors, it may be possible to synthesize assemblies with a different connectivity to break the symmetry of the cluster and reduce its magnetic moment.

#### SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the complete information on magnetic moments at various sites, and coordinates of atoms and total energies in various structures.

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