Ligand Control of Manganese Telluride Molecular Cluster Core Nuclearity

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S *Supporting Information*

ABSTRACT: We report the synthesis, structural diversity, and chemical behavior of a family of manganese telluride molecular clusters whose charge-neutral cores are passivated by two-electron donor ligands. We describe three different core structures: a cubane-type Mn_4Te_4, a prismane Mn_6Te_6, and a dicubane Mn_8Te_8. We use various trialkylphosphines and N-heterocyclic carbenes (NHCs) as surface ligands and demonstrate that the formation of the different cluster core structures is controlled by the choice of ligand: bulky ligands such as P^iPr_3, PCy_3, or $^iPr_2NHC$ ($^iPr_2NHC$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) form the cubane-type core, while the smaller PMe_3 produces the prismane core. The intermediate-sized PEt_3 produces both cubane and prismane species. These manganese telluride molecular clusters are labile, and the capping phosphines can be replaced by stronger ligands, while the internal core structure of the cluster remains intact. The interplay of structural diversity and ligand versatility and lability makes these clusters potentially useful building blocks for the assembly of larger aggregates and extended structures. We demonstrate the simplest prototype of these solid-forming reactions: the direct coupling of two $Mn_4Te_4(^iPr_2NHC)_4$ units to form the dicubane $Mn_8Te_8(^iPr_2NHC)_6$. We also postulate the prismatic Mn_6Te_6 as the common ancestor of both Chevrel-type M_6E_8 and octanuclear rhombododecahedral M_8E_6 molecular clusters (M = transition metal and E = chalcogen), and we discuss the core structure of our molecular clusters as recognizable building units for the zinc blende and the hypothetical wurtzite lattices of MnTe.
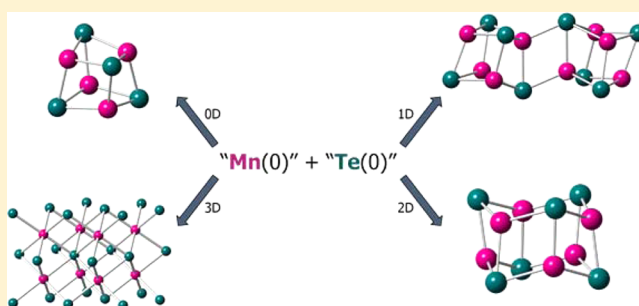
INTRODUCTION

We recently reported the preparation of several new materials that form when electron-rich metal chalcogenide molecular clusters combine with complementary electron poor molecular clusters such as fullerenes[1,2] or metal oxide clusters.[3] We have thus far focused our attention on electrically neutral transition metal chalcogenide molecular cluster building blocks of a single extended family: ligand-passivated, roughly 14-atom spherical cages.[4−8] With M = V, Cr, Fe, Co, and Ni; E = S, Se, and Te; and L = two-electron donor ligand, this family includes the Chevrel-type cage $M_6E_8L_6$,[9−11] the inverse structure $M_8E_6L_8$,[12] as well as their respective chalcogen- and metal-filled analogues, $M_6E_9L_6$[13] and $M_9E_6L_8$.[14] While the chemistry of manganese oxide molecular clusters is rich,[15−17] there is only a small handful of known manganese clusters containing heavier chalcogens (i.e., S, Se, and Te), and none that are passivated with L-type two-electron donor ligands. Noteworthy examples include $[Mn_4(SPh)_{10}]^{2−}$,[18] $[Mn_4Se_4(SeSiMe_3)_4]^{4−}$,[19] $[Mn_4Sn_4Se_{17}]^{10−}$,[20] and $[Mn_4Te_4(E^iPr)_4]^{4−}$ (E = S, Se, Te).[21,22] Here, we describe a new family of neutral manganese telluride molecular clusters that are stabilized by two-electron donor ligands. Our interest in synthesizing and studying these

manganese clusters is also motivated by the reports of remarkable magnetic[23−25] and catalytic[26,27] properties in manganese oxide clusters and by the promising uses of MnTe in the preparation of dilute magnetic semiconducting alloys,[28,29] in the fabrication of X-ray and γ-ray detectors,[30,31] and as magnetic impurities in nanocrystals.[32,33]

We report the synthesis, structure, and chemical behavior of a family of manganese telluride molecular clusters, $[MnTe]_n$ (n = 4, 6, 8). We demonstrate that the size of the capping ligand controls the structure of the inorganic core: bulky ligands such as L = P^iPr_3 or PCy_3 generate a $Mn_4Te_4L_4$ cubane-type cluster, while the smaller L = PMe_3 produces the prismane $Mn_6Te_6L_6$. The PEt_3 ligand is intermediate in size, and its use yields both cubane and prismane clusters. We also describe the preparation of a manganese telluride cubane cluster capped with N-heterocyclic carbene (NHC) ligands, and we used this cluster to form the dicubane $Mn_8Te_8L_6$. We find the hexanuclear $Mn_6Te_6L_6$ to be particularly interesting: it is the first demonstration of a neutral prismane cluster that is capped

entirely by L-type two-electron donating ligands, and its cylindrical, rather than spherical, shape offers an opportunity to design and prepare anisotropic solids. At first glance the $Mn_6Te_6L_6$ cluster does not appear to be a member of the family of 14-atom cage clusters, but a closer inspection suggests that it should be viewed as the common ancestor of the entire family: when the two-dimensional M_6E_6 core is completed, top and bottom, with E atoms, $M_6E_8L_6$ results; when it is completed, top and bottom, with M atoms, $M_8E_6L_8$ results.

■ EXPERIMENTAL SECTION

General Information. Anhydrous manganese(II) chloride, trimethylphosphine, triethylphosphine, triisopropylphosphine, and tellurium powder were purchased from Strem Chemicals. Allyl magnesium chloride (1.7 M solution in tetrahydrofuran (THF)), tricyclohexylphosphine, and all other reagents and solvents were purchased from Sigma-Aldrich. Dry and deoxygenated solvents were prepared by elution through a dual-column solvent system (MBraun SPS). All reactions and sample preparations were performed under inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox. $Mn(\eta^4$-butadiene$)_2PMe_3$,[34] Me_2NHC,[35] $^iPr_2NHC$,[35] $^iPr_2NHCTe$,[36] and R_3PTe (R = Et, ^iPr, and Cy)[37,38] were prepared according to published protocols.

Instrumentation. ^1H and ^{31}P NMR spectra were recorded using a Bruker DRX400 NMR spectrometer. All elemental analyses were performed by Roberston Microlit Laboratories. Electronic absorption measurements were performed on a Shimadzu UV-1800 spectrophotometer. The samples were dissolved in dichloromethane, loaded in a quartz cuvette in the glovebox, and sealed under nitrogen. Single-crystal X-ray diffraction data were collected on an Agilent SuperNova diffractometer using mirror-monochromated Cu Kα or Mo Kα radiation. Powder X-ray diffraction data were collected on a PANalytical X'Pert3 Powder diffractometer. Complete instrumentation and characterization details can be found in the Supporting Information.

Synthesis. We describe the preparation of $Mn_4Te_4(P^iPr_3)_4$. Full synthetic details for all new compounds are provided in the Supporting Information.

$Mn_4Te_4(P^iPr_3)_4$. Method A. To a solution of $Mn(\eta^4$-butadiene$)_2PMe_3$ (150 mg, 0.62 mmol) in 7 mL of THF was added $^iPr_3PTe$ (180 mg, 0.62 mmol) and P^iPr_3 (1000 mg, 6.24 mmol). The reaction was heated at reflux for 2 h. Once it cooled to room temperature, the mixture was filtered through a 0.2 μm syringe filter and concentrated in vacuo. The solution was cooled to −35 °C, and dark orange crystals grew over 24 h. The supernatant solution was decanted, and the recovered dark orange crystals were dried in vacuo. Yield: 100 mg (46%).

Method B. A suspension of anhydrous $MnCl_2$ (600 mg, 4.77 mmol) in 50 mL of THF was treated with P^iPr_3 (760 mg, 4.77 mmol). The mixture was cooled to −78 °C, and allyl magnesium chloride (5.6 mL, 1.7 M in THF, 9.53 mmol) was added dropwise. After this mixture was stirred at −78 °C for 2 h, a solution of freshly prepared $^iPr_3PTe$ (760 mg, 4.77 mmol of P^iPr_3 and 610 mg, 4.77 mmol of Te in 20 mL of THF) was added to the reaction mixture, which was subsequently warmed slowly to room temperature. After it was stirred for 5 h, the reddish-brown reaction mixture was evaporated to dryness in vacuo. The product was dissolved in 40 mL of toluene, and the mixture was filtered through a medium frit over Celite. The filtrate was concentrated in vacuo and filtered through a 0.2 μm syringe filter. The solution was cooled to −35 °C, and dark orange crystals grew over 24 h. The supernatant solution was decanted, and the recovered dark orange crystals were dried in vacuo. Yield: 760 mg (44%).

■ RESULTS

The hard, high-spin Mn(II) ion interacts very weakly with soft organophosphine ligands,[39] and as a result, ionic MnX_2 (X = Cl, Br or I) precursors proved to be a poor choice for the synthesis of phosphine-capped manganese telluride clusters. For example,

the reaction of $MnCl_2$, bis(*tert*-butyldimethylsilyl)telluride and a large excess of P^iPr_3 resulted in the formation of an insoluble, amorphous solid that, when pyrolyzed, yields bulk α-MnTe. In light of these results, we turned to an alternative chemical approach in which we react a low-valent manganese organometallic complex with a source of functionally "low-valent" tellurium to give the targeted molecular clusters. Trialkylphosphine tellurides (R_3PTe)[37,38] have been used as reactive sources of "low-valent" tellurium to form metal−tellurium bonds with several low-valent transition metal complexes, including $Co_2(CO)_8$,[10] $Cr(DMPD)_2$,[9] and $Fe(COT)_2$[40] (DMPD = 2,4-dimethylpentadienyl; COT = cyclooctatetraene). When the reaction conditions were controlled, stable polynuclear metal chalcogenide clusters were intercepted in the molecules-to-solids process.

We found that the 17-electron complex $Mn(\eta^4$-butadiene$)_2PMe_3$[34] reacts with $^iPr_3PTe$ in refluxing THF in the presence of a large excess of P^iPr_3 (10 equiv) to form a brown solution from which dark orange crystals grew at −35 °C over 24 h. The absorption spectrum of this compound in dichloromethane (Figure S2) shows a single characteristic peak centered at ∼520 nm. Single-crystal X-ray diffraction (SCXRD) reveals that this compound manganese telluride cluster with a cubane-type core, $Mn_4Te_4(P^iPr_3)_4$ (Figure 1).

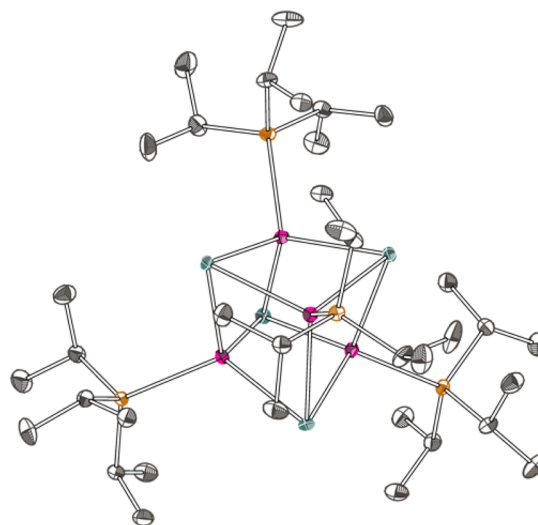**Figure 1.** Molecular structure of $Mn_4Te_4(P^iPr_3)_4$ showing thermal ellipsoids at 50% probability. Magenta, manganese; teal, tellurium; orange, phosphorus; black, carbon. Hydrogen atoms and a toluene of solvation are removed to clarify the view.

The core is a tetrahedron of Mn atoms with each face capped with a Te atom forming a larger tetrahedron; four phosphine ligands passivate this inorganic core, forming again a tetrahedron. As in the closely related cluster $Fe_4Te_4(P^iPr_3)_4$,[11] the cubane core of $Mn_4Te_4(P^iPr_3)_4$ is severely distorted; the Mn_2Te_2 rhombs are nonplanar with mean Te−Mn−Mn−Te torsion angle of 156.7°. Other important mean bond distances and angles are listed in Table 1.

Because the preparation and isolation of $Mn(\eta^4$-butadiene$)_2$-PMe_3 can be both time-consuming and challenging, we sought a more convenient precursor for the preparation of this molecular cluster. Analogous to the previously reported use of the complex $(Et_3P)_2Cr(allyl)_2$ as a source of reactive, low-valent chromium,[9] we treated a suspension of anhydrous $MnCl_2$ in THF with 1 equiv of P^iPr_3 and 2 equiv of allylmagnesium

Table 1. Mean[a] Bond Distances (Å) and Angles (deg) for $[MnTe]_n$ (n = 4, 6, 8) Clusters

	distances (Å)			angles (deg)	
	Mn−Mn	Mn−Te	Mn−L (L = P, C)	Mn−Te−Mn	Te−Mn−Mn−Te[b]
$Mn_4Te_4(PEt_3)_4$[c]	3.029	2.712	2.479	67.9	155.2
$Mn_4Te_4(P^iPr_3)_4$	3.118(18)	2.738(9)	2.533(5)	69.4(5)	156.7(13)
$Mn_4Te_4(PCy_3)_4$	3.10(6)	2.732(17)	2.527(17)	69.1(14)	156(3)
$Mn_4Te_4(Me_2NHC)_4$	3.22(5)	2.741(18)	2.185(14)	72.1(13)	159(3)
$Mn_6Te_6(PMe_3)_6$	3.07(3)	2.714(16)	2.512(17)	68.9(6) (rhomb)	162.6(4)
				99(3) (hexagon)	
$Mn_6Te_6(PEt_3)_6$	3.010(17)	2.720(7)	2.540(12)	69.5(3) (rhomb)	164.3(6)
				101(2) (hexagon)	
$Mn_8Te_8(^iPr_2NHC)_6$	3.27(12)[d]	2.77(4)[d]	2.175(6)	72(3)	159(6)
				69.3[c] (bridge)	180.0[c] (bridge)

[a]We list average geometric parameters and their standard deviations. Crystallographic estimated standard deviation values of individual measurements are typically much smaller; they are 0.01−0.02 Å for Mn−C distances, 0.001−0.005 Å for other distances, and 0.01−0.1° for angles. Full details are available in the Supporting Information, CIF file. [b]The Te−Mn−Mn−Te torsion angle is the dihedral between two fused Mn_2Te rings. The angle would be 180° for a perfectly planar rhomb. [c]No standard deviation is listed when a measurement has only one independent value. [d]The bridging Mn−Mn and Mn−Te distances, respectively 3.1715(18) and 2.7513(10) Å, are omitted from these averages.

chloride at −78 °C. After ~2 h, we obtained a dark brown mixture (which we believe contains a manganese diallyl compound or a reactive equivalent thereof) to which we added 1 equiv of $^iPr_3PTe$. The reaction warmed to room temperature and was stirred for ~5 h. The mixture was concentrated to dryness and recrystallized from toluene to afford dark orange crystals of $Mn_4Te_4(P^iPr_3)_4$ identical to the compound prepared from $Mn(\eta^4\text{-butadiene})_2PMe_3$. In contrast to our original approach, this one-pot synthesis does not require a large excess of phosphine and employs commercially available precursors.

We prepared cubane-type clusters $Mn_4Te_4L_4$, capped with various trialkylphosphines (L = PEt_3, P^iPr_3, PCy_3), using both approaches (Scheme 1). The cores of $Mn_4Te_4(PCy_3)_4$ (Figure S25) and $Mn_4Te_4(PEt_3)_4$ (Figure S23) are similar to that of $Mn_4Te_4(P^iPr_3)_4$, but the Mn−Mn, Mn−Te, and Mn−P distances in $Mn_4Te_4(PEt_3)_4$ are shorter than those in

Scheme 1. Synthesis and Reactivity of Manganese Telluride Molecular Clusters

$Mn_4Te_4(P^iPr_3)_4$ and $Mn_4Te_4(PCy_3)_4$, reflecting the smaller cone angle of PEt_3[41,42] (Table 1).

We found that the reaction of $Mn(\eta^4\text{-butadiene})_2PMe_3$ with Et_3PTe in the presence of a large excess of PEt_3 produces a mixture of two clusters of different nuclearity: $Mn_4Te_4(PEt_3)_4$ and $Mn_6Te_6(PEt_3)_6$. These compounds were separated based on their difference in solubility; during the course of the reaction, $Mn_6Te_6(PEt_3)_6$ precipitates from refluxing THF as a brown solid. We filter this solid and recrystallize it from dichloromethane at −35 °C. Figure 2 shows the molecular
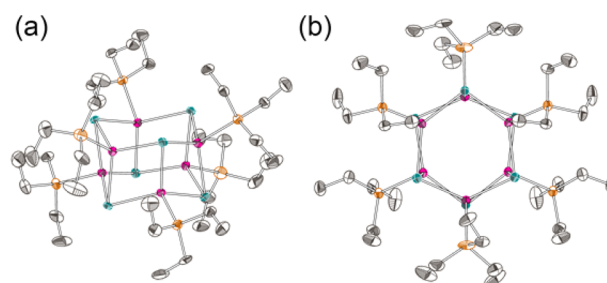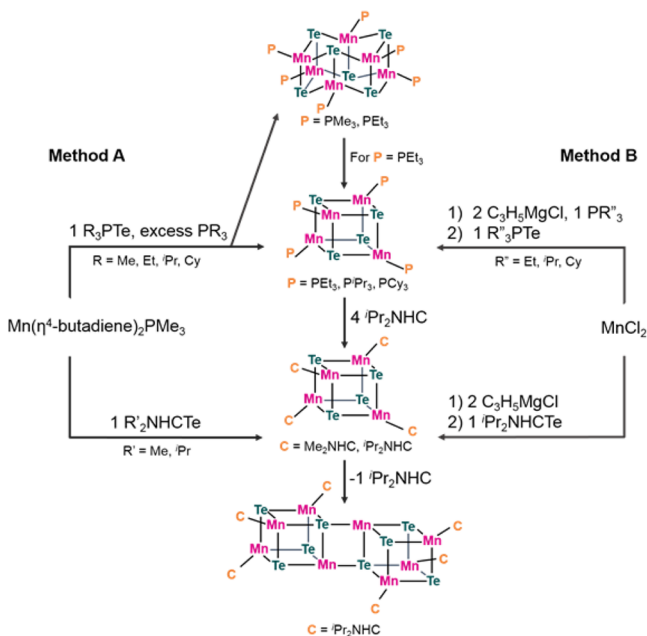
Figure 2. Molecular structure of $Mn_6Te_6(PEt_3)_6$ (a) side view and (b) top view showing thermal ellipsoids at 50% probability. Color scheme is the same as in Figure 1. Hydrogen atoms and a dichloromethane of solvation were removed to clarify the view.

structure of $Mn_6Te_6(PEt_3)_6$ as determined by SCXRD. The cluster has a cylindrical prismane core built from two face-sharing hexagonal Mn_3Te_3 puckered rings with alternating Mn and Te atoms at the vertices; each Mn atom is further coordinated by one PEt_3. The Mn_2Te_2 rhombs that form the lateral surfaces of the cylinder are nonplanar but to a lesser degree than in the cubane-type structures; the mean Te−Mn−Mn−Te torsion angle is 164.3° in $Mn_6Te_6(PEt_3)_6$, while it is 155.2° in $Mn_4Te_4(PEt_3)_4$. The Mn−Mn, Mn−Te, and Mn−P distances in $Mn_6Te_6(PEt_3)_6$ are similar to those of $Mn_4Te_4(PEt_3)_4$ (Table 1).

Our findings thus far suggest that the core structure of these manganese telluride clusters is controlled by the size of the capping ligand. Phosphines with a large cone angle (P^iPr_3 or PCy_3) form clusters with a small radius of curvature, $Mn_4Te_4L_4$. The intermediate-sized phosphine PEt_3 produces a mixture of $Mn_4Te_4(PEt_3)_4$ and $Mn_6Te_6(PEt_3)_6$. (In addition, we found

that the prismane $Mn_6Te_6(PEt_3)_6$ is metastable, reorganizing into the cubane-type $Mn_4Te_4(PEt_3)_4$ when left in solution for ~one week at −35 °C.) Our hypothesis predicts that smaller capping ligands favor the formation of clusters with larger radii of curvature, and we find this to be the case with the smallest trialkylphosphine ligand, PMe_3. This ligand gives the prismane $Mn_6Te_6(PMe_3)_6$ (as determined by SCXRD; see Figure S26). We used powder X-ray diffraction (PXRD) to confirm, more importantly, that using PMe_3 forms $Mn_6Te_6(PMe_3)_6$ exclusively (Figure S22); we do not see any evidence of the cubane-type cluster or of the conversion of the prismane to the related (and as yet hypothetical) $Mn_4Te_4(PMe_3)_4$ cluster.

The capping phosphines on these manganese telluride molecular clusters are labile, and in solution, ligand dissociation leads to the precipitation of an insoluble orange solid. The stability of the cubane-type compounds $Mn_4Te_4(PR_3)_4$ is strongly influenced by the choice of capping ligand, solvent, and temperature. While $Mn_4Te_4(PEt_3)_4$ decomposes within minutes when dissolved in dichloromethane at room temperature, $Mn_4Te_4(P^iPr_3)_4$ and $Mn_4Te_4(PCy_3)_4$ remain unchanged in solution for ~16 h in noncoordinating solvents such as dichloromethane or toluene. The same cluster solutions are stable indefinitely when kept at −35 °C, and the addition of free phosphine increases their lifetime at room temperature. All of these $Mn_4Te_4(PR_3)_4$ compounds react immediately in coordinating solvents such as THF to form larger insoluble cluster aggregates.

Lability and ligand substitution are essential features of cluster-based catalytic systems,[43] but they often make solution-based studies and applications challenging. The coordinating characteristics of NHCs[44] are similar to those of phosphines.[45−48] Importantly, they are generally stronger σ-donor ligands than phosphines and form more stable bonds to metals.[49] Despite the ready availability of NHCs, very few examples of NHC complexes of Mn(II) are known.[50−52] We explored whether a "carbene telluride" (NHCTe), analogous to a phosphine telluride, could transfer a tellurium atom to a low-valent manganese to form a manganese−tellurium bond while liberating an NHC that could bind to the metal to form an NHC-capped manganese telluride molecular cluster. To examine this reaction, we prepared the precursor $^iPr_2NHCTe$[36] from the corresponding carbene $^iPr_2NHC$ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)[35] and elemental Te, and used this carbene telluride in our cluster synthesis. We employed $^iPr_2NHCTe$ in both synthetic approaches (Methods A and B) and obtained the cubane-type cluster $Mn_4Te_4(^iPr_2NHC)_4$ (Figure 3). In contrast to phosphine-capped clusters, whose syntheses require an excess of free phosphine, only a stoichiometric amount of $^iPr_2NHCTe$ is required to form $Mn_4Te_4(^iPr_2NHC)_4$. Using the same synthetic approach we prepared $Mn_4Te_4(Me_2NHC)_4$, where Me_2NHC = 1,3,4,5-tetramethylimidazol-2-ylidene.[35]

SCXRD shows that the cores of $Mn_4Te_4(Me_2NHC)_4$ and $Mn_4Te_4(^iPr_2NHC)_4$ are similar to that of $Mn_4Te_4(PR_3)_4$. Orientational disorder within the single crystals of $Mn_4Te_4(^iPr_2NHC)_4$ precluded detailed metrical analysis of this complex, but $Mn_4Te_4(Me_2NHC)_4$ (Figure S28) gave a higher-quality single-crystal structure, and we list the mean bond distances and angles of this cluster in Table 1. Because of the instability of the Me_2NHC in solution, we use $^iPr_2NHC$ in subsequent substitution reactions (see below). The Mn−Te distances in the Me_2NHC-capped cluster are similar to those in the phosphine-capped clusters, although the Mn−Mn distances
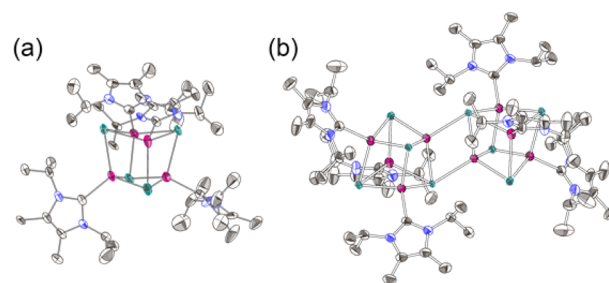

Figure 3. Molecular structures of (a) $Mn_4Te_4(^iPr_2NHC)_4$ and (b) $Mn_8Te_8(^iPr_2NHC)_6$ showing thermal ellipsoids at 50% probability. Magenta, manganese; teal, tellurium; blue, nitrogen; black, carbon. Hydrogen atoms and toluene molecules of solvation are removed to clarify the view.

are slightly longer (Table 1). The average Mn−C(NHC) bond length is 2.185 Å, suggesting a Mn−C(NHC) single bond with negligible Mn → C(NHC) back-bonding contributions.[50]

The stronger binding of the NHC to the tetrahedral Mn(II) manifests itself in the increased solution-phase stability of $Mn_4Te_4(^iPr_2NHC)_4$ vis-à-vis that of $Mn_4Te_4(PR_3)_4$. We further demonstrate the affinity of the cubane core for NHC in a ligand-substitution reaction. When we treat a d_8-toluene solution of $Mn_4Te_4(P^iPr_3)_4$ with 4.5 equiv of $^iPr_2NHC$ at room temperature the solution turns from red to orange, and ^1H NMR spectroscopy verifies that $^iPr_2NHC$ replaces the erstwhile cluster-bound P^iPr_3 (Figure 4). The ^1H NMR spectrum of $Mn_4Te_4(P^iPr_3)_4$ (Figure 4a) exhibits two broad resonances centered at 3.5 and 6.8 ppm (corresponding to methyl and methine groups of P^iPr_3 bound to Mn, respectively). We always observe a small amount of free P^iPr_3 at 1.0 and 1.6 ppm in the ^1H NMR and at −17.5 ppm in the ^{31}P NMR. Upon addition of a slight excess of $^iPr_2NHC$, the peaks due to free P^iPr_3 increase in intensity, and the peaks at 3.5 and 6.8 ppm completely disappear (Figure 4b). Two new broad peaks emerge at 5.4 and 7.5 ppm, corresponding to the cluster-bound $^iPr_2NHC$ isopropyl methyl and olefinic methyl groups. These new broad resonances at 5.4 and 7.5 ppm match those of $Mn_4Te_4(^iPr_2NHC)_4$ synthesized from $^iPr_2NHCTe$ and low-valent manganese (Figure 4c). After the addition of $^iPr_2NHC$, the ^{31}P NMR spectrum shows the disappearance of a broad peak at −11 ppm corresponding to P^iPr_3 bound to the cluster. These results indicate that the stronger NHC ligand replaces the weaker phosphine on our molecular cluster.

While the NHC ligands can replace phosphines, they themselves remain labile, and in solution their dissociation from the cluster leads to the dimerization of the cubane. After several weeks at −35 °C a toluene solution of $Mn_4Te_4(^iPr_2NHC)_4$ deposits the dicubane cluster $Mn_8Te_8(^iPr_2NHC)_6$, which forms subsequently to the loss of one of the NHC caps from each of two cluster monomers. The structure of the dicubane cluster (Figure 3) is composed of two $[Mn_4Te_4]^0$ cores directly linked via two Mn−Te bonds. The bridging Mn_2Te_2 rhomb is strictly planar, featuring distances Mn−Mn (3.172 Å) and Mn−Te (2.751 Å) and angle Mn−Te−Mn (69.3°).

When the phosphine-capped clusters lose sufficient amounts of phosphine, they aggregate to form an insoluble orange precipitate that is highly air-sensitive and amorphous as determined by PXRD. We performed pyrolysis on the solid that forms when THF is added to a toluene solution of $Mn_4Te_4(P^iPr_3)_4$. The orange solid was weighed and sealed

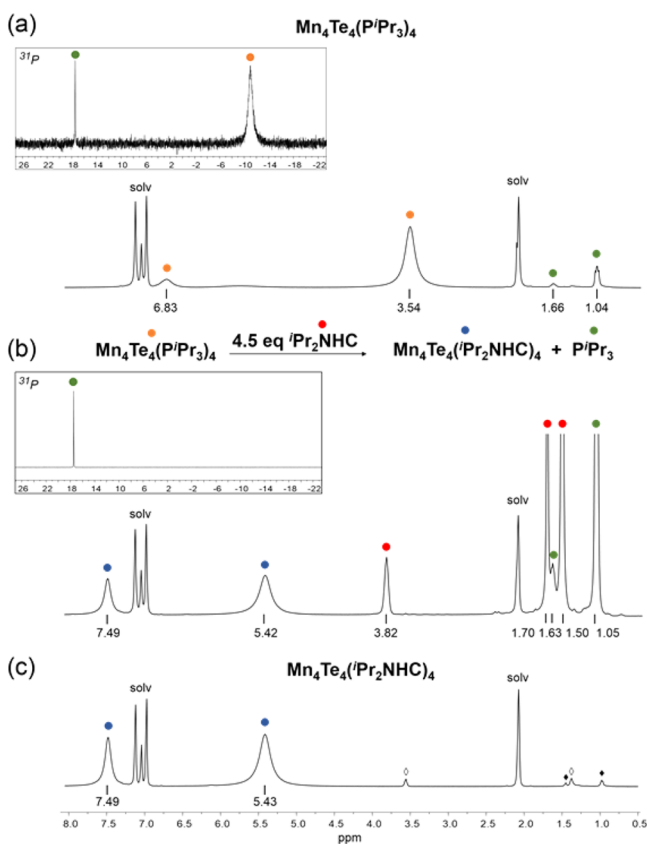**Figure 4.** ^{1}H NMR spectra of (a) $Mn_4Te_4(P^iPr_3)_4$, (b) product of the reaction of $^iPr_2NHC$ with $Mn_4Te_4(P^iPr_3)_4$, and (c) $Mn_4Te_4(^iPr_2NHC)_4$ as directly synthesized in C_7D_8 at 240 K. ^{31}P NMR spectra are shown in the inset of (a) and (b). (c) Minor solvent impurities are visible ($\lozenge$, THF; $\blacklozenge$, hexanes). The peaks are color-coded according to the reaction scheme above (orange, $Mn_4Te_4(P^iPr_3)_4$; red, $^iPr_2NHC$; blue, $Mn_4Te_4(^iPr_2NHC)_4$; green, P^iPr_3). We consistently observe free P^iPr_3 peaks in $Mn_4Te_4(P^iPr_3)_4$.

under vacuum in a 20 cm long Pyrex tube. The sample was slowly heated to 300 °C in a tube furnace, keeping one end of the sample tube at room temperature. The orange solid turned black at ∼200 °C, and a clear liquid condensed at the cold end. The PXRD pattern of the black powder (80−90% of the initial mass) corresponds to that of hexagonal α-MnTe with NiAs lattice (Figure S31), and the condensed liquid contained free P^iPr_3 as identified by ^{1}H and ^{31}P NMR. From the mass of the solid pre- and postpyrolysis, we calculate that the composition of the aggregation product ranges from $(MnTe)(P^iPr_3)_{0.25}$ to $(MnTe)(P^iPr_3)_{0.17}$.

■ DISCUSSION

We have demonstrated that a variety of molecular clusters are formed from the reaction of functionally low-valent manganese and functionally low-valent tellurium. Our results suggest that the choice of capping ligand promotes the formation of one type of cluster while suppressing the formation of another one. The larger ligands such as P^iPr_3, PCy_3, and $^iPr_2NHC$ select the smaller, cubane-type clusters $Mn_4Te_4L_4$, while the smaller PMe_3 exclusively generates the larger prismane $Mn_6Te_6L_6$. The intermediate-sized ligand PEt_3 does not discriminate toward one compound but instead leads to the formation of a mixture of cubane and prismane clusters that can be separated based on

solubility; $Mn_6Te_6(PEt_3)_6$ is insoluble in THF and precipitates from the reaction mixture.

The cubane geometry is pervasive throughout molecular cluster chemistry, and we compare $Mn_4Te_4L_4$ to several related compounds. The only reported manganese telluride cubane is the ionic cluster $[Mn_4Te_4(EC_3H_7)_4]^{4-}$ (E = S, Se, Te), which is capped with chalcogenolate ligands.[21,22] As in our neutral $Mn_4Te_4L_4$ clusters, the core of $[Mn_4Te_4(EC_3H_7)_4]^{4-}$ is significantly distorted from a perfect cube, and the Mn−Te distances are within the typical range for such bonds. The mean Mn−Mn separation in all $Mn_4Te_4L_4$ (∼3.1 Å) is significantly longer than the nearest-neighbor distance of 2.73 Å in elemental Mn and lies between that of traditional singly bonded manganese dimers (e.g., ∼2.9 Å in $Mn_2(CO)_{10}$)[53,54] and that of $[Mn_4Te_4(EC_3H_7)_4]^{4-}$ (∼3.3 Å),[22] which exhibits no Mn−Mn interactions. We can also view the $Mn_4Te_4L_4$ cluster as an illustration of the topological self-duality of the tetrahedron: the cubane core is the intersection of two concentric tetrahedra, Mn_4 and Te_4, that have different edge lengths (∼3.1 Å and ∼4.4 Å, respectively).

In contrast to $[Mn_4Te_4(EC_3H_7)_4]^{4-}$, which does not participate in ligand-substitution reactions, the $Mn_4Te_4L_4$ clusters are labile and may be used as starting materials for the preparation of new derivatives and larger aggregates. In this respect, the behavior of $Mn_4Te_4L_4$ is similar to that of the cubane-type $Fe_4S_4L_4$ (L = P^iPr_3, P^tBu_3, PCy_3).[55,56] We have shown that $Mn_4Te_4(P^iPr_3)_4$ reacts with $^iPr_2NHC$ to afford $Mn_4Te_4(^iPr_2NHC)_4$. NHC ligands have been used on Co_4S_4 and Fe_4S_4 clusters to access oxidation states that are unstable with phosphine ligands.[57,58] In our case, the use of NHC ligands enabled the isolation and characterization of the dicubane $Mn_8Te_8(^iPr_2NHC)_6$. (The synthesis of $Mn_8Te_8(PR_3)_6$ analogue proved unsuccessful.) The scope of this reaction is under further investigation as a way to prepare cluster aggregates of larger nuclearity.

The compound $Mn_6Te_6L_6$ forms when small cone angle phosphines (L = PEt_3, PMe_3) are employed. The prismane core is assembled from three nonplanar Mn_2Te_2 rhombs that are analogous to the ones in $Mn_4Te_4L_4$. This Mn_6Te_6 structural unit is reminiscent of the $[Fe_6S_6]^{2+/+}$ cluster,[59−62] but to the best of our knowledge, $Mn_6Te_6L_6$ is the first example of a prismane chalcogenide cluster with a fully reduced core, that is, an inorganic core that has no formal charge. It is also the only prismane cluster containing either Mn or Te. $Mn_6Te_6(PEt_3)_6$ is metastable and converts to $Mn_4Te_4(PEt_3)_4$ in solution over a period of several days at −35 °C (in this it behaves like $[Fe_6S_6]^{2+/+}$[63−65]); however, the use of the smaller PMe_3 ligand leads to the formation of a stable $Mn_6Te_6(PMe_3)_6$.

We examine the structure of $Mn_6Te_6L_6$ as a potential common ancestor of the 14-atom cage family of clusters that we use as superatomic building blocks[1−3] (Figure 5). Each member of this family may be viewed as formed from an exoskeleton of six metal atoms and six chalcogens that assemble to form a stack of two chair-type six-membered rings analogous to our Mn_6Te_6 prismane. Supplementing this hexagonal core with two metals produces the M_8E_6 cluster (e.g., Ni_8Se_6[12]). The inverse structure or Chevrel-type M_6E_8 is obtained by shifting the metal atoms toward the center of each hexagonal ring and complementing this slightly deformed prismane core with two chalcogen atoms (e.g., Cr_6Te_8,[9] Fe_6Te_8,[11] and Co_6Te_8[10]). In addition to these basic structures, the M_8E_6 and M_6E_8 cores can be filled with an additional metal atom (e.g., Ni_9Te_6[14]) and with an oxygen atom (e.g., V_6Se_8O[13]), respectively.
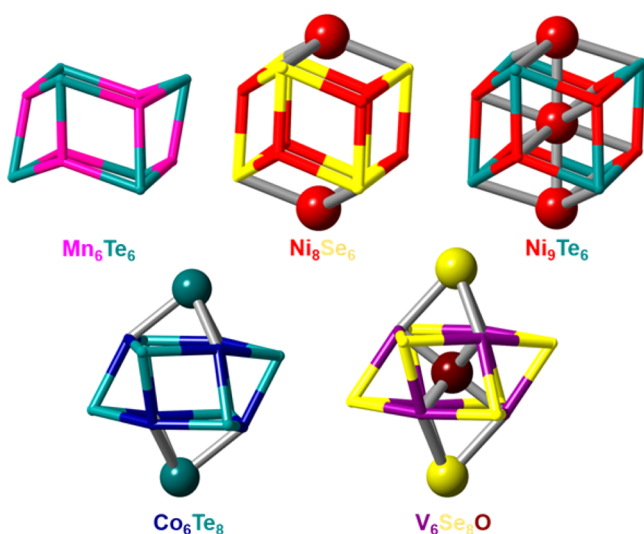
Figure 5. A family of 14-atom cage clusters with M_6E_6 core.

We also consider our manganese telluride molecular clusters as reconstructed fragments of the associated solid-state compound MnTe. Though the properties of the molecular clusters show fundamental differences with those of their corresponding bulk compound, the study of the formation of molecular clusters is a valuable model for understanding the bulk structure and vice versa. MnTe typically crystallizes in its most energetically favored hexagonal NiAs lattice type,[66] but it can also adopt a metastable zinc blende structure when grown as films by molecular beam epitaxy at low temperature[67,68] or when alloyed with II−VI semiconductors.[69−71] Consistent with these observations, theoretical calculations have suggested that the energy difference between the zinc blende and NiAs structures is small,[72] while the wurtzite lattice, which has been postulated but has never been experimentally observed,[73] is significantly higher in energy.

On the basis of these experimental and theoretical studies, we examine the cubic $Mn_4Te_4L_4$ and hexagonal $Mn_6Te_6L_6$ clusters as fragments of the zinc blende and wurtzite structures, respectively. Similar M_4E_4 and M_6E_6 clusters (M = Zn, Cd and E = S, Se, Te) have been postulated as a base for the growth of zinc blende and wurtzite lattices,[74,75] and both of these species have been observed experimentally by mass spectrometry of ZnS clusters obtained by laser ablation of bulk ZnS.[76] Figure 6 illustrates the relationship between the prismane core and the wurtzite structure. A set of simple transformations can be used to generate a hexagonal fragment of the wurtzite lattice from the core of $Mn_6Te_6L_6$. At first sight, the link between the Mn_4Te_4 cubane and the zinc blende structure is less apparent.
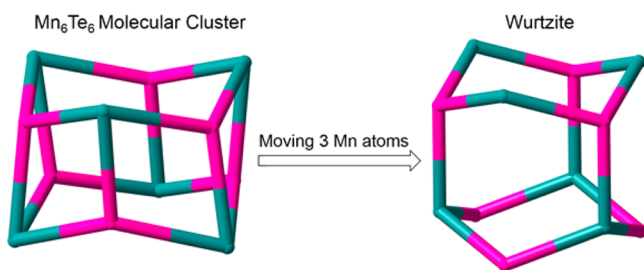

Figure 6. Pictorial comparison of Mn_6Te_6 cluster and a fragment of solid-state wurtzite lattice type.

The Mn_4Te_4 core structure has cubic symmetry, suggesting that it can form rock salt or zinc blende lattices. These structures are related structurally by a simple shift of cations from an octahedral environment in the rock salt to a tetrahedral environment in the zinc blende, but we note that the rock salt structure of MnTe is postulated to be much higher in energy than either zinc blende or wurtzite structures.[72] Our work highlights the importance of the capping ligands on the internal structure of the cluster, but it also suggests that in the molecular cluster regime, the cubic zinc blende and hexagonal wurtzite structures are relatively close in energy. These results provide insight into the structural reconstruction taking place during the molecule-to-solid transformation.

CONCLUSION

We have described the synthesis and characterization of a family of manganese telluride molecular clusters whose neutral inorganic cores are stabilized by two-electron donor capping ligands. We prepare these clusters by treating a functionally low-valent organometallic complex of manganese with a source of functionally low-valent tellurium. Using this approach, we are able to control both the core structure of the clusters and the ligands that decorate their surfaces. We report three structural types of manganese telluride: the cubane-type Mn_4Te_4, the prismane Mn_6Te_6, and the dicubane Mn_8Te_8. Our polynuclear compounds are labile, and this feature enables ligand substitution reactions that preserve the internal core structure of the cluster. While ligand dissociation leads to rapid core aggregation, the use of strong NHC capping ligands slows this reaction and allows us to isolate a stable intermediate of the aggregation process. Being structurally varied and chemically flexible, the clusters reported in this work form an exciting new class of building blocks for the assembly of solid-state compounds.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01020.

> Synthetic and characterization details, elemental analysis, electronic absorption spectroscopy, single-crystal X-ray diffraction, powder X-ray diffraction, crystal structures, pyrolysis experiment, and additional references. (PDF)
> X-ray crystallographic information in CIF files. (ZIP)

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Notes

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