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Clusters in the step-by-step growth of solids

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Abstract

We show that $Pd_2Te_2(PEt_3)_4$ (**1**) converts to $Pd_6Te_6(PEt_3)_8$ (**2**) on standing at room temperature in toluene, and that $Ni_9Te_6(PEt_3)_8$ (**3**) reacts with $TePEt_3$ at room temperature in toluene to form $Ni_{20}Te_{18}(PEt_3)_{12}$ (**4**). We have shown previously that each of these molecular clusters can be isolated from reactions which, under more forcing reactions, give the corresponding solid state compounds, PdTe and NiTe. We have also shown that each of the clusters can be viewed as an isolated, passivated molecular fragment of the extended solid and for this reason the reactions which take the smaller clusters to the larger ones may be viewed as the molecular equivalents of solid state crystal growth reactions.

Introduction

We have reported molecule-based syntheses of the inorganic solid state compounds PdTe [1] and NiTe [2]. One of the goals of that work was to elucidate pathways along which molecular compounds react to form extended solids, and therefore we sought to isolate compounds which might be considered intermediates in the molecules-to-solids transformations. In each case we were able to isolate and characterize two molecular intermediates. In the study of PdTe we isolated the compounds $Pd_2Te_2(PEt_3)_4$ (**1**) and $Pd_6Te_6(PEt_3)_8$ (**2**). In the study of NiTe we isolated the compounds $Ni_9Te_6(PEt_3)_8$ (**3**) and $Ni_{20}Te_{18}(PEt_3)_{12}$ (**4**). We rationalized the structures of these clusters in terms of the associated extended solids [1, 3]. In each case we showed that there are both structural similarities and differences between the cluster and fragments of the solid state material. Analysis of the differences between the molecular compounds and the extended solids shows the nature of the reconstructions required in the change from an excised fragment of a three-dimensional solid to a 'zero-dimensional' molecule.

In this paper we support our suggestion that the clusters **1**–**4** be viewed as reconstructed fragments of the bulk solids by showing that each of these clusters can be converted to extended solid state compounds, and that the smaller clusters (**1** and **3**) can be converted to the larger clusters (**2** and **4**, respectively). Each cluster being a fragment of the extended solid, we view the cluster-to-cluster transformations as early steps in the growth of the solids.

Experimental

Unless noted to the contrary all manipulations were conducted under inert atmosphere using conventional techniques. Triethylphosphine (Aldrich) and bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) (Strem) were used as received. Solvents were anhydrous and used as received from Aldrich. Tetrakis(triethylphosphine)-palladium [4] and triethylphosphine telluride [5] were prepared using literature methods. Nuclear magnetic resonance spectra were recorded using a GE QE-300 spectrometer. UV–Vis absorption spectra were recorded on an HP 8451 A spectrophotometer. Powder X-ray diffraction measurements used a Rigaku Miniflex diffractometer (Cu Kα radiation).

Preparation of $Pd_2Te_2(PEt_3)_4$

$Pd(PEt_3)_4$ (2.25 g, 3.89 mmol), $TePEt_3$ (0.96 g, 3.89 mmol) and PEt_3 (1.87 g, 15.56 mmol) were combined in toluene (10 ml). The resulting green mixture was stirred for 1 h at room temperature and then filtered into a Schlenk vessel. The solution was evaporated *in vacuo* to approximately 7 ml and then cooled to −20 °C for 24 h. The product formed as a green crystalline

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solid (1.41 g, 1.50 mmol, 77%). This material was identical to $Pd_2Te_2(PEt_3)_4$ prepared as in ref. 1. $^{31}P\{^1H\}$ NMR (C_6D_6): single resonance 8.2 ppm downfield from PEt_3*. UV–Vis (toluene): broad bands at 334 and 376 nm with a significant tail out to longer wavelengths. The solid softens and evolves PEt_3 at approximately 100–115 °C. Differential scanning calorimetry (DSC) shows two endotherms, one centered at 111 °C corresponding to the process just described, the other centered at 155 °C. *Anal.* Calc. for $C_{24}H_{60}P_4Pd_2Te_2$: C, 30.65; H, 6.43; P, 13.17; Pd, 22.62; Te, 27.13. Found: C, 30.51; H, 6.26; P, 13.13; Pd, 22.40; Te, 26.85%.

Conversion of $Pd_2Te_2(PEt_3)_4$ *to* $Pd_6Te_6(PEt_3)_8$

$Pd_2Te_2(PEt_3)_4$ (0.35 g, 0.37 mmol) and PEt_3 (0.17 g, 1.5 mmol) were combined in toluene. The mixture was stirred at room temperature for 1 h and filtered. Heptane (20 ml) was layered onto this solution and the two phases were allowed to interdiffuse at room temperature. The product formed as a deep red crystalline solid (0.19 g, 0.081 mmol, 66%). This material was identical to $Pd_6Te_6(PEt_3)_8$ prepared as in ref. 1. *Anal.* Calc. for $C_{48}H_{120}P_8Pd_6Te_6$: C, 24.54; H, 5.15; P, 10.55; Pd, 27.17; Te, 32.59. Found: C, 24.81; H, 5.14; P, 10.65; Pd, 27.30; Te, 32.30%. Powder X-ray diffraction from this crystalline solid matched that from the material described in ref. 1.

Thermolysis of $Pd_2Te_2(PEt_3)_4$

(A) $Pd_2Te_2(PEt_3)_4$ (0.161 g, 0.171 mmol) was dissolved in toluene (10 ml) and the resulting solution was heated to reflux during which time a dark powdery solid formed. After 10 min the mixture was cooled to room temperature and filtered. The solid was washed with pentane and dried. This gave 0.079 g (99% based on eqn. (2)) of polycrystalline PdTe (assayed by powder X-ray diffraction [6]).

(B) $Pd_2Te_2(PEt_3)_4$ (0.097 g, 0.103 mmol) was sealed in an evacuated pyrex tube and heated to 170 °C for 1.5 h. At the end of that time the tube was cooled and opened. The resulting black solid was collected, washed with pentane and dried (yield: 0.047 g = 97% based on eqn. (2)). Powder X-ray diffraction showed only PdTe (NiAs structure type) [6].

Preparation of $Ni_9Te_6(PEt_3)_8$

$Ni(COD)_2$ (7.80 g, 28.4 mmol), $TePEt_3$ (3.55 g, 14.5 mmol) and PEt_3 (35 ml, 237 mmol) were combined in pentane (70 ml). The mixture was stirred approximately 30 min and then filtered into a fresh vessel. The product formed as a dark crystalline solid (3.05 g, 1.36 mmol, 56%). This material is identical in all respects to $Ni_9Te_6(PEt_3)_8$ prepared and analyzed as in ref. 2. The compound is soluble in toluene and thf, giving deep brown solutions. The room-temperature optical absorption spectrum of the cluster in solution shows a peak at 363 nm with a tail extending across the entire visible range and into the IR. There are barely defined features at 405, 467 and approximately 600 nm. This solid does not melt, however DSC of the solid shows a single endothermic process occurring between 130 and 150 °C.

Preparation of $Ni_{20}Te_{18}(PEt_3)_{12}$

A solution of $Ni(COD)_2$ (0.52 g, 1.9 mmol) and PEt_3 (0.23 g, 1.9 mmol) in toluene (10 ml) was treated with a solution of $TePEt_3$ (0.47 g, 1.9 mmol) in toluene (5 ml). The resulting black mixture was allowed to stand at room temperature for three days after which time a small amount of black solid had precipitated. This solid was removed by filtration and pentane (40 ml) was carefully layered onto the filtered toluene solution. After four days the layers had interdiffused and a black, crystalline solid has formed (0.12 g, 26%). The characterization of this material, $Ni_{20}Te_{18}(PEt_3)_{12}$, is given in ref. 2. This cluster is slightly soluble in toluene, giving black solutions whose optical absorption spectra are featureless across the visible into the IR. The crystalline solid does not melt, however, DSC of the solid shows a single exotherm at 165–170 °C. Powder X-ray diffraction of the material which had been heated through this exotherm showed it to be polycrystalline δ-NiTe. (The δ phase of NiTe occurs as a pure phase between $NiTe_{1.09}$ and $NiTe_2$ [7].)

Conversion of $Ni_9Te_6(PEt_3)_8$ *to* $Ni_{20}Te_{18}(PEt_3)_{12}$

$Ni_9Te_6(PEt_3)_8$ (250 mg, 0.11 mmol) and PEt_3 (150 mg, 1.27 mmol) were combined in toluene (20 ml) and the mixture was stirred for 30 min to ensure complete dissolution. At this point $TePEt_3$ (75 mg, 0.31 mmol) was added as a solid to the deep brown solution and the resulting solution was stirred magnetically at room temperature for 24 h. The solution, which has slowly turned black, was filtered to remove a small amount of black solid. Pentane (40 ml) was carefully layered onto the toluene solution and the two phases were allowed to interdiffuse slowly. After 10 days large black crystals had formed and were collected. This crystalline product is identical to $Ni_{20}Te_{18}(PEt_3)_{12}$ prepared as in ref. 2. Single crystal X-ray diffraction shows this material to have the same unit cell as that in ref. 2 and powder X-ray diffraction shows $Ni_{20}Te_{18}(PEt_3)_{12}$ to be the only product (yield: 100 mg = 42%).

Thermolysis of $Ni_9Te_6(PEt_3)_8$

$Ni_9Te_6(PEt_3)_8$ (88.2 mg, 3.93×10^{-5} mol) was sealed in an evacuated pyrex tube and heated to 200 °C for

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*In ref. 1 the chemical shift of the ^{31}P NMR resonance for 1 was erroneously given as upfield from PEt_3.

1 h. The tube was then cooled and opened. The black solid was washed with pentane and dried (yield: 50.5 mg, 99% based on eqn. (4)). Powder X-ray diffraction showed weak interferences attributable to Ni_3Te_2 [7]*. The material was annealed under vacuum at 400 °C for an additional 18 h after which much stronger diffraction was observed.

Thermolysis of $Ni_{20}Te_{18}(PEt_3)_{12}$

$Ni_{20}Te_{18}(PEt_3)_{12}$ (88.3 mg, 1.80×10^{-5} mol) was sealed in an evacuated pyrex tube and heated to 200 ° for 1 h. The tube was then cooled and opened. The black solid was washed with pentane and dried (yield: 62.6 mg, 100% based on eqn. (3)). Powder X-ray diffraction showed δ-NiTe (NiAs structure type) to be the only crystalline solid product. After further annealing (400 °C, 18 h) interfaces due to γ-NiTe ($Ni_{1+x}Te$) appeared.

Results and discussion

We previously reported a preparation of the solid state compound PdTe that used the molecular compounds ($Pd(PPh_3)_4$ and $TePEt_3$ ($Ph = C_6H_5$ and $Et = C_2H_5$) as starting materials. In that publication we reported that when the two reagents were combined in refluxing toluene the solid state compound formed quickly and precipitated. We also showed that two molecular compounds could be formed by conducting the same reaction under less forcing conditions. When $Pd(PPh_3)_4$ and $TePEt_3$ were combined in toluene at room temperature $Pd_2Te_2(PEt_3)_4$ (**1**) (Fig. 1) and $Pd_6Te_6(PEt_3)_8$ (**2**) (Fig. 2), were formed in low yield. We were able to show that **2** could be converted thermally to PdTe, but owing to the poor yield of **1** from this reaction we were not able to study its condensation to give either **2** or PdTe. Herein we address those omissions.

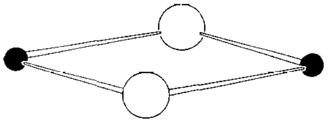

Fig. 1. Diagram of the inorganic core of $Pd_2Te_2(PEt_3)_4$. Filled circles represent Pd atoms, open circles represent Te atoms and the phosphine ligands have been omitted for clarity. Full details of the structure are given in ref. 1.

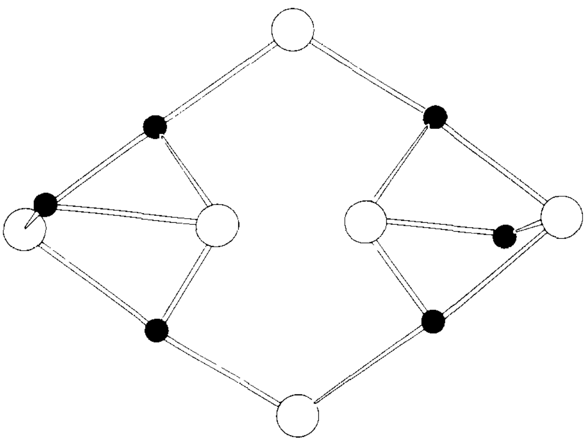

Fig. 2. Diagram of the inorganic core of $Pd_6Te_6(PEt_3)_8$. Filled circles represent Pd atoms, open circles represent Te atoms and the phosphine ligands have been omitted for clarity Full details of the structure are given in ref. 1.

We presumed that low yields of **1** and **2** were due to the presence in the reaction environment of two different phosphine ligands, PPh_3 and PEt_3, and reasoned that if the PPh_3 were removed from the system the process would be simplified and the yields improved. This has been the case. When $Pd(PEt_3)_4$ and $TePEt_3$ are combined in toluene at room temperature a green solution results from which **1** can be crystallized in high yield (eqn. (1)). Compound **1** is very soluble in toluene and not soluble in pentane. As befits its molecular structure compound **1** shows simple NMR spectra: the ^1H spectrum shows the ethyl groups of the coordinating ligands, and the ^{31}P spectrum shows one singlet (no ^{125}Te satellites could be identified).

$$2Pd(PEt_3)_4 + 2TePEt_3 \longrightarrow Pd_2Te(PEt_3)_4 \qquad (1)$$

Several compounds that are similar to **1** have been reported. Adams *et al.* [9] prepared $(Ph_3P)_4Pt_2Te_2$ from $(Bu_4N)_4Hg_4Te_{12}$ and $Pt(PPh_3)_4$, and Dahl and co-workers [10] have prepared $(Et_3P)_4Pt_2Te_2$ from $[Pt_3(CO)_6]_n{}^{2-}$ and $TePEt_3$. In each case the structure of the Pt_2Te_2 compound was determined, and the general features of the three $M_2Te_2L_4$ structures are the same. By way of contrast, Dahl *et al.* have found that $Pt_2Te_2(PEt_3)_4$ can be oxidized to give $Pt_2Te_2(PEt_3)_4{}^{2+}[SbF_6{}^-]_2$, and that a Te–Te bond forms in the latter complex. The presence of Te–Te bonding in the M_2Te_2 array is reminiscent of that seen in $Ni_2Te_2(triphos)_2$ and in $LNi(Te_2)$ (L = triphos or bis(2-diphenylphosphinoethyl)phenylphosphorane) by Di Vaira *et al.* [11, 12]. Apparently the electronic structure of these complexes is not as simple as their formulae suggest.

The thermal behavior of compound **1** is noteworthy. When the solid is heated two endothermic processes are apparent by DSC. In the lower temperature of the two (at approx. 110 °C) the material softens and triethylphosphine can be observed to evolve from the solid. In the higher temperature process (at approx. 155 °C) the material turns black as it resolidifies. Bulk thermolysis shows that the result of the high temperature

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*Three structures occur in the Ni–Te phase diagram at or near Ni_3Te_2. The three are very closely related and are based on the unit shown in Fig. 3(b) [8].

process is PdTe (as a polycrystalline solid). Thermolysis of **1** in solution also gives PdTe. Polycrystalline PdTe forms in quantitative yield after 10 min when a solution of **1** in toluene is heated to reflux (eqn. (2)). In our original report [1] we proposed that **1** was an intermediate in the production of PdTe from the solution-phase co-thermolysis of the two zerovalent reagents, $Pd(PPh_3)_4$ and $TePEt_3$, but we were not able to substantiate this by subjecting **1** to the same thermolysis conditions and showing that the same solid state compound results. While the results of the present experiments do not require that **1** is an alternative in the synthesis of PdTe, they do confirm that **1** can be such an intermediate.

$$Pd_2Te_2(PEt_3)_4 \longrightarrow (PdTe)_s + 4PEt_3 \qquad (2)$$

In our original paper we described how the structure of PdTe can be visualized as an ordered assembly of Pd_2Te_2 units, and we compared the Pd_2Te_2 units from **1** and PdTe, showing the similarities as well as differences between the two rhombi. It is tempting to suggest that the solid state compound is actually formed from solution by the sequential, direct linking of Pd_2Te_2 units from **1**, however our evidence does not support this view. We find that under reaction conditions milder than those required to generate PdTe, compound **1** condenses to form compound **2**, $Pd_6Te_6(PEt_3)_8$, a compound which is not a simple assembly of Pd_2Te_2 rhombi.

When compound **1** is dissolved in toluene in the presence of PEt_3 and allowed to stand at room temperature for a short time **2** forms and the latter crystallizes upon the slow addition of heptane. It is not convenient to follow this process either by UV–Vis or by NMR spectroscopy – in neither case does the spectrum of **2** present useful features – therefore this reaction can be described only qualitatively. The conversion of **1** to **2** occurs at a convenient rate and in good yield at room temperature; increasing the temperature to 65 °C decreases the yield of **2**. Added PEt_3 appears to assist in the conversion of **1** to **2**. The yields of **2** from **1** are high; this is a more effective way to prepare **2** than the method we described earlier. A complex whose structure is similar to **2**, $Pd_6Se_4Cl_4(PPh_3)_6$, has recently been reported by Fenske *et al.* [13].

We have shown that **2** can be seen as a fragment of bulk PdTe by associating it with a Te-centered fragment of the extended lattice [1]. We have also discussed the substantial reconstructions which are required to convert from the structure of the molecule to that of the idealized molecular fragment of the solid. Since we have now shown that **1** transforms easily to **2**; that **2** can be converted to PdTe; and that both **1** and **2** are small fragments of the extended solid, the reaction that takes **1** to **2** can be viewed as a very early step in the growth of PdTe from the original mononuclear reagents.

The chemical process which leads from **1** to **2** must be rather complicated and we do not have enough information to draw many conclusions about the mechanisms of the process. The one point that is clear is that at least one-third of the $Pd_2Te_2(PEt_3)_4$ units effectively break up into smaller fragments at some point during the conversion to **2**. For this reason it does not appear that bulk PdTe is formed by the simple and direct stacking of the Pd_2Te_2 units from **1**.

We have shown in another earlier publication [2] that the solid state compound NiTe can be prepared by combining $Ni(COD)_2$, $TePEt_3$ and PEt_3 in refluxing toluene. In our study of this molecules-to-solids process we isolated and identified two molecular clusters $Ni_9Te_6(PEt_3)_8$ (**3**) (Fig. 3(a)) and $Ni_{20}Te_{18}(PEt_3)_{12}$ (**4**) (Fig. 4). The molecular compounds were formed by combining the same molecular reagents under less forcing reaction conditions. We have also shown [3] that each of the molecular clusters can be viewed as a reconstructed fragment of the extended NiTe crystal lattice.

The relationships between **3**, **4** and the solid state tellurides of nickel are more than simply structural. We find that when **4** is heated in the solid state to modest temperatures the stabilizing phosphine ligands are liberated and the extended solid NiTe is formed (eqn. (3)) [7]. The solid mass recovery from this pyrolysis indicates that the PEt_3 is removed quantitatively and powder X-ray diffraction indicates that δ-NiTe is the only crystalline product formed. The pyrolysis of **3** is conducted similarly, however in this case an Ni_3Te_2 phase is formed as the polycrystalline solid product (eqn. (4)). This result might be expected in view of Ni/Te stoichiometry in **3**. Powder diffraction shows only Ni_3Te_2 in the pyrolyzate, and as in the case of **4** the mass recovery indicates that the phosphine is completely removed.

$$Ni_{20}Te_{18}(PEt_3)_{12} \longrightarrow (NiTe)_s + 12PEt_3 \qquad (3)$$

$$Ni_9Te_6(PEt_3)_8 \longrightarrow (Ni_3Te_2)_s + 8PEt_3 \qquad (4)$$

The pyrolyses of **3** and **4** show that the clusters can be chemically as well as structurally connected to the Ni–Te solid state phase diagram; the two clusters are also chemically connected to one another in the sense that **3** can be converted to **4**. When **3** is dissolved in toluene and treated with $TePEt_3$ in the presence of ancillary PEt_3, **4** is formed and can be isolated by the addition of heptane (eqn. (5)). The element ratios and absolute concentrations used for the **3**→**4** transformation were chosen to mimic those used in the synthesis of **4** from $Ni(COD)_2$ and $TePEt_3$ directly, and we have not optimized the yield of **4**.

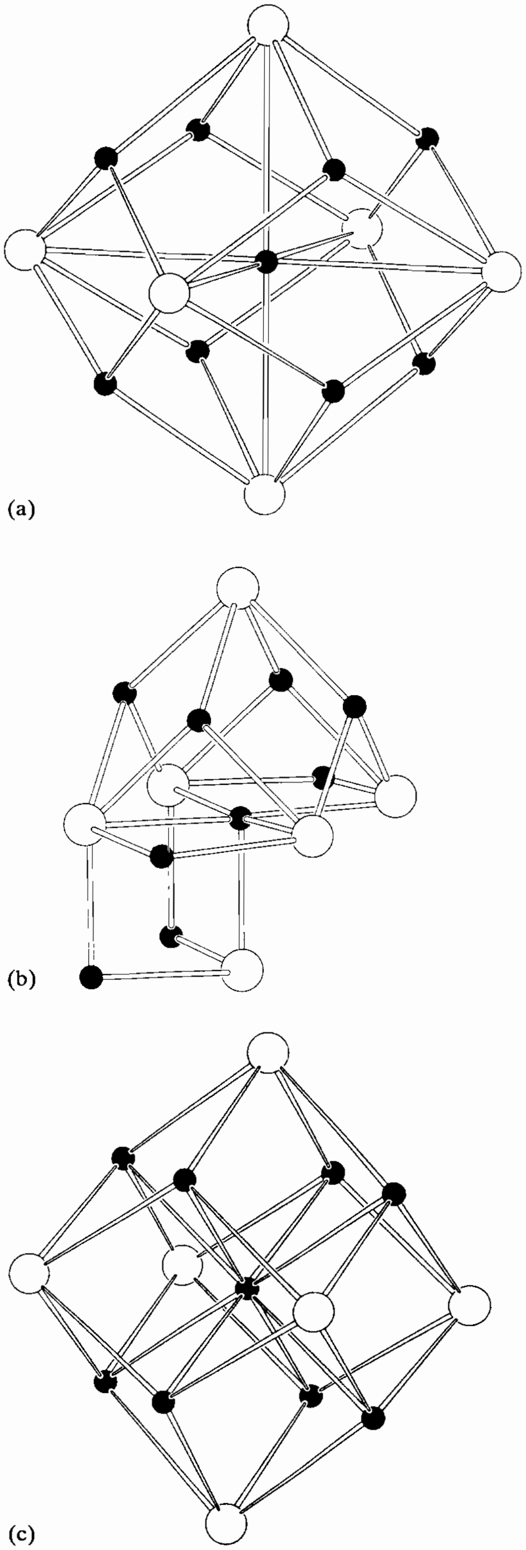

Fig. 3. (a) Diagram of the inorganic core of $Ni_9Te_6(PEt_3)_8$. Filled circles represent Ni atoms, open circles represent Te atoms and the phosphine ligands have been omitted for clarity. Full details of the structure are given in ref 2. (b) Diagram of a Ni-centered fragment of Ni_3Te_2. Structural parameters were taken from refs. 7a and 8 and atom identifications are as in (a). (c) Diagram (a) redrawn to emphasize Ni–Ni bonding.

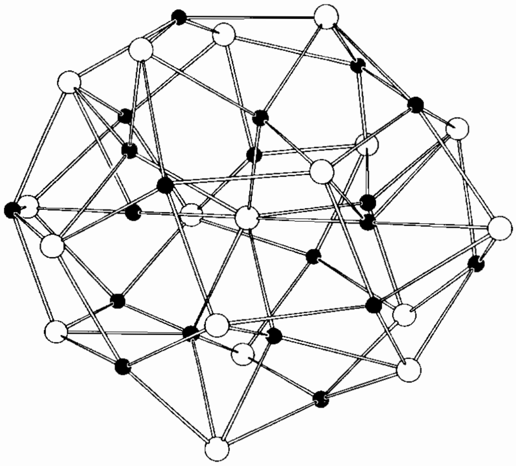

Fig. 4. Diagram of the inorganic core of $Ni_{20}Te_{18}$ Filled circles represent Ni atoms, open circles represent Te atoms and the phosphine ligands have been omitted for clarity. Complete details of the structure are given in ref. 2.

$$20Ni_9Te_6(PEt_3)_8 + 42TePEt_3 \longrightarrow 9Ni_{20}Te_{18}(PEt_3)_{12} \qquad (5)$$

The microscopic process that takes **3** to **4** is certainly very complex, and, as in the Pd/Te case above, we can claim little concerning reaction mechanisms. There is one point that the Ni/Te case appears to have in common with the Pd/Te case: comparison of the stoichiometries of **3** and **4** indicates that at least some fraction of the $Ni_9Te_6(PEt_3)_8$ reactant must fragment at some point in the transformation. The extent to which the feedstock cluster must disintegrate is not clear.

Since we have shown that $Ni_9Te_6(PEt_3)_8$ and $Ni_{20}Te_{18}(PEt_3)_{12}$ are both identifiable as fragments of the NiTe (NiAs-type) solid state structure we suggest that the reaction which takes the smaller cluster to the larger cluster is an early step in the molecule-based synthesis of the extended solid. However, since **3** and **4** have different Ni:Te ratios, the association of both of them with the same point in the Ni–Te solid state phase diagram is equivocal. This is particularly true since the solid phase thermolyses of the two cluster compounds give different solid products (eqns. (3) and (4)). The ambiguity is stressed when the structure of **3** is examined in more detail.

In Fig. 3(a) we show the inorganic core of **3**. Bonds are drawn between the central Ni atom and the peripheral Te atoms in order to emphasize the fact that the central Ni atom is octahedrally coordinated by six Te atoms. Since each Ni atom in δ-NiTe is in the same octahedral Te_6 environment [14, 15] this representation of **3** underscores the geometrical relationship between **3** and the NiAs-type NiTe phase. What goes unsaid in the foregoing analysis is that six of the eight peripheral

Ni atoms must be relocated in order to change from the Ni_9Ti_6 core of **3** to an Ni_9Te_6 site in δ-NiTe [3].

The drawing in Fig. 3(a) obscures the fact that **3** is also structurally related to Ni_3Te_2. In Fig. 3(b) we show a Ni-centered fragment of Ni_3Te_2 [7, 8]. There is a noticeable similarity between the fragment of Ni_3Te_2 and the inorganic core of **3**. Only two changes need to be made to connect the Ni_9Te_6 unit in Fig. 3(b) to that in Fig. 3(a): (i) the four lower Ni atoms must be moved, and (ii) the Ni_{center}–Te distances must be equalized. It is unclear whether **3** bears more resemblance to NiTe or to Ni_3Te_2.

The drawing in Fig. 3(a) is also misleading because the central Ni atom is actually closer to the peripheral Ni atoms than to the Te atoms. In describing the bonding in **3**, Fig. 3(c) may be more accurate. The average Ni_{center}–Ni_{outer} distance in **3** is 2.47 Å .This is shorter than the nearest neighbor distance in elemental Ni (2.49 Å) therefore it is reasonable to invoke Ni–Ni bonding in **3**. Taken *in toto* Fig. 3 shows that there exist similarities between **3** and extended solids, but that the identification of **3** as a fragment of an extended solid is not unique; the cluster resembles Ni_3Te_2, δ-NiTe and elemental Ni, each in a different sense.

The identification of **4** as a fragment of δ-NiTe is unique in the sense that we have not been able to find other members of the Ni–Te phase diagram whose structures contain an $Ni_{20}Te_{18}$ unit that looks like the core of **4**. While **3** is too small to be conclusively identified with a single solid phase, by the time **3** has grown into **4** (via eqn.(5)) the selection of δ-NiTe as the 'target' phase has been made.

Conclusions

This report has centered on two systems in which extended inorganic solid state materials have been made from simple molecular precursors. In each system we had previously isolated two clusters by moderating the reactions which led from the molecular reagents to the solid state products. Here we have shown that in each case the smaller of the two clusters can be converted to the larger under appropriate reaction conditions. We have argued that since each cluster can be identified as a fragment of the extended lattice the cluster-to-cluster reactions can be identified as a rudimentary step in the growth of the solid state compound from the molecular reagents. In connection with this we have also argued that the structural features of the ultimate solid state compound are more apparent in the larger clusters than in the smaller.

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