work may be related to this high symmetrical structure.

Supplementary Material Available: Tables A–F, listing atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **2** and **3** (14 pages). Tables G and H, listing observed and calculated structure factors for **2** and **3**, respectively (42 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Takumi Konno*
Ken-ichi Okamoto
Jinsai Hidaka

Received January 3, 1991

$(Et_3P)_6Co_6Te_8$ and a Connection between Chevrel Clusters and the NiAs Structure

We have shown several examples[1] of molecule-to-solid transformations in which we have been able to intercept and characterize reaction intermediates. In some of these cases,[1a,b] we have isolated molecule intermediates that bear no particular resemblance to the ultimate solid products; however, in other instances[1c–e], we have found cluster intermediates that are identifiable fragments of the solid lattice. In this communication we report a molecular precursor synthesis of β-cobalt telluride and the interception of the intermediate $(Et_3P)_6Co_6Te_8$ (**1**). We show that this core is, furthermore, a simply distorted fragment of the CoTe (NiAs-type) lattice.

Since dicobalt octacarbonyl[2] and triethylphosphine telluride[3] are convenient sources of Co(0) and Te(0), respectively, we attempted to find the conditions under which the combination of the two would yield cobalt telluride. We found[4] that the reaction of $Co_2(CO)_8$ with Et_3PTe in a 3:8 molar ratio gave cluster **1**. The compound is a very dark red, crystalline solid that is soluble in common organic solvents. We determined the molecular structure of the compound,[5] and a drawing of that structure is shown in Figure 1. The structure is composed of an octahedron of Co atoms with a Te atom on each octahedral face. The surface of the cluster is passivated by a triethylphosphine ligand bound to each cobalt. This cluster is a member of the growing family of Chevrel-type[6]

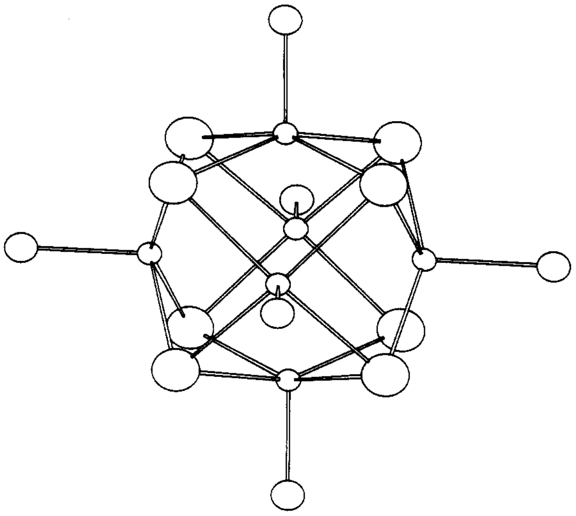

Figure 1. Molecular structure of $Co_6Te_8(PEt_3)_6$. Small circles represent Co atoms. Large circles represent Te atoms. Intermediate circles represent P atoms. C_2H_5 groups are omitted for clarity. Selected averages: r(Co–Te) = 2.521 (4) Å (average of 34, std dev = 0.008 Å); r(Te–Te) = 3.483 (3) Å (average of 19, std dev = 0.014 Å), r(Co–P) = 2.139 (9) Å (average of 6, std dev = 0.010 Å), θ(Co–Te–Co) = 79.53 (13)° (average of 24, std dev = 0.46°), θ_{cis}(Te–Co–Te) = 87.38 (13)°, std dev = 0.58°), θ_{trans}(Te–Co–Te) = 155.29° (average of 12, std dev = 0.53°), θ(Te–Co–P) = 102.3 (3)° (average of 24, std dev = 1.8°). There are two independent clusters in the unit cell. The structures of the two are essentially identical.

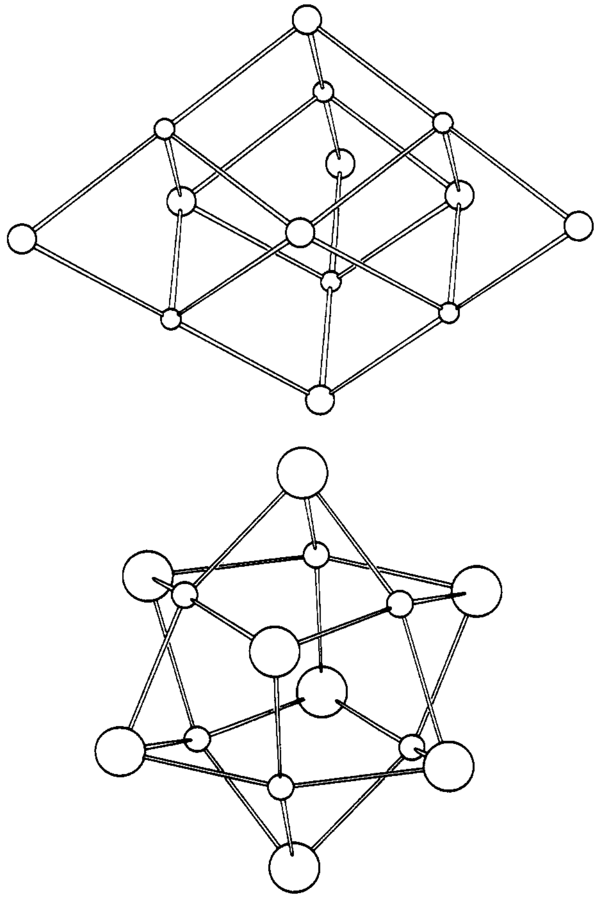

Figure 2. (a) Top: Void site in the CoTe lattice. Large circles represent Te; small circles represent Co. (b) Bottom: Co_6Te_8 core of **1** redrawn to stress relationship with the void site shown in part a.

---

(1) (a) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228. (b) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52. (c) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141. (d) Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240. (e) Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 9233.

(2) Wender, I.; Pino, P. *Organic Synthesis via Metal Carbonyls*; Wiley-Interscience: New York, 1968; Vol. 1.

(3) Zingaro, R. A.; Stevens, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320–3.

(4) The synthesis of **1** was as follows. Dicobalt octacarbonyl (2.06 g, 6.0 mmol) was dissolved in toluene (40 mL) and treated with triethylphosphine (4 mL, 27 mmol) and triethylphosphine telluride (4.12 g, 16.8 mmol). The resulting mixture was heated to reflux for 2 h, then cooled to room temperature, and filtered. The toluene solution was concentrated in vacuo, and pentane was added. Crystallization at –20 °C gave 2.60 g of a dark, crystalline solid. Residual CO (shown by infrared spectroscopy) was exchanged as follows: A portion of the crude product (1.89 g) was dissolved in toluene (30 ml) and treated with triethylphosphine (2.8 ml, 19 mmol). The mixture was heated to reflux 17 hr. Crystallization as above gave **1** (1.65 g, 55% effective overall yield) as a black-red crystalline solid. The infrared spectrum of this solid showed no CO. The compound was characterized as follows IR (CS_2): in addition to the trace CO band (1930 cm^{-1}), there are only absorptions characteristic of coordinated Et_3P. $^{31}P\{^1H\}$ NMR (C_6D_6): 88.1 ppm downfield from (external) 85% H_3PO_4; fwhm = 710 Hz. UV–vis (toluene), λ_{max} (ϵ): 398 (37 000), 474 (23 700), 538 nm (20 000). The compound decomposes without melting. (The thermal behavior of this compound is discussed in the text.) Anal. (Analytische Laboratorien). Found (calcd for $C_{36}H_{90}Co_6P_6Te_8$): C, 20.86 (20.75); H, 4.23 (4.35); Co, 17.10 (16.97); P, 8.74 (8.92); Te, 49.00 (49.00).

(5) Compound **1** crystallizes in the $P\bar{1}$ space group. Lattice constants: a = 12.2460 (10) Å, b = 13.1120 (10) Å, c = 20.4420 (20) Å, α = 88.790 (10)°, β = 86.480 (10)°, γ = 70.780 (10)°, Z = 2, V = 3093.6 (5) $Å^3$. There are two independent clusters in the unit cell. Data collection and reduction: $2\theta_{max}$ = 44.8°, 5729 reflections with $I > 2.5\sigma I$. The last least-squares cycle was calculated with 56 atoms, 326 parameters, and 5729 out of 7999 reflections; R = 0.069, R_w = 0.058.

0020-1669/91/1330-2256$02.50/0

clusters, $(Et_3P)_6M_6X_8$ (M = Co, X = S,[7] Se;[8] M = Fe,[9] Mo,[10] W,[11] X = S). Comparison of this structure to the sulfur and selenium analogues verifies the conclusion advanced by Zanello[12] that bonding in the cobalt clusters is dominated by the cobalt–chalcogen bonds. The large Co–Co and Te–Te separations preclude significant metal–metal or chalcogen–chalcogen bonding. As expected on the basis of atomic sizes the Co/Te cluster is larger than the corresponding Co/S and Co/Se clusters. (We have isolated ions of the $(Et_3P)_6Co_6Te_8$ cluster, and will report their syntheses and characterizations separately.)

We examined the thermal behavior of **1** by differential scanning calorimetry (DSC). This showed a broad endotherm between approximately 225 and 275 °C. In order to determine the source of this endotherm, we conducted the thermolysis on a preparative scale and found that heating **1** in a sealed tube to 300 °C for 45 min gives polycrystalline β-CoTe.[13] This molecule-based preparation of the solid is summarized in eq 1.

$$3Co_2(CO)_8 + 8TePEt_3 \xrightarrow[-PEt_3]{-CO} Co_6Te_8(PEt_3)_6 \xrightarrow[-PEt_3]{\Delta} \beta\text{-CoTe} \qquad (1)$$

It is important to see if there is any structural relationship between compound **1** and the solid product CoTe, for at least two reasons. First, it will help elucidate the chemical processes by which molecular starting materials are converted to solid-state products. Second, when studying the particle-size dependence of properties of a solid,[14] one must know at what point a molecule is of the right size and shape to be considered a small piece of a solid. We can identify the Co_6Te_8 nucleus of **1** as a reconstructed fragment of bulk CoTe in the following way.

Cobalt telluride, $Co_{1-x}Te$, forms in the NiAs structure over a wide range of x. The NiAs structure consists of an hexagonal close-packed array of anions with cations filling the octahedral holes in the anion lattice.[15] A complementary description of the structure is the regular combination of three sites: the anion, the cation, and the remaining interstitial void. Each anion in the lattice is at the center of a trigonal prism of cations; each cation is at the center of an octahedron of anions, and each interstitial site is defined equivalently by either a second trigonal prism of cations or by a trigonal bipyramid of anions. (Occupation of this site gives the "filled NiAs structure"—the Ni_2In structure type[16]). Figure 2a shows a drawing of this interstitial site.

To arrive at the structure in Figure 2a, we included the void site and its first and second nearest neighbors. This gives the formula Co_6Te_8. For comparison the Co_6Te_8 core of **1** is shown in Figure 2b. These figures show that the CoTe fragment results from a 60° twist of one face of the Co_6 octahedron of **1**, thereby generating a Co_6 trigonal prism. In conjunction with this, the six Te atoms involved in the twist reorganize; three cap the rectangular faces of the trigonal prism, and three span the vertical edges of the prism.

This analysis shows that **1** can be viewed as a small, distorted fragment of the CoTe structure. While the reorganization that connects the two structures in Figure 2 is qualitatively drastic, it is conceptually simple. Comparison of the two structures hints at the pathway the molecular reagents, cobalt carbonyl, and the phosphine telluride take to get to the solid product and shows some of the reconstruction CoTe can undergo as the particle size becomes very small. We are studying the reactions which lead to **1** and from **1** to other CoTe clusters in order to further characterize the molecules-to-solids transformation.

It is interesting to note in passing that there is such a relationship between the NiAs structure and the M_6X_8 cluster that is the building block of the Chevrel phases.

Acknowledgment. We gratefully acknowledge P. Trevor for X-ray fluorescence measurements.

Supplementary Material Available: Tables listing crystallographic data, positional and thermal parameters, and significant distances and angles for $(Et_3P)_6Co_6Te_8$, a diagram showing the packing of **1** in the crystal, and a DSC trace of the thermal behavior of **1** (10 pages); a table of calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page.

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

M. L. Steigerwald*
T. Siegrist
S. M. Stuczynski

Received January 9, 1991

---

[6] Yvon, K. *Current Topics in Materials Science*; Kaldis, E., Ed.; North-Holland: Amsterdam, 1979; Vol. 3, pp 53–129.

[7] (a) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *Polyhedron* **1986**, *5*, 2021. (b) Diana, E.; Gervasio, G.; Rossetti, R.; Valdemarin, F.; Bor, G.; Stranghellini, P. L. *Inorg. Chem.* **1991**, *30*, 294.

[8] Fenske, D.; Ohmer, J.; Hachengenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993.

[9] Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1987**, 831.

[10] (a) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 1646. (b) Saito, T.; Yamamoto, N.; Nagase, T.; Tsuboi, T.; Kobayashi, K.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1990**, *29*, 764.

[11] Saito, T.; Yoshikawa, A.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1989**, *28*, 3588.

[12] Zanello, P. *Coord. Chem. Rev.* **1988**, *83*, 199.

[13] Compound **1** (400 mg; 0.19 mmol) was sealed in Pyrex under vacuum and heated in a tube furnace at 300 °C for 45 min. This gave triethylphosphine and a shiny black solid. The tube was cooled and the solid was collected, washed with pentane, and dried (yield = 264 mg = 100% based on the second reaction in eq 1). Powder X-ray diffraction shows only β-CoTe. Anal. (Analytische Laboratorien). Found (calcd for $Co_{0.75}Te$): C, 0.60 (0.0); H, 0.03 (0.0); P, 0.88 (0.0); Co, 25.15 (25.73); Te, 70.60 (74.27).

[14] Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471.

[15] (a) Wells, A. F. *Structural Inorganic Chemisry*, 5th ed.; Clarendon Press: Cambridge, U.K., 1984; Chapter 17. (b) West, A. R. *Solid State Chemistry and its Applications*; John Wiley & Sons: Chichester, U.K., Chapter 7. (c) Haraldsen, H.; Gronvold, F.; Hurlen, T. *Z. Anorg. Allg. Chem.* **1956**, *283*, 143.

[16] Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley-Interscience: New York, 1972; p 530 f.

High-Nuclearity Platinum–Osmium Alloy Cluster Complexes. Synthesis and Structural Characterizations of $Pt_4Os_6(CO)_{22}(COD)$ and $Pt_5Os_6(CO)_{21}(COD)_2$

The discovery that platinum alloy clusters have catalytic properties that are far superior to those of pure platinum has led to major improvements in the process of petroleum reforming.[1] This has resulted in an increased interest in the study of the structure, bonding, and reactivity of mixed-metal cluster complexes containing platinum.[2] To date, however, there have been very few reports of high-nuclearity alloy cluster complexes containing platinum.[3-5] We now wish to report the first examples of what may prove to be a series of new high-nuclearity platinum–osmium carbonyl cluster complexes having structures based upon alternating layers of platinum and osmium.

Three products were formed when a hexane solution of $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**)[6] (COD = 1,5-cyclooctadiene) (24.0 mg

---

[1] (a) Sinfelt, J. H. *Bimetallic Catalysts. Discoveries, Concepts and Applications*; Wiley: New York, 1983. (b) Sinfelt, J. H. *Sci. Am.* **1985**, *253*, 90. (c) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15. (d) Sachtler, W. M. H. *J. Mol. Catal.* **1984**, *25*, 1. (e) Ponec, V. *Adv. Catal.* **1983**, *32*, 149.

[2] Farrugia, L. J. *Adv. Organomet. Chem.* **1990**, *31*, 301.

[3] (a) Fumagalli, A.; Martinengo, S.; Ciani, G. *J. Organomet. Chem.* **1984**, *273*, C46. (b) Fumagalli, A.; Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1381. (c) Fumagalli, A.; Martinengo, S.; Ciani, G.; Marturano, G. *Inorg. Chem.* **1986**, *25*, 592.

[4] (a) Ceriotti, A.; Demartin, F.; Longoni, G.; Manassero, M.; Marchionna, M.; Piva, G.; Sansoni, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 697. (b) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 7973.

[5] (a) Couture, C.; Farrar, D. H.; Goudsmit, R. J. *Inorg. Chim. Acta* **1984**, *89*, L29. (b) Couture, C.; Farrar, D. H. *J. Chem. Soc., Chem. Commun.* **1985**, 197. (c) Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2245. (d) Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2253. (e) Adams, R. D.; Wu, W. *Organometallics* **1991**, *10*, 35.

[6] Adams, R. D.; Chen, G.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 1007.

0020-1669/91/1330-2257$02.50/0