Electrochemical Synthesis of a New Gallium Telluride containing One-dimensional Chains: Structure Of $[(C_6H_5)_4P]GaTe_2(en)_2$ (en = ethane-1,2-diamine)

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The cathodic dissolution of a Ga_2Te_3 electrode in an ethane-1,2-diamine solution of tetraphenylphosphonium bromide yields the novel gallium telluride $[(C_6H_5)_4P]GaTe_2(en)_2$ **1** which consists of one-dimensional $GaTe_2(en)_2^-$ chains held together by NH···Te hydrogen bonds.

There are very few examples of compounds of gallium and the heavier group 16 elements in the literature. While the binary compounds GaTe, Ga_2Te_3, and Ga_2Te_5 have been known for a long time, most of the recent interest in this area has been directed toward the organometallic compounds of gallium with group 15 elements. Compounds such as $R_3Ga{\cdot}XR'_3$[1] (X = N, P, As) and $(R_2Ga{\cdot}XR'_2)_2$[2] (X = P, As), for example, are of current interest as possible precursors to thin films of III–V materials.[3] The first example of a compound containing a Ga–Te bond was reported by Coates[4] in the adduct formed from the reaction of $GaMe_3$ with $TeMe_2$. Since then, the compounds $[(Me_3CCH_2)_2GaTePh]_2$, which was prepared from the reaction of $Ga(CH_2CMe_3)_2Cl$ with LiTePh in Et_2O[5] and $[(Bu^t)_2Ga(\mu\text{-}TeBu^t)]_2$, which was prepared by the ambient temperature reaction of $Ga(Bu^t)_3$ with metallic tellurium,[6] appear to be the only examples of Ga–Te compounds with organic ligands. Isolated Ga–Te anions are even rarer with $K_6Ga_2Te_6$ prepared by the high temperature fusion of the elements[7] apparently being the only known example. Related work in the semiconductor industries has produced the compounds $XGaTe_2$ (X = Cu, Ag, In, Tl),[8] XGa_2Te_4 (X = Cd, Hg),[9a,b] and $Ag_2Ga_6Te_{10}$[10] which have been studied for their optical, thermal and electrophysical properties. We report here the electrochemical synthesis of the new gallium telluride compound $[(C_6H_5)_4P]GaTe_2(en)_2$ **1** which exists in the solid state as one-dimensional hydrogen-bonded chains.

We have previously reported the novel electrochemical synthesis of the gold tellurides $[(n\text{-}C_4H_9)_4N]_3Au_3Te_4$ and $[(C_6H_5)_4P]_2Au_2Te_4$, which were prepared by the cathodic dissolution of $AuTe_2$ alloy electrodes.[11a] We have also isolated the compounds $[(n\text{-}C_3H_7)_4N]_4Sb_4Te_4$ and $[n\text{-}C_3H_7)_4N]_3Sb_9Te_6$,[11b] $[(n\text{-}C_4H_9)_4N]_2In_2Te_4$,[11c] and others from the Hg and As telluride systems using a similar cathodic dissolution process. This technique, which was inspired by the early work of Zintl and Kaiser[12] and others,[13a,b] has allowed us to prepare structurally characterized solids which may not be accessible by standard hydrothermal and high temperature elemental fusion techniques. Using this technique, we have extended this chemistry to include the synthesis of the title compound by the electrochemically controlled cathodic dissolution of a Ga_2Te_3 electrode.

The synthesis of **1** requires a Ga_2Te_3 electrode which is made by melting stoichiometric amounts of the elements under N_2 in a quartz tube. When melting, these elements react violently erupting in bright orange flames and leaving a shiny black solid as a product.† The regulus is then crushed into a fine powder and fabricated into electrodes in accordance with the procedure reported for the Au–Te system.[11a] Compound **1** was observed as bright orange needle-shaped crystals which grew from a galvanostated Ga_2Te_3 cathode running at a current density of *ca.* 300 μA cm^{-2} for 6 days in a solution of 0.5 mol dm^{-3} tetraphenylphosphonium bromide in ethane-1,2-diamine.‡ A two compartment, liquid junction, air-tight electrochemical cell equipped with a nickel plate counter electrode was utilized for this purpose, the ethane-1,2-diamine was purified before use by distillation from a red solution of K_4Sn_9, and all manipulations were performed in a high purity (<1 ppm O_2) He atmosphere. The use of nickel as a counter electrode is a modification to our previous technique (in which Pt was used) and is advantageous in that it generates an insoluble purple precipitate (the qualitative microprobe analysis of which showed Ni and Br in a 1 : 2 molar ratio) in the anode chamber. This prevents cross-contamination of the cathode chamber with oxidation products from the anode chamber thus allowing the reactions to run for longer periods of time.

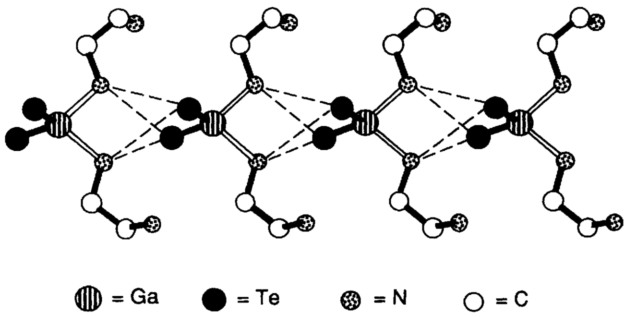

Fig. 1 Structure of $GaTe_2(en)_2^-$ **1** showing one-dimensional doubly hydrogen-bonded chains

X-Ray structural analysis of **1**§ revealed the novel $GaTe_2(en)_2^-$ anion which is shown in Fig. 1. The anion consists of Ga^{III} in a distorted tetrahedral coordination environment. The Ga atom lies on the Wyckoff 4e special position in space group *C2/c* on a twofold axis and is bonded to two crystallographically equivalent terminal Te atoms. The Ga–Te bond distance is 2.509(1) Å, which is 0.11 Å shorter than the sum of the Ga and Te covalent radii, 2.62 Å.[14] Owing to the paucity of structurally characterized Ga-Te compounds, it is difficult to make extensive comparisons with this Ga–Te bond distance. The four-membered Ga_2Te_2 ring in $[(Me_3CCH_2)_2GaTePh]_2$ has Ga–Te bond distances in the range 2.7435(8)–2.7623(8) Å,[5] and $K_6Ga_2Te_6$ is composed of two edge-sharing $GaTe_4$ tetrahedra with Ga–Te bond distances of 2.591 $Å_{(terminal)}$ and 2.680 $Å_{(bridging)}$.[7] In the solid state phases, the average Ga–Te bond distances in GaTe (monoclinic),[15a,b] GaTe (hexagonal),[16] Ga_2Te_3[17] and Ga_2Te_5[15b] are 2.665, 2.61, 2.56, and 2.641 Å respectively. Therefore, it would appear that the $GaTe_2(en)_2^-$ anion has the shortest Ga–Te bond distance thus far recorded.

The Te–Ga–Te bond angle of 125.7(1)° is greatly distorted from the ideal tetrahedral angle of 109.5° by the repulsion of the large Te atoms which are 4.465 Å apart. The N–Ga–N angle is 85.2(4)°, bringing the inner ethylenediamine N atoms to within 2.816 Å of each other. The Te–Ga–N angles are 110.0(2) and 109.2(2)°.

The complete structure of the compound **1** consists of $GaTe_2(en)_2^-$ anions which are doubly hydrogen bonded into one-dimensional chains as shown in Fig. 1. Unlike the corresponding sulfides and selenides, there are few examples of hydrogen bonding to telluride anions. Hydrogen bonding of an ethane-1,2-diamine molecule to Te_3^{2-} has been observed[18] with an N–Te distance of 3.46(6) Å, and MeOH has also been observed to hydrogen bond to the ends of a Te_4^{2-} anion[19] with the O–Te distance being 3.585(7) Å. The criterion for determining the existence of a hydrogen bond in a crystalline

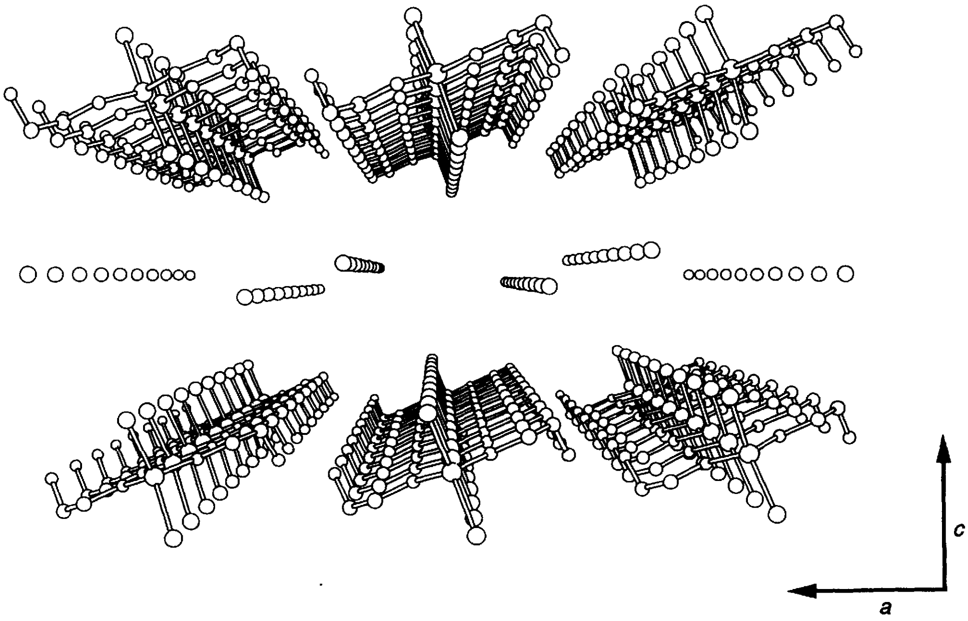

Fig. 2 Perspective view of $[(C_6H_5)_4P]GaTe_2(en)_2$ down the crystallographic *b* axis showing the one-dimensional $GaTe_2(en)_2^-$ chains separated by tetraphenylphosphonium cations (P atoms only shown)

solid was suggested by Hamilton and Ibers[20] as the observation of a distance between two nonhydrogen atoms, one of which is capable of donating electrons (tellurium in this case) and one of which is electronegative and bonded to hydrogen, which is less than the sum of the van der Waals radii. According to Pauling[14] this sum is 3.70 Å for Te–N, which is just 0.050 Å shorter than the closest Te–N contact of 3.750(7) Å and only 0.093 Å shorter than the longer Te–N contact of 3.793(7) Å. In $[(C_6H_5)_4P]GaTe_2(en)_2$, however, we are dealing with two hydrogen bonds per tellurium atom and a formal Te^{2-} anionic radius instead of a Te atomic radius, both reasons of which may contribute to the longer observed hydrogen bonding distances.

The individual chains of $GaTe_2(en)_2^-$ run parallel to the crystallographic *b* axis in sheets which are effectively isolated from one another by tetraphenylphosphonium cations (see Fig. 2). Individual chains within these rows have terminal ethylenediamine N–N contacts of 3.456 Å, and are clearly not related by hydrogen bonding interactions. The Te–Te distance between rows of $GaTe_2(en)_2^-$ chains is 9.789 Å.

The mechanism of formation of $GaTe_2(en)_2^-$ from the reaction of a Ga_2Te_3 cathode is not clear at this time, but may involve the dissolution of a $GaTe_2$ fragment to which ethylenediamine molecules can then coordinate (in a monodentate fashion, as they are excess), thus forming a stable tetrahedral Ga^{III} moiety. There is no evidence of an excess of polytellurides in the catholyte solution (which was light orange in colour), and evaporation of the ethane-1,2-diamine results in the formation of an orange powder, the qualitative microprobe analysis of which shows Ga and Te in a 1:2 molar ratio. By simply exposing this orange solution to the air, we obtained a black powder which contains Ga and Te. We are currently in the process of characterizing this material.

The authors thank Michael J. Souza for the construction of the electrochemical cells used in our experiments.

Received, 15th July 1993; Com. 3/04150F

Footnotes

† CAUTION: Owing to the extreme exothermic nature of this reaction, it must be done in a fume hood equipped with a fire extinguishing device and a safety shield and/or safety face shield must be used.

‡ The cathodic dissolution reaction results in the formation of a bright orange powder and a small number of orange needle-shaped crystals which grow both on the Ga_2Te_3 electrode and on the walls of the cathode chamber. Reactions have typically yielded less than 0.01 g of crystals (an average yield of 8% based on moles of Ga). The reactions are stopped when the insulating orange powder layer prevents further passage of current through the cell, and much of the Ga_2Te_3 electrode is left intact at the end of the experiment. The electrochemical yield (mol of crystalline product/mole e- passed) is typically less than 1%, but as much as 12–15% if the powder is included. This powder, which may also be $[(C_6H_5)_4P]GaTe_2(en)_2$, has not yet been characterized except for qualitative microprobe analyses which have yielded Ga : Te ratios of between 1 : 1.85–1 : 2.06.

§ *Crystal data* for **1**: $C_{28}H_{36}GaN_4PTe_2$, $M = 784.5$, monoclinic, space group *C2/c* (No. 15), $a = 20.680(3)$, $b = 5.3877(9)$, $c = 27.192(5)$ Å, $\beta = 90.13(2)°$, $V = 3029.6(8)$ Å^3 and $D_c = 1.720$ g cm^{-3}. Data were measured on a Siemens P4 diffractometer equipped with an LT-2 low temperature device and graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Lattice parameters at 235 K were determined from the setting angles of 25 centred reflections having $25 \leq 2\theta \leq 34°$. The 3095 measured reflections were corrected for Lorentz and polarization effects, but not for absorption or extinction. Merging equivalents gave 2689 unique reflections ($R_{int} = 0.0226$) of which 1889 having $F > 3.0\sigma(F)$ were considered observed. The structure was solved by heavy-atom methods and refined on *F* by full-matrix least-squares using the Siemens SHELXTL PLUS program package. The atoms of the tetraphenylphosphonium cation were disordered and assigned site occupancy factors of a half with the phenyl rings modelled as regular hexagons and refined as rigid groups. The refinments converged to $R(F) = 0.0479$, $wR(F) = 0.0522$ and $S = 1.05$ with 228 variables and 8.3 reflections per refined parameter. Axial photographs of the *b* axis and diffuse scans along [010] were taken on a rotating anode system (Rigaku AFC7R) in order to confirm the short axial length and look for possible signs of doubling. No evidence of doubling along this axis was found.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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