Inorg. Chem. **1995**, *34*, 6417−6418

$[Fe(en)_3]_2(Hg_2Te_9)$: A Novel Tellurometalate Containing One-Dimensional Chains of Weakly Bound Zintl Anions $(Hg_2Te_9)^{4-}$

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Received July 27, 1995

A tremendous amount of research has been conducted on tellurometalates during the last decade. A number of techniques have been developed and employed in the synthesis of this class of compounds. As a result, many new phases have been prepared and characterized. Thus, solvent extraction of intermetallic alloys has generated polytelluride anions such as $(HgTe_2)^{2-}$,[1] $(Au_9Te_7)^{5-}$,[2] $(Au_4Te_4)^{4-}$,[2] $(Hg_2Te_5)^{2-}$,[3] $[Hg_4Te_2(Te_2)_2(Te_3)_2]^{4-}$,[3] $[Au_2(Te_2)_2]^{2-}$,[4] $(As_{10}Te_3)^{2-}$,[5] $(Cu_4SbTe_{12})^{3-}$,[6] $(Hg_2Te_4)^{2-}$,[7] $[Hg_3Te_7(en)_{0.5}]^{4-}$,[7] and $(Au_2Te_{12})^{4-}$.[8] Nonaqueous solution phase reactions have produced compounds containing $[Cr_3(Te_4)_6]^{3-}$,[9] $(NbTe_{10})^{3-}$,[9] $[Mo_4Te_{16}(en)_4]^{2-}$,[10] $[M(Te_4)_2]^{2-}$, M = Pd,[11−13] Hg,[14,15] Cd,[14,15] and Zn,[15] $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$,[16] $[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]^{4-}$, M = Cu and Ag,[17] $[Pt_4Te_4(Te_3)_6]^{4-}$,[18] $(AuTe_7)^{3-}$,[19] $(Sn_2Te_6)^{4-}$,[20] $(MTe_7)^{3-}$, M = Ag,[21] Hg,[21,22] and Zn,[21] $[M(Te_4)]^-$, M = Cu and Ag,[23] $(M_2Te_{12})^{4-}$, M = Cu and Ag,[24] and $(M_4Te_{12})^{4-}$, M = Cd and Hg.[25] Electrochemical synthesis has resulted in Zintl anionic clusters of $(Au_3Te_4)^{3-}$,[26] $(Sb_4Te_4)^{4-}$,[27] $(Sb_9Te_6)^{3-}$,[27] $(GaTe_2(en)_2)^-$,[28] $(Sb_2Te_5)^{4-}$,[29] $(Sb_6Te_9)^{4-}$,[29] $(As_2Te_5)^{2-}$,[30] and $(As_2Te_6(en)_2)^{4-}$.[30] In addition to these simple tellurometalates,[31] many other new metal tellurides have also been obtained using chemical vapor transport (CVT) reactions and the molten salt (flux growth) technique.[32] In contrast, the hydrothermal (solvothermal) reactions have not yet been extensively applied to the synthesis of telluride compounds. Although several metal selenides[33] and a few metal carbonyl polytelluride clusters[34] have been recently prepared employing this technique, there is virtually no report on the hydrothermal (solvothermal) studies of metal tellurides. Herein we describe our preparation and structure characterization of the first tellurometalate containing mercury and tellurium via this method.

The compound $[Fe(en)_3]_2Hg_2Te_9$ (**1**) was synthesized by reaction of HgCl (59 mg, 0.25 mmol), $FeCl_2$ (32 mg, 0.25 mmol), Rb_2Te (75 mg, 0.25 mmol), and Te (96 mg, 0.75 mmol) in ethylenediamine (en) at 160 °C. The starting materials were mixed in a glovebox and loaded in a Pyrex tube containing ~3.7 mL of ethylenediamine. The tube was then evacuated and sealed with a torch. The sample was heated at 160 °C for 7 days and then cooled to room temperature. The product was washed with ethanol (95%) followed by diethyl ether (100%). The black, columnlike crystals of **1** were manually selected and analyzed by single-crystal X-ray diffraction methods.

The diffraction analysis[35] revealed that **1** contains a novel one-dimensional chain of loosely bound Zintl anions $(Hg_2Te_9)^{4-}$ separated by iron tris(ethylenediamine) cations. The anion, formally written as $[(Hg^{2+})_2(Te^{2-})(Te_2^{2-})(Te_3^{2-})_2]$, consists of a five-membered ring Hg_2Te_3 with two bent $(Te_3)^{2-}$ bonded to the two Hgs in the 1 and 3 positions of the ring (see Figure 1). The Te(1) bridging the two Hg atoms is tilted with respect to the plane of Hg_2Te_2 by 0.52 Å, resulting in an envelope conformation. The mercury atoms have trigonal planar coor-

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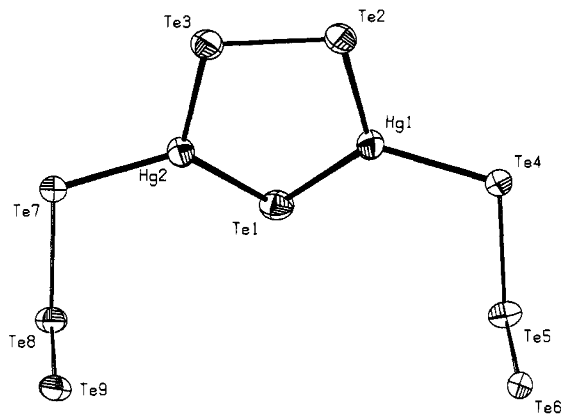

Figure 1. Structure of the anion $(Hg_2Te_9)^{4-}$. Averaged bond distances (Å) 2 × Hg−Te(1) 2.694, 4 × Hg−Te 2.755, 3 × Te−Te(short) 2.734, 2 × Te−Te(long) 2.769. Important angles (deg): Hg(1)−Te(1)−Hg(2) 91.99(4), Te(3,2)−Hg(1,2)−Te(1) 120.2, Hg(1)−Te(2)−Te(3) and Hg(2)−Te(3)−Te(2) 101.9, Te(4,7)−Hg(1,2)−Te(1) 129 (see text for definitions of long and short).

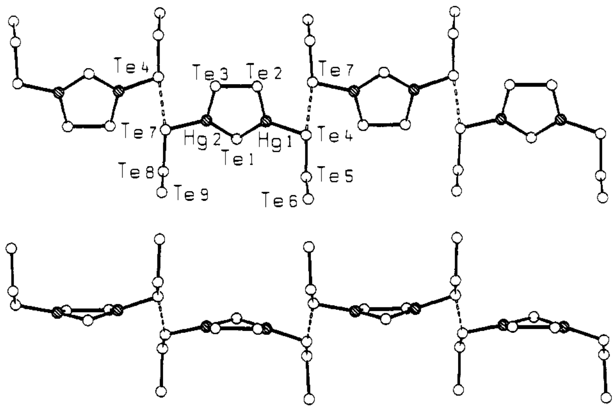

Figure 2. View of the 1-D chain of $(Hg_2Te_9)^{4-}$ anions showing intermolecular contacts (top). Profile of the chain (bottom). Important bond distances (Å) and angles (deg) Te(4)···Te(7) 3.488(2); Te(6)−Te(5)−Te(4), 106.89(5); Te(5)−Te(4)···Te(7), 153.69(5); Te(4)···Te(7)−Te(8), 152.05(5); Te(7)−Te(8)−Te(9), 104.73(5).

dination. The two parallel $(Te_3)^{2-}$ arms define two planes oriented almost perpendicular to the plane of the ring (88° average). The Hg−Te and Te−Te distances are comparable with those found in $(Hg_4Te_{12})^{4-}$,[3,25] $(Hg_2Te_5{}^{2-})_n$,[3] $(Hg_3Te_7{}^{4-})_n$,[7] and $(Hg_2Te_4{}^{2-})_n$.[7] The anion may also be described as a "cut" from $(Hg_4Te_{12})^{4-}$, by removal of one Hg_2Te_3 ring.[3,7] The ubiquity of the five-membered Hg_2Te_3 ring in all the mercurotellurates cited above should be noticed.

The unique screw axis parallel to **b** generates an infinite 1-D chain of $(Hg_2Te_9)^{4-}$ anions as shown in Figure 2. These anions are connected by weak intermolecular interactions between Te(4) and Te(7) at a distance of 3.488(2) Å, which is considerably shorter than the sum of the van der Waals radii of 4.12 Å,[36] thus indicating secondary bonding interactions.[37] This weak interaction is comparable to the intramolecular ones observed in $[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]^{4-}$, M = Cu and Ag (3.48 Å average),[17,24] but longer than those in $(AuTe_7)^{3-}$ (3.25 Å average).[19] Intermolecular secondary interactions with Te−Te distances shorter than 3.5 Å have been described for $(Te_4)^{2-}$,[38] $(Te_8)^{2-}$,[39] and for $(Ni_4Te_{20})^{4-}$, which has a short intercluster contact of 3.40 Å.[16] To the best of our knowledge, these are the only examples of such secondary interactions observed in the known tellurometalates. The effect of the secondary bonding interaction between Te(4) and Te(7) in **1** is lengthening of the Te-Te bonds involving these atoms, thus Te(4)−Te(5) and Te(7)−Te(8) (2.77 Å average) are slightly longer than other three Te−Te bonds (2.73 Å average). Similar elongation is also found in all the examples cited above.

In addition to the novel structure of the anion, no other tellurometalates have ever been isolated with a transition metal complex as counterion.[40] Further studies have shown that use of ethylenediamine as solvent may be important for the synthesis of mercurotellurates containing other transition metal complexes.[41] More peculiarly, the crystal structure of the iron tris-ethylendiamine has never been reported previously. The cation $[Fe(en)_3]^{2+}$ is present with two independent molecules in the more stable conformation *lel*₃.[39] Given the centrosymmetric space group of the structure, both enantiomers $\Lambda(\delta\delta\delta)$ and $\Delta(\lambda\lambda\lambda)$ are present.[42] The coordination of the ethylendiamine is analogous to the cobalt derivatives of the same type and presents an N−C−C−N dihedral angle of average 57° and bite angles N−Fe−N of average 79°.[40] Formal oxidation state assignment suggests that iron is divalent and the average Fe−N distance of 2.21 Å is in agreement with high spin Fe(II) amine complexes (see ref 43 and references therein). Currently, plans are being made to confirm this by ESR studies.

Acknowledgment. The support of the National Science Foundation (Grant No. DMR-9310431) for the work at Rutgers University is gratefully acknowledged. This research has made use of the microprobe and X-ray facilities at Rutgers University and at University of Milan, Italy.

Supporting Information Available: Summary of crystal data (Table S1), atomic positional parameters (Table S2), bond distances and bond angles (Table S3), thermal displacement parameters (Table S4), hydrogen coordinates (Table S5), and a drawing of the tris-(ethylenediamine) cation (8 pages). Ordering information is given on any current masthead page.

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(35) Crystal data for $[Fe(en)_3]_2Hg_2Te_9$: monoclinic, $P2_1/c$ (No. 14), a = 11.915(2) Å, b = 19.105(5) Å, c = 18.180(5) Å, β = 98.64(1)°, V = 4092(2) Å³, Z = 4, D_c = 3.282 Mg·m⁻³, Mo Kα radiation (λ = 0.710 73 Å), μ = 144.91 cm⁻¹. The data collection was performed at 293K on an Enraf-Nonius CAD-4 diffractometer, by the ω-scan method, within the limits $3 < \theta < 25°$. The structure was solved by direct methods (SIR92) and refined by full- matrix least-squares methods (SHELX93). The final agreement indices were R = 0.039 and wR2 = 0.0937 for 3988 independent significant ($I > 3\sigma(I)$) absorption corrected data. Anisotropic thermal factors were assigned to all non-hydrogen atoms. EDX analysis gave a Fe/Hg/Te ratio in agreement with the molecular formula.

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