

# Tellurometalates

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The chemistry of oxometalates and thiometalates was initiated at almost the same time in the early nineteenth century by Berzelius, who synthesized what turned out to be the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  and  $[\text{MoS}_4]^{2-}$  anions. Since then, research in oxometalates has progressed steadily,<sup>3,4</sup> owing to their remarkable, accessible structural chemistry. Some of these compounds show potential in catalysis<sup>5,6</sup> and in medicine.<sup>7</sup> The corresponding chemistry of thiometalates has received serious attention only during the last two decades, although some species, such as  $[\text{Pt}(\text{S}_6)_3]^{2-}$ , have been known for nearly a century.<sup>8</sup> This work on thiometalates has produced many new structure types and coordination modes. While this in itself is *raison d'être* for such research, other factors in its development include the importance of thiometalates as starting materials for the synthesis of models for metalloenzymes<sup>9,10</sup> and for the synthesis of hydrodesulfurization catalysts.<sup>11-14</sup>

Surprisingly, the chemistry of the metalates of the accessible higher congeners of sulfur, namely, selenium and tellurium, has been essentially neglected until recently, presumably owing to the assumption (which turns out to be false) that the chemistry would be similar to that of the sulfur systems. Now the coordination chemistry of selenide, and to a lesser extent telluride, ligands is expanding rapidly. In a very recent review,<sup>15</sup> a large percentage of the 254 references are from the last five years. Earlier reviews<sup>16,17</sup> are out of date. It has become apparent that in going from sulfur to tellurium the chemistry of the chalcogenometalates changes gradually but distinctly. There are some resemblances but far more dissimilarities, in part as a result of decreasing electronegativity and increasing covalency down the family. A beautiful illustration of subtle differences may be found in the three related chalcogenometalates  $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$  (Figure 1A),  $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$  (Figure 1B), and  $[\text{Fe}_{14}\text{Te}_{22}]^{6-}$  (Figure 1C). These anions conceptually are constructed from similar edge-sharing "Fe<sub>2</sub>Q<sub>2</sub>" units (Q = S, Se, Te) that form rings, but each structure is unique. It has also become apparent that a vast new coordination chemistry of selenium and especially tellurium remains to be discovered, rationalized, and systematized. Excitement about this prospect is fueling the rapid growth in the field.

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The objective of this Account is to give a sense of this excitement through the description of the known chemistry of the tellurometalates of general formula  $[\text{M}_x\text{Te}_y]^{z-}$ . This chemistry is very new; most of the species to be discussed are not covered in the most recent review.<sup>15</sup> The results arise almost entirely from intuitive synthetic efforts; the chemistry has not been rationalized, let alone systematized. But as the organometallic chemistry that emanated from the discovery of ferrocene illustrates, synthesis of new compounds, often through serendipity, necessarily precedes rationalization and systematization. Why did we select the tellurometalates for discussion? Conceptually, these are simple species, comprising a single type of metal atom and tellurium. But, as we shall show, their chemistry is turning out to be distinct and structurally very rich. Few of the species have selenium analogues and none have sulfur or oxygen analogues. Many of the bonding arrangements defy simple description. This reflects the propensity of tellurium, compared with its lighter congeners, to enter into a wide range of bonding interactions. This trend is also evident in solid-state tellurides,<sup>21-23</sup> although such compounds are not discussed here.

## Review of the Earlier Literature

This Account is concerned with tellurometalates of general formula  $[\text{M}_x\text{Te}_y]^{z-}$ , species, sometimes described as "soluble", that contain *only* a metal M and tellurium. We thus exclude solid-state tellurides, even

- (1) Berzelius, J. J. *Poggendorff's Ann. Phys. Chem.* 1826, 6, 369-392.
- (2) Berzelius, J. J. *Poggendorff's Ann. Phys. Chem.* 1826, 7, 262-288.
- (3) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
- (4) Day, V. W.; Klemperer, W. G. *Science* 1985, 228, 533-540.
- (5) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* 1989, 1483-1489.
- (6) Renneke, R. F.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* 1990, 112, 6585-6594.
- (7) Hill, C. L.; Weeks, M. S.; Schinazi, R. F. *J. Med. Chem.* 1990, 33, 2767-2772.
- (8) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* 1903, 36, 3090-3093.
- (9) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* 1986, 19, 363-370.
- (10) Coucouvanis, D. *Acc. Chem. Res.* 1991, 24, 1-8.
- (11) Müller, A. *Polyhedron* 1986, 5, 323-340.
- (12) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* 1981, 67, 430-445.
- (13) Harris, S.; Chianelli, R. R. *J. Catal.* 1984, 86, 400-412.
- (14) Chianelli, R. R.; Pecoraro, T. A.; Halbert, T. R.; Pan, W.-H.; Steifel, E. I. *J. Catal.* 1984, 86, 226-230.
- (15) Roof, L. C.; Kolis, J. W. *Chem. Rev.* 1993, 93, 1037-1080.
- (16) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* 1990, 100, 223-266.
- (17) Kanatzidis, M. G. *Comments Inorg. Chem.* 1990, 10, 161-195.
- (18) You, J.-F.; Snyder, B. S.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* 1990, 112, 1067-1076.
- (19) You, J.-F.; Holm, R. H. *Inorg. Chem.* 1991, 30, 1431-1433.
- (20) Flomer, W. A.; Roof, L. C.; Pennington, W. T.; Kolis, J. W. Work in progress.
- (21) Keane, P. M.; Ibers, J. A. *Inorg. Chem.* 1991, 30, 1327-1329.
- (22) Mar, A.; Jobic, S.; Ibers, J. A. *J. Am. Chem. Soc.* 1992, 114, 8963-8971.
- (23) Jobic, S.; Brec, R.; Rouzel, J. *J. Solid State Chem.* 1992, 96, 169-180.

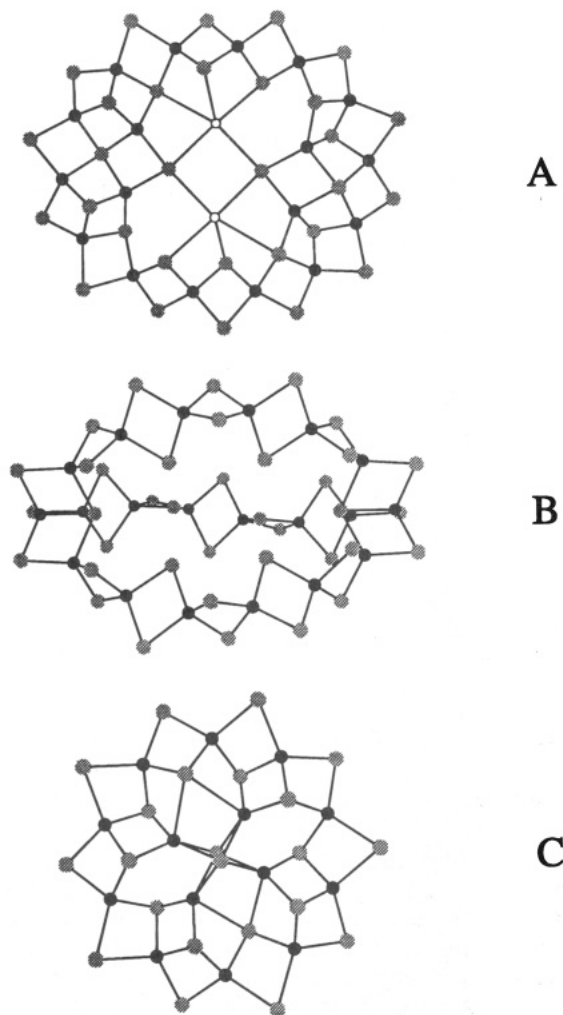


Figure 1. (A) The  $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{6-}$ ,<sup>18</sup> (B)  $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$ ,<sup>19</sup> and (C)  $[\text{Fe}_{14}\text{Te}_{22}]^{6-20}$  anions.

though in some instances, e.g.,  $\text{K}_6(\text{MnTe}_4)$ ,<sup>24</sup> a distinct  $[\text{M}_x\text{Te}_y]^{z-}$  species can be discerned. Pioneering work on tellurometalates was carried out primarily by Haushalter and co-workers and by Kolis and co-workers. In the late transition metals Haushalter and co-workers prepared species mainly from the solubilization of solid-state materials, a method first used in tellurometalates by Burns and Corbett to synthesize the  $[\text{HgTe}_2]^{2-}$  anion.<sup>25</sup> The species synthesized include  $[\text{Au}_4\text{Te}_4]^{4-}$ ,<sup>26</sup>  $[\text{Au}_9\text{Te}_7]^{5-}$ ,<sup>26</sup>  $[\text{Au}_2(\text{Te}_2)_2]^{2-}$ ,<sup>27</sup>  $[\text{Hg}_4\text{Te}_2(\text{Te}_2)_2(\text{Te}_3)_2]^{4-}$ ,<sup>28</sup>  $[\text{Hg}_2\text{Te}_5]^{2-}$ ,<sup>28</sup> and  $[\text{Pd}(\text{Te}_4)_2]^{2-}$ .<sup>29</sup> In the early transition metals Kolis and co-workers prepared species mainly through nonaqueous solution chemistry. The species synthesized include  $[\text{NbTe}_{10}]^{3-}$ ,<sup>30</sup>  $[\text{Cr}_3(\text{Te}_4)_6]^{3-}$ ,<sup>31</sup> and  $[\text{Fe}_{14}\text{Te}_{22}]^{6-20}$  (Figure 1C).

### Synthetic Routes to Tellurometalates

There is no general route for the synthesis of tellurium-containing compounds, let alone of telluro-

(24) Bronger, W.; Balk-Hardtdegen, H. *Z. Anorg. Allg. Chem.* 1989, 574, 89–98.

(25) Burns, R. C.; Corbett, J. D. *Inorg. Chem.* 1981, 20, 4433–4434.

(26) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 432–433.

(27) Haushalter, R. C. *Inorg. Chim. Acta* 1985, 102, L37–L38.

(28) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 433–435.

(29) Adams, R. D.; Wolfe, T. A.; Eichhorn, B. W.; Haushalter, R. C. *Polyhedron* 1989, 8, 701–703.

(30) Flomer, W. A.; Kolis, J. W. *J. Am. Chem. Soc.* 1988, 110, 3682–3683.

metalates. A variety of different reagents have been used. The important routes involve the reaction of metal fragments with (i) elemental tellurium,<sup>32</sup> (ii) the unstable  $\text{H}_2\text{Te}$  gas,<sup>33</sup> (iii) naked polycationic species,<sup>34,35</sup> and (iv) tellurium-releasing reagents, such as  $\text{Te}(\text{SiR}_3)_2$ <sup>36</sup> and  $\text{TePR}_3$ .<sup>37,38</sup> The extraction of Zintl phases<sup>25,26</sup> has also proved effective. Perhaps the most widely used method for the synthesis of  $[\text{M}_x\text{Te}_y]^{z-}$  species is the reaction in a nonaqueous solvent of metal salts (e.g., halides<sup>30</sup> or xanthates<sup>39</sup>) with polytelluride solutions. More recently, we have found that the reaction of  $\text{TePR}_3$  with thiometalates and selenometalates provides a very convenient route to the synthesis of a host of new species.

### Tellurometalates $[\text{M}_x\text{Te}_y]^{z-}$

**Nickel Triad.** The Ni triad forms many interesting chalcogenometalates. Sulfides of the Ni triad include  $[\text{M}(\text{S}_4)_2]^{2-}$  ( $\text{M} = \text{Ni}$ ,<sup>40,41</sup>  $\text{Pd}$ <sup>40</sup>),  $[\text{PdS}_{11}]^{2-}$ ,<sup>42,43</sup>  $[\text{Pd}_2(\text{S}_7)_4]^{4-}$ ,<sup>44</sup>  $[\text{Pt}(\text{S}_5)_2]^{2-}$ ,<sup>45</sup>  $[\text{Pt}(\text{S}_5)(\text{S}_6)_2]^{2-}$ ,<sup>46</sup>  $[\text{Pt}(\text{S}_6)_3]^{2-}$ ,<sup>47</sup> and the well-known inorganic chiral anion  $[\text{Pt}(\text{S}_5)_3]^{2-}$ .<sup>8,46,48</sup> Subsequently, we synthesized a number of selenometalates of this triad, including  $[\text{M}(\text{Se}_4)_2]^{2-}$  ( $\text{M} = \text{Ni}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ),<sup>49,50</sup>  $[\text{Pd}(\text{Se}_5)_2]^{2-}$ ,<sup>49</sup>  $[\text{Pt}(\text{Se}_4)_3]^{2-}$ ,<sup>49,51</sup> and  $[\text{Ni}_4\text{Se}_4(\text{Se}_3)_5(\text{Se}_4)]^{4-}$ .<sup>39,52</sup> a remarkable Ni(IV) cubane. Note that there are marked differences between the sulfur and selenium species. Encouraged by our synthesis of the  $[\text{Ni}_4\text{Se}_4(\text{Se}_3)_5(\text{Se}_4)]^{4-}$  anion we began a systematic search for a tellurometalate(IV) species. This culminated in the synthesis of the  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  anion.<sup>39</sup>

The  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  anion<sup>39</sup> (Figure 2) was obtained as its  $\text{NET}_4^+$  salt by the reaction in DMF of stoichiometric amounts of  $\text{Ni}(\text{S}_2\text{COEt})_2$  and polytel-

(31) Flomer, W. A.; O'Neal, S. C.; Pennington, W. T.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1702–1703.

(32) Cowley, A. H.; Jones, R. A.; Harris, P. R.; Atwood, D. A.; Contreras, L.; Burek, C. J. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1143–1145.

(33) Herrmann, W. A.; Hecht, C.; Herdtweck, E.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 132–134.

(34) Faggiani, R.; Gillespie, R. J.; Campana, C.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* 1987, 7, 485–486.

(35) Seigneurin, A.; Makani, T.; Jones, D. J.; Rozière, J. *J. Chem. Soc., Dalton Trans.* 1987, 2111–2116.

(36) Fenske, D.; Grissinger, A. *Z. Naturforsch., B: Chem. Sci.* 1990, 45b, 1309–1313.

(37) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* 1988, 110, 4228–4231.

(38) Ma, A. L.; Thoden, J. B.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* 1992, 1516–1518.

(39) McConnachie, J. M.; Ansari, M. A.; Ibers, J. A. *Inorg. Chim. Acta* 1992, 198–200, 85–93.

(40) Müller, A.; Krickemeyer, E.; Bögge, H.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 1006–1007.

(41) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* 1985, 24, 24–31.

(42) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* 1904, 37, 245–249.

(43) Haradem, P. S.; Cronin, J. L.; Krause, R. A.; Katz, L. *Inorg. Chim. Acta* 1977, 25, 173–179.

(44) Müller, A.; Schmitz, K.; Krickemeyer, E.; Penk, M.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 453–454.

(45) Wickenden, A. E. E.; Krause, R. A. *Inorg. Chem.* 1969, 8, 779–783.

(46) Gillard, R. D.; Wimmer, F. L.; Richards, J. P. G. *J. Chem. Soc., Dalton Trans.* 1985, 253–258.

(47) Sillanpää, R.; Cartwright, P. S.; Gillard, R. D.; Valkonen, J. *Polyhedron* 1988, 7, 1801–1806.

(48) Jones, P. E.; Katz, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1969, 25, 745–753.

(49) McConnachie, J. M.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* 1993, 32, 3250–3255.

(50) Ansari, M. A.; Mahler, C. H.; Chorghade, G. S.; Lu, Y.-J.; Ibers, J. A. *Inorg. Chem.* 1990, 29, 3832–3839.

(51) Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* 1989, 28, 4068–4069.

(52) McConnachie, J. M.; Ansari, M. A.; Ibers, J. A. *J. Am. Chem. Soc.* 1991, 113, 7078–7079.

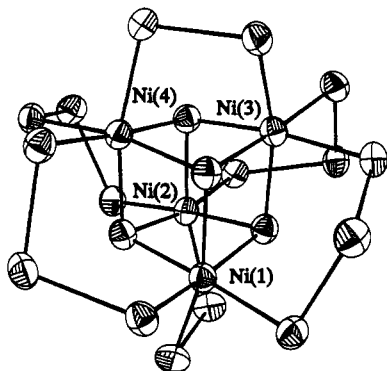
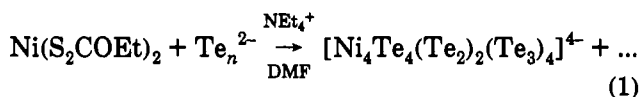
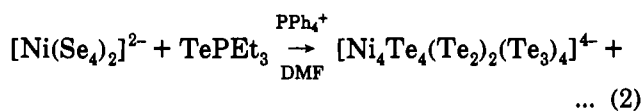


Figure 2. The  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  anion.<sup>39</sup>

luride solution (generated *in situ* by mixing  $\text{Li}_2\text{Te}$  with Te powder) in the presence of  $\text{NEt}_4\text{Cl}$ .



In this reaction Ni(II) is oxidized to Ni(IV) with a concomitant reduction of the polytelluride.<sup>53</sup> The anion comprises Ni atoms in a distorted octahedral geometry, being coordinated by three Te atoms in the cubane framework and three Te atoms belonging to chains that crisscross the cubane faces and connect the Ni atoms. There are four  $\text{Te}_3^{2-}$  chains about the equator and two  $\text{Te}_2^{2-}$  chains at the poles. This cubane differs from  $[\text{Ni}_4\text{Se}_4(\text{Se}_3)_5(\text{Se}_4)]^{4-}$ <sup>39</sup> in chalcogen ring size. The only known sulfidometalate cubane is  $[\text{Re}_4\text{S}_4(\text{S}_3)_6]^{4-}$ ,<sup>56</sup> a Re(IV) species. Note that the Ni cubanes ( $d^6$ ,  $t_{2g}$  completely filled) and the Re cubane ( $d^3$ ,  $t_{2g}$  half-filled) are both electronically symmetrical. The  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  anion, which appears to be the thermodynamic product, has also been obtained as its  $\text{PPh}_4^+$  salt by the following reaction:<sup>57</sup>



Synthesis of the  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  anion from  $\text{M}(\text{Se}_4)_2^{2-}$  and  $\text{TePEt}_3$  was a pleasant surprise. Here not only has substitution of Se by Te taken place but also structural rearrangement. We presume that similar reactions with other known thio- and selenometalates will produce new tellurometalates with unusual structures and reaction chemistry.

Our attempts to synthesize similar Pd cubanes have failed, despite the fact that Pd(IV) species are generally more stable than Ni(IV) species. We have isolated only the known  $[\text{Pd}(\text{Te}_4)_2]^{2-}$  anion.<sup>29,58</sup> This anion, which has an analogue in both sulfur and selenium chemistry,

(53) It is important to note that a polychalcogenide solution contains a variety of  $\text{Q}_n^{2-}$  species, perhaps with  $n \leq 6$ .<sup>54</sup> A given  $\text{Q}_n^{2-}$  species has oxidation state  $-2/n$ . Hence redox chemistry, including "internal redox chemistry",<sup>55</sup> is characteristic of polychalcogenide solutions and adds to the complexity of the chemistry.

(54) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* 1988, 27, 73-80.

(55) Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* 1980, 102, 5102-5104.

(56) Müller, A.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 272-273.

(57) McConnachie, J. M.; Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* 1993, 32, 3923-3927.

(58) Kanatzidis, M. G. *Acta Crystallogr.* 1991, C47, 1193-1196.

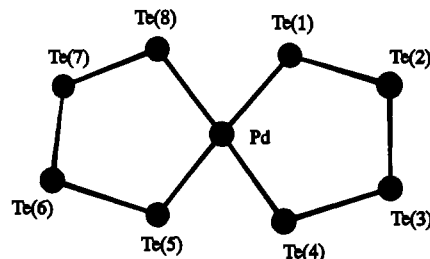


Figure 3. The  $[\text{Pd}(\text{Te}_4)_2]^{2-}$  anion.<sup>29,58</sup>

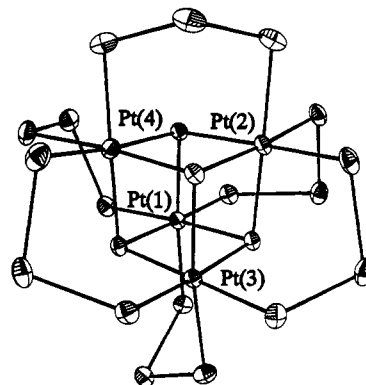


Figure 4. The  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  anion.<sup>57</sup>

consists of a square-planar Pd(II) center coordinated to two bidentate  $\text{Te}_4^{2-}$  ligands (Figure 3).

Usually platinum produces Pt(IV) chalcogenoplatinates, e.g.,  $[\text{Pt}(\text{S}_5)_3]^{2-}$ ,<sup>48</sup>  $[\text{Pt}(\text{S}_5)(\text{S}_6)_2]^{2-}$ ,<sup>46</sup> and  $[\text{Pt}(\text{Se}_4)_3]^{2-}$ .<sup>49,51</sup> Such species can often be reduced to afford Pt(II) anions, such as  $[\text{Pt}(\text{S}_5)_2]^{2-}$ <sup>46</sup> and  $[\text{Pt}(\text{Se}_4)_2]^{2-}$ .<sup>50</sup> In the tellurium system we failed to isolate a monometallic tellurometalate species. Rather, we isolated the highly symmetric cubane  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$ <sup>57</sup> (Figure 4). The compound  $[\text{PPh}_4]_4[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$ <sup>57</sup> was obtained by the reaction of  $[\text{PPh}_4]_2[\text{Pt}(\text{Se}_4)_3]$  with  $\text{TePEt}_3$ , whereas  $[\text{NEt}_4]_4[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  was obtained by the reaction of  $\text{Pt}(\text{S}_2\text{COEt})_2$  with polytelluride in the presence of  $\text{NEt}_4\text{Cl}$ . Since the  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  anion was obtained by two different routes and crystallized with different cations, we conclude that it is the thermodynamic product. The  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  anion consists of a  $[\text{Pt}_4\text{Te}_4]^{8+}$  core with the Pt centers being bridged by six  $\text{Te}_3^{2-}$  chains. The  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  cubane is an analogue of the  $[\text{Re}_4\text{S}_4(\text{S}_3)_6]^{4-}$  and a variant of the  $[\text{Ni}_4\text{Te}_4(\text{Te}_2)_2(\text{Te}_3)_4]^{4-}$  cubanes. All these cubanes contain M(IV) centers, unexceptional for Pt or Re, but exceptional for Ni. Why do we find  $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$  but not its Ni analogue  $[\text{Ni}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$ ? Two explanations occur to us: (i) the lengthening of the M-Te bond on descending from Ni to Pt helps accommodate the  $\text{Te}_3^{2-}$  ligand; (ii) Ni(IV) is harder than Pt(IV) and should prefer the  $\text{Te}_2^{2-}$  ligand, which has electron density spread over fewer atoms than does the  $\text{Te}_3^{2-}$  ligand.

**Zinc Triad.** This family possesses the simplest and the earliest tellurometalate known, the  $[\text{HgTe}_2]^{2-}$  anion, which was obtained by extraction with ethylenediamine of the ternary alloy  $\text{KHgTe}$  in the presence of 2,2,2-crypt.<sup>25</sup> As expected, this anion is linear. Extraction with ethylenediamine of another ternary alloy,  $\text{K}_2\text{Hg}_2\text{Te}_3$ , in the presence of  $\text{NBu}_4\text{Br}$  and  $\text{PPh}_4\text{Br}$  affords  $[\text{Hg}_4\text{Te}_2(\text{Te}_2)_2(\text{Te}_3)_2]^{4-}$  and polymeric  $[\text{Hg}_2\text{Te}_5]^{2-}$ , respectively.<sup>28</sup> The  $[\text{Hg}_4\text{Te}_2(\text{Te}_2)_2(\text{Te}_3)_2]^{4-}$  anion (Figure

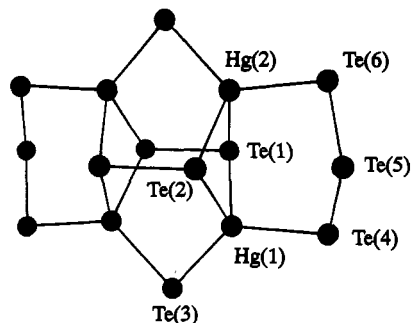


Figure 5. The  $[\text{Hg}_4\text{Te}_2(\text{Te}_2)_2(\text{Te}_3)_2]^{4-}$  anion.<sup>28</sup>

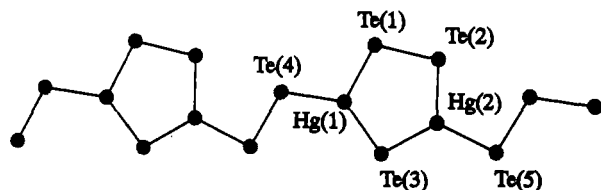


Figure 6. The one-dimensional  $\frac{1}{2}[\text{HgTe}_5]^{2-}$  species.<sup>28</sup>

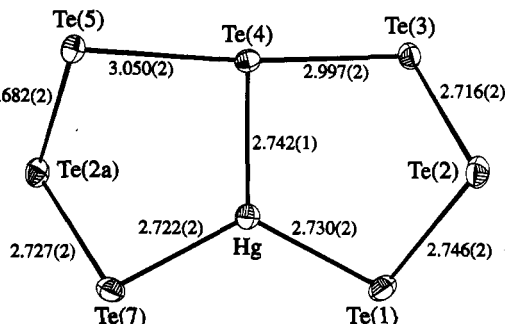


Figure 7. The  $[\text{HgTe}_7]^{2-}$  anion.<sup>61,62</sup> Estimated standard deviations on the distances<sup>61</sup> (in Å) are shown in parentheses.

5) has four Hg atoms almost in the same plane coordinated to two  $\text{Te}^{2-}$ , two  $\text{Te}_2^{2-}$ , and two  $\text{Te}_3^{2-}$  ligands. The one-dimensional  $\frac{1}{2}[\text{Hg}_2\text{Te}_5]^{2-}$  species has two crystallographically independent Hg atoms in trigonal-planar geometry, bridged by  $\text{Te}^{2-}$  and  $\text{Te}_2^{2-}$  ligands (Figure 6).

In our studies of the Zn triad we have isolated the expected  $[\text{M}(\text{Te}_4)_2]^{2-}$  anions ( $\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$ ).<sup>17,59</sup> While the  $[\text{Hg}(\text{Te}_4)_2]^{2-}$  anion has been synthesized<sup>17</sup> in a conventional way by reacting  $\text{Hg}^{2+}$  with polytelluride solution, we have synthesized it and its Zn and Cd analogues by the reaction of the corresponding  $[\text{M}(\text{Se}_4)_2]^{2-}$  anions with excess  $\text{TePET}_3$ .<sup>57</sup> Reaction of  $[\text{Hg}(\text{Se}_4)_2]^{2-}$  with limited quantities of  $\text{TePET}_3$  causes stepwise substitution of Se by Te,<sup>60</sup> to afford  $[\text{HgSe}_{8-n}\text{Te}_n]^{2-}$ . In these reactions the driving force is probably the relative strength of the Q-PR<sub>3</sub> bond, which is in the order S-P > Se-P > Te-P. The remarkable  $[\text{HgTe}_7]^{2-}$  species has also been isolated as the  $\text{PPh}_4^+$  (Figure 7) and the (15-crown-5)<sup>+</sup> salt.<sup>62</sup> The nature of this anion is discussed below.  $[\text{15-Crown-5}]_2[\text{ZnTe}_7]$  is also known.<sup>62</sup>

**Copper Triad.** The word *chalcogen* has its origin in the Greek word *chalkos* meaning copper or brass

(59) McConnachie, J. M.; Bollinger, J. C.; Ibers, J. A. Unpublished results.

(60) Bollinger, J. C.; Salm, R. J.; Ibers, J. A. Unpublished results.

(61) McConnachie, J. M.; Ansari, M. A.; Bollinger, J. C.; Salm, R. J.; Ibers, J. A. *Inorg. Chem.* 1993, 32, 3201-3202.

(62) Müller, U.; Grebe, C.; Neumüller, B.; Schreiner, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* 1993, 619, 500-506.

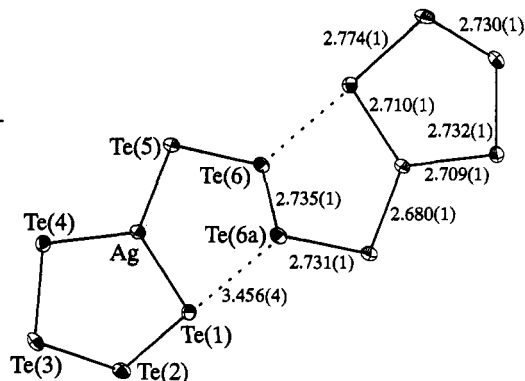


Figure 8. The  $[(\text{Te}_4)\text{Ag}(\mu\text{-Te}_4)\text{Ag}(\text{Te}_4)]^{4-}$  anion.<sup>66,67</sup> The anion<sup>66</sup> has a crystallographically imposed center of symmetry. The analogous Cu species<sup>66,67</sup> has the identical structure.

and *genes* meaning born. In keeping with the name, the copper triad has proved to be the richest area of chalcogenide chemistry.<sup>16,17,63,64</sup> A large number of thiocuprates<sup>63,65</sup> and selenocuprates<sup>16</sup> are known, but until very recently no tellurometalates of Cu or Ag were known, although the species  $[\text{Au}_4\text{Te}_4]^{4-}$ ,<sup>26</sup>  $[\text{Au}_9\text{Te}_7]^{5-}$ ,<sup>26</sup> and  $[\text{Au}_2(\text{Te}_2)_2]^{2-}$ <sup>27</sup> were known.

The tellurometalate anions  $[(\text{Te}_4)\text{M}(\mu\text{-Te}_4)\text{M}(\text{Te}_4)]^{4-}$  ( $\text{M} = \text{Cu}, \text{Ag}$ ),<sup>66,67</sup> (Figure 8) have recently been synthesized. These are related to the  $[(\text{S}_6)\text{M}(\mu\text{-S}_6)\text{M}(\text{S}_6)]^{4-}$  ( $\text{M} = \text{Cu},^{68} \text{Ag}^{69}$ ) and  $[(\text{Se}_4)\text{Cu}(\mu\text{-Se}_5)\text{Cu}(\text{Se}_5)]^{4-}$ <sup>70</sup> anions. Note the decreasing ring size in going from S to Se to Te. The  $\text{Te}_n^{2-}$  rings and chains are often shorter than the  $\text{Se}_n^{2-}$  units in the corresponding selenometalates, for example in the cubanes discussed above. The chalcogenoaurates, where S,<sup>71</sup> Se,<sup>72,73</sup> and Te<sup>27</sup> species are known, provide another example. In the  $[(\text{Te}_4)\text{M}(\mu\text{-Te}_4)\text{M}(\text{Te}_4)]^{4-}$  ( $\text{M} = \text{Cu}, \text{Ag}$ ) anions the ring atom Te(1) interacts with a bridging atom Te(6a) at distances of 3.488(4) and 3.456(4) Å, respectively,<sup>66</sup> considerably shorter than the Te...Te van der Waals interaction of about 4 Å. Below we describe the  $[\text{AgTe}_7]^{3-}$  anion. This anion has the structure that would result from the formation of a Te(1)-Te(6a) bond with a concomitant cleavage of the Te(6a)-Te(5a) bond and loss of the  $\text{AgTe}_5$  fragment.

The structural chemistry and bonding in tellurometalates of the coinage metals turn out to be more interesting and very different from those of the thio-metalates and selenometalates. This is especially apparent in the  $[\text{MTe}_7]^{n-}$  species ( $\text{M} = \text{Ag},^{61} \text{Hg},^{61,62}$

(63) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* 1987, 31, 89-122.

(64) Keane, P. M.; Lu, Y.-J.; Ibers, J. A. *Acc. Chem. Res.* 1991, 24, 223-229.

(65) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 742-757.

(66) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* 1993, 32, 1746-1748.

(67) Fenske, D.; Schreiner, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* 1993, 619, 253-260.

(68) Müller, A.; Baumann, F.-W.; Bögge, H.; Römer, M.; Krickemeyer, E.; Schmitz, K. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 632-633.

(69) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Baumann, F.-W.; Schmitz, K. *Inorg. Chim. Acta* 1984, 89, L7-L8.

(70) Müller, U.; Ha-Eierdanz, M.-L.; Kräuter, G.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* 1990, 45, 1128-1132.

(71) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Schmitz, K. *Inorg. Chim. Acta* 1984, 85, L39-L41.

(72) Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* 1991, 30, 3572-3575.

(73) Kanatzidis, M. G.; Huang, S.-P. *Inorg. Chem.* 1989, 28, 4667-4669.

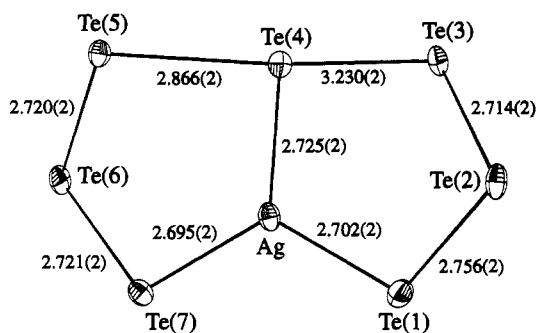


Figure 9. The  $[\text{AgTe}_7]^{3-}$  anion.<sup>61</sup>

Zn,<sup>62</sup> and Au<sup>74</sup>). The  $[\text{AgTe}_7]^{3-}$  anion (Figure 9) is closely related structurally to the  $[\text{HgTe}_7]^{2-}$  anion (Figure 7). It features a trigonal-planar Ag(I) atom chelated to a single  $\text{Te}_7$  unit. The trigonal-planar geometry around the Ag(I) and Hg(II) centers in these anions is not as surprising as the bonding pattern. The  $\text{Te}(3)\text{--Te}(4)\text{--Te}(5)$  moieties are almost linear ( $\angle(\text{Te}(3)\text{--Te}(4)\text{--Te}(5))$  is  $174.12(5)^\circ$  for Ag and  $174.52(5)^\circ$  for Hg). While the  $\text{M}\text{--Te}(4)$  distances in the two compounds are similar to the other  $\text{M}\text{--Te}$  distances, the  $\text{Te}(4)\text{--Te}$  distances are significantly longer than the other  $\text{Te}\text{--Te}$  distances in the two compounds. Longer bond lengths around the  $\text{Te}(4)$  atom are expected if atoms  $\text{Te}(3)$ ,  $\text{Te}(4)$ , and  $\text{Te}(5)$  are connected by a three-center four-electron bond. The bonding around atom  $\text{Te}(4)$  is symmetric in the Hg compound whereas it is unsymmetric in the Ag compound. But in  $[\text{15-crown-5}]_2[\text{HgTe}_7]^{62}$  the bonding around atom  $\text{Te}(4)$  (as labeled in Figure 7) is unsymmetric, with  $\text{Te}(4)\text{--Te}$  distances of 2.962(2) and 3.258(8) Å. The related  $\text{I}_3^-$  anion shows both symmetric and unsymmetric bonding modes.<sup>75</sup> Thus both the Ag and Hg anions seem to possess the unprecedented  $\eta^3\text{-Te}_7^{4-}$  ligand. An  $\eta^3\text{-S}_7^{2-}$  ligand is known in the compounds  $(\text{Me}_3\text{P})_3\text{MS}_7$  ( $\text{M} = \text{Ru}, \text{Os}$ ),<sup>76</sup> but the three-coordinate S atom adopts a normal geometry and the moiety is described as  $\text{S}_7^{2-}$ .

A number of sulfido- and selenoaurates are known, including  $[\text{AuS}_9]^-$ ,<sup>77</sup>  $[\text{Au}_2(\text{S}_4)_2]^{2-}$ ,<sup>71</sup>  $[\text{Au}_2(\text{Se}_2)(\text{Se}_3)]^{2-}$ ,<sup>72</sup>  $[\text{Au}_2(\text{Se}_2)(\text{Se}_4)]^{2-}$ ,<sup>72</sup> and  $[\text{Au}_2\text{Se}_2(\text{Se}_4)_2]^{2-}$ ,<sup>73</sup> but the bonding in all of these is conventional, consisting of  $\text{Q}_n^{2-}$  moieties ( $\text{Q} = \text{S}, \text{Se}; n \geq 1$ ). Reaction of Au(I) with a polytelluride solution in the presence of phosphine affords the remarkable planar  $[\text{AuTe}_7]^{3-}$ <sup>74</sup> anion. This anion, though different from the  $[\text{AgTe}_7]^{3-}$  and  $[\text{HgTe}_7]^{2-}$  anions, also exhibits an unprecedented coordination mode. It features a Au(III) center in

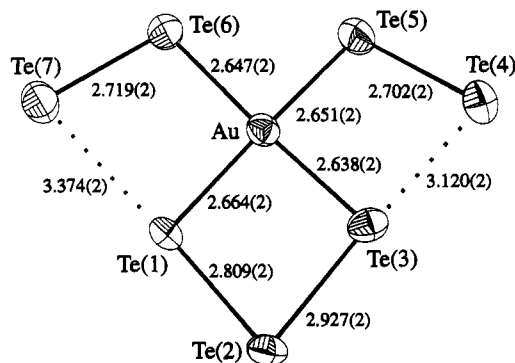


Figure 10. The planar  $[\text{AuTe}_7]^{3-}$  anion, better described as the  $[\text{Au}(\eta^1\text{-Te}_2)(\eta^3\text{-Te}_5)]^{3-}$  anion.<sup>74</sup>

square-planar geometry coordinated to a  $\text{Te}_3$  ring and two  $\text{Te}_2$  arms in an end-on ( $\eta^1$ ) fashion (Figure 10). We describe the  $\text{Te}(3)\cdots\text{Te}(4)$  interaction as a bond and formulate the ion as  $[\text{Au}(\eta^1\text{-Te}_2)(\eta^3\text{-Te}_5)]^{3-}$ , which then possesses the unprecedented  $\eta^3\text{-Te}_5^{4-}$  and  $\eta^1\text{-Te}_2$  ligands. The  $\eta^3\text{-Te}_5^{4-}$  ligand shows some similarities to the  $\eta^3\text{-Te}_7^{4-}$  ligand found in the  $[\text{AgTe}_7]^{3-}$  and  $[\text{HgTe}_7]^{2-}$  anions described above. The "T"-type arrangement around atom  $\text{Te}(3)$  is similar, and the  $\text{Te}(2)\text{--Te}(3)\text{--Te}(4)$  group is essentially linear ( $\angle(\text{Te}(2)\text{--Te}(3)\text{--Te}(4)) = 175.9(1)^\circ$ ). The bonding in this remarkable anion is currently the subject of an extended Hückel calculation.<sup>78</sup>

## Conclusions

Although the chemistry of tellurometalates is in its early stages, it is being developed rapidly. Five years ago we believed that additional ligands would be required to stabilize species of the type  $[\text{M}_x\text{Te}_y]^{z-}$ . We now have many counterexamples. Above all, the chemistry of tellurometalates is distinct and structurally rich, with several examples of unconventional bonding, for example,  $\eta^1\text{-Te}_2^{2-}$ ,  $\eta^3\text{-Te}_5^{4-}$ , and  $\eta^3\text{-Te}_7^{4-}$ . Recent results, both in solid-state and in solution chemistry, make clear that tellurium exhibits a greater propensity, as compared to its lighter congeners, to adopt unusual bonding and coordination modes.

Synthetic explorations in tellurometalates will continue to be a driving force for new chemistry. But now is a propitious time for studies of the spectroscopy, reaction chemistry, and bonding in these species. We hope that this Account will encourage such studies.

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(74) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3838–3839.

(75) Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry*, 1st ed.; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 2, Chapter 26, pp 1534–1563.

(76) Gotzig, J.; Rheingold, A. L.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 814–815.

(77) Marbach, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 246.

(78) Pichko, V.; Hoffmann, R. Unpublished results.