

$\text{Cs}_3\text{Te}_{22}$, THE ONE WE NOW KNOW

Roald Hoffmann

I'm supposed to be a theoretical chemist, but really I'm a scavenger of interesting molecules. My picking ground is in scientific journals; *Chemical Abstracts* says there were 687,789 articles last year that I should have read. Because I have access to what used to be the best library in the world (until financial stringencies took their toll), and because I have conditioned myself to feel guilty if I don't look at as many new articles as I can, I glance at 18.56 percent of them. I look at a molecule, and if I understand it from a theoretical point of view, I go on to the next.

With 35 years experience and lots of molecules in my head, most seem like variations on a theme. I don't disregard them, useful or beautiful as they are. But their geometries fit a pattern. They are not strange; they are friends. I go on to find the one I do not know. Here I tell you of one such encounter.

In a February 1995 issue of *Angewandte Chemie* (this journal, a close competitor with the *Journal of the American Chemical Society* for the title of "best chemistry journal in the world," is published simultaneously in German and English), William S. Sheldrick and Michael Wachhold from the Ruhr University of Bochum published a paper on the synthesis and structure of a cesium (Cs) and tellurium (Te) compound, $\text{Cs}_3\text{Te}_{22}$. Now tellurium has a profligate chemistry; could I recommend only one element for a solid-state chemist to work on, an element that forms a myriad of compounds with other elements, almost every one a puzzle, it would be Te. (Indium would be a close second.) Tellurium, lying under oxygen, sulfur and selenium in the periodic table, between antimony and iodine, just has a ball, entering into a great range of weak-bonding interactions with itself. Carbon, by comparison, is abstinence itself, forming strong—oh, so strong—bonds (fortunately, for us). With carbon, for the most part, either a bond is made or it isn't. Carbon forms single bonds, double, triple bonds, or no bonds at all. For tellurium, there is constant flirtation with other tellurium partners, in the range between a bond and no bond.

So, at the time of the Sheldrick and Wachhold paper, in addition to $\text{Cs}_3\text{Te}_{22}$ (a weird stoichiometry that we wouldn't dare show our beginning students—what's the oxidation state of Te?), some nine other compounds were also known. These ranged from tellurium-rich CsTe_4 to cesium-rich Cs_3Te_2 . Two more have been made since.

Life Imitates Escher

These compounds are not discrete molecules, weakly held together in a molecular crystal. They are extended structures, in which networks of atoms, bonded in part by covalent, in part by ionic forces, march in orderly fashion through the crystal. But I've been withholding the structure too long. Figure 1 shows it in a perspective view (Cs are dark balls, Te light).

The first feature one discerns are the crown-shaped eight-membered rings of tellurium

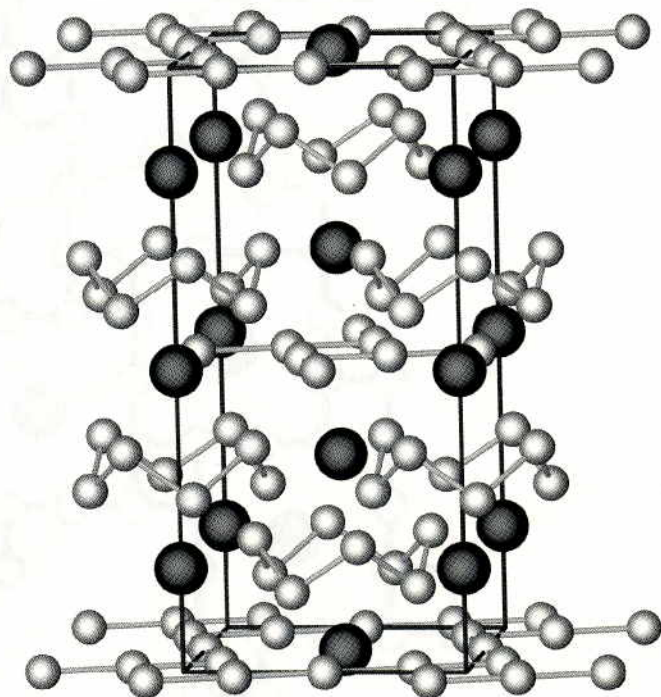


Figure 1. One-unit cell of the structure of $\text{Cs}_3\text{Te}_{22}$ is outlined. (Cs atoms are black.)

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atoms. I look at this, searching for similarities and differences with other known structures, as do the synthesizers of the molecule, who know just as many structures as I do.

And then I remember that sulfur, for which a host of allotropes is known (now *there* is an interesting story—that of the 16 sulfurs of Erämetsä) readily forms such eight-sulfur crowns. And so does selenium. That's similarity à la Mendeleev. But for tellurium such a ring had never been seen! A surprise, but not a surprise. Still, what a weird thing—to find in a tellurium *compound* a geometry that *elemental* tellurium should show. This is the fun of chemistry, and why the field gets along with a smallish number of theoreticians. Who would have predicted Te_8 rings in $\text{Cs}_3\text{Te}_{22}$?

And no one predicted the other piece of the structure, an incredible planar CsTe_6 sublattice, which you can see "side-on" in Figure 1, and which is shown "end-on" in Figure 2. To get to the CsTe_6 formula, you can look at the "unit cell" (the repeating unit of the net), drawn as a box in both figures, and count up the atoms in it.

If you like symmetry, this neat structure is for you. This is a rare two-dimensional net. Yes, Es-

cher has drawn a pattern with this symmetry, and I think it is in the Alhambra. But I had not seen it in any molecule. The only symmetry elements of this net are fourfold and twofold rotational axes.

Now for some electron counting: Since, as alkali metals, cesium atoms are prone to give up their one valence electron each and bond ionically in this solid (and the Cs-Te distances are consistent with this), and the two Te_8 rings per $\text{Cs}_3\text{Te}_{22}$ formula are happy as neutral, elemental Te_8 , the only place to go for the three electrons that the cesium atoms give up is into that Te_6 net. To put it another way, $\text{Cs}_3\text{Te}_{22} = (\text{Cs}^+)_3 (\text{Te}_8)_2 \text{Te}_6^{3-}$.

T Shapes

Once I'm through admiring the symmetry of the Te_6 net, I look at its structural features, to see whether I understand them. There are squares of tellurium. Aha! I remember John D. Corbett of Iowa State University and Ronald J. Gillespie of McMaster University and their coworkers had made Te_4 (and Se_4) squares a quarter of a century ago. But their compounds were isolated molecules, each tellurium two-coordinate, and they

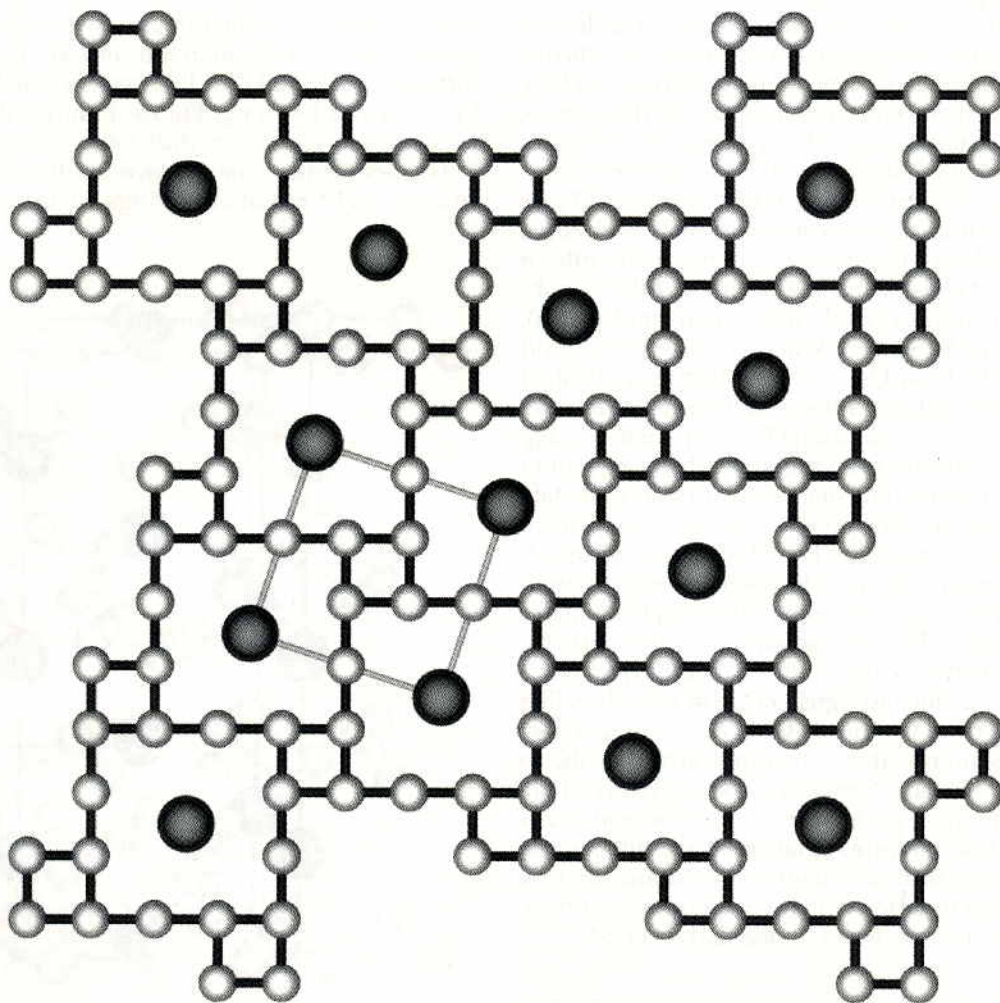


Figure 2. CsTe_6 net in $\text{Cs}_3\text{Te}_{22}$ is shown. One unit cell is outlined.

carried a $2+$ charge overall. The telluriums in the squares in the Sheldrick and Wachhold compound are three-coordinate, and negatively charged. And the coordination geometry is weird—not trigonal or trigonal pyramidal (all Te–Te–Te angles equal, 120 degrees or less), but, what we can loosely call, planar T-shaped.

For each Te_6 unit there are four such T-shaped structures. Connecting these are two-coordinate telluriums. That seems as it should be—tellurium's normality is expressed by forming two bonds, except ... the usual Te–Te–Te angle in those normal tellurium compounds (the analogues of water, alcohols or ethers) are near 90 degrees. In the Te_6 net in $\text{Cs}_3\text{Te}_{22}$, these angles are 180 degrees.

This is where I wake up, as did my coworkers Qiang Liu from China and Norman Goldberg from Germany. Not that we needed waking up, for no one had seen such a net before. But now that we realized how strange the seemingly innocent geometries of the net components were, we knew we had to understand this molecule. Having the tools in hand, we tried.

Not Classically Non-Classical

Our theoretical story will appear in a journal around the time you read this. In part, it is a computational tale—we specialize in the kind of approximate solutions to Schrödinger's equation

to which all other computations are superior. And we bootstrap ourselves out of the lowest reaches of quality of computation by constructing portable explanations based on molecular-orbital arguments. We read the clues in this structure: T-shaped tellurium configuration (that reminds us of BrF_3 , also T-shaped), linearity where bending would have been expected (that reminds us of linear I_3^- and XeF_2) and electron richness (Te_6^{3-}). All of these features, geometrical and electronic, point to what chemists sometimes call hypervalence, and also to a framework of ideas under the rubric of "electron-rich three-center bonding." There is a surprise, in that these compounds don't quite fit these non-classical extensions of normal bonding—they are not classically non-classical!

For the rest of the story you will have to read our paper. We understand the bonding in the end, or at least tell a good story about it. We predict some further structures, and incredibly one of these has been made. The theory is in some ways unimportant here, for we were followers and rationalizers. What matters is that the molecule has been made, in its dazzling interest.

The next time I see that net, in another compound, it will be—to me—just a little bit less interesting. That's fine: Another issue of *Angewandte Chemie* is on its way.