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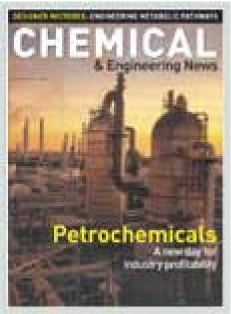

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SULFUR'S TURN FOR MULTIPLE BONDS

'Triple-bond' compounds have highest bond order for multiply bonded main-group elements

STEPHEN K. RITTER, C&EN WASHINGTON

The synthesis of compounds with multiple bonds between main-group elements in the third row or lower of the periodic table has brought much excitement to inorganic and theoretical chemists. But Canadian chemist Jack Passmore, whose group has prepared some of the compounds, has felt a bit like a spectator. That's because the spotlight mainly has been on alkene and alkyne analogs of group 14 elements silicon, germanium, tin, and lead, while Passmore and his colleagues have focused on group 16 and 17 elements, particularly sulfur.

After years of work, Passmore, a professor at the University of New Brunswick, Fredericton, now believes he has definitive experimental evidence that the $S_2I_4^{2+}$ cation in $S_2I_4(MF_6)_2$, where M = As or Sb, contains a sulfur-sulfur bond with the highest bond order for a homonuclear multiple bond involving a heavy main-group element (*Inorg. Chem.* **2005,** *44,* 1660). The research was carried out by graduate student Scott Brownridge, postdoc Carsten Knapp, and others in Passmore's group; T. Stanley Cameron of Dalhousie University, Halifax; J. Mikko Rautiainen, a graduate student at the University of Jyväskylä, in Finland; and colleagues in Germany.

The arsenic and antimony salts of the sulfur iodide have sulfur-sulfur bond orders of 2.4 and 2.7, respectively, which are comparable to that of compounds containing a silicon-silicon triple bond (disilyne) reported by other groups last year. The disilyne has been given credit as having an effective silicon-silicon triple bond, even though the bond order falls short of the 3.0 expected for a "true" triple bond.

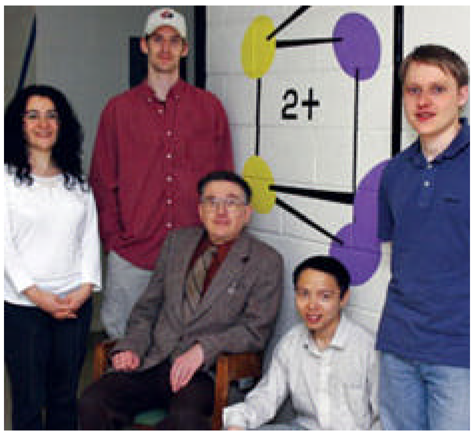
The $S_2I_4^{2+}$ cation has some triple-bond character, and a valence bond resonance structure with a sulfur-sulfur triple bond can be drawn for it. Yet knowing that multiple bonding in main-group elements has at times been a controversial topic, Passmore doesn't call his sulfur-sulfur bond a triple bond. He prefers to just stick with the experimental evidence that his sulfur compound has a high bond order, he says. And to be extra cautious, he ends the first part of the title of the Inorganic Chemistry paper with a question mark.

Multiple bonding in group 16 and 17 elements has been known for a long time, but these compounds "seem to have escaped the notice of most of the reviewers of the field," Passmore laments. "Many folks want to pretend that multiple-bonded sulfur compounds don't exist." He allows that chemists perhaps assume sulfur chemistry is well-known and that there's no expectation of seeing anything new. Passmore hopes his work will change that perception and broaden the multiple-bonding spotlight to include other main-group elements.

"Sulfur has been overlooked, there's no doubt about it," observes Philip P. Power, a chemistry professor at the University of California, Davis. "I was skeptical about the bonding in this compound at first, but the more I have looked at it, the more convinced I have become that the bond order is pretty high and that it's similar to the disilyne." Power's group synthesized the germanium, tin, and lead alkyne analogs in 2000 and 2002, and he's the *Inorganic Chemistry* editor who processed Passmore's paper.

There was a time when chemists believed that elements below the second row of the periodic table weren't capable of forming multiple bonds because they were unstable with respect to the single-bond alternatives, Passmore says. Inorganic chemists relished the idea of trying to make these supposedly unattainable compounds, however.

ONE AREA of focus naturally was to make multiple-bond carbon analogs from the heavier group 14 elements. A tin-tin double-bond compound (distannene) synthesized in 1976 was the first heavy main-group multiple-bond compound to be made, followed by a silicon-silicon double-bond compound (disilene) in 1981. Today, homonuclear double-bond compounds have been prepared for nearly all the elements in groups 13 to 17.


IN THE LOOP Passmore (seated) poses with some members of his group and the structure of $S_2I_4^{2+}$ on the wall outside his laboratories. From left are postdoc Nilgün Akkus and graduate students Aaron Mailman, Xinping Wang (kneeling), and Konstantin Shuvaev.

COURTESY OF JACK PASSMORE

Preparation of triple-bond compounds has proven more difficult. Following Power's work to isolate the germanium, tin, and lead compounds, the elusive disilyne was finally confirmed last year by chemistry professor Akira Sekiguchi and coworkers of the University of Tsukuba, in Japan, and independently by chemistry professor Nils Wiberg of the University of Munich, in Germany.

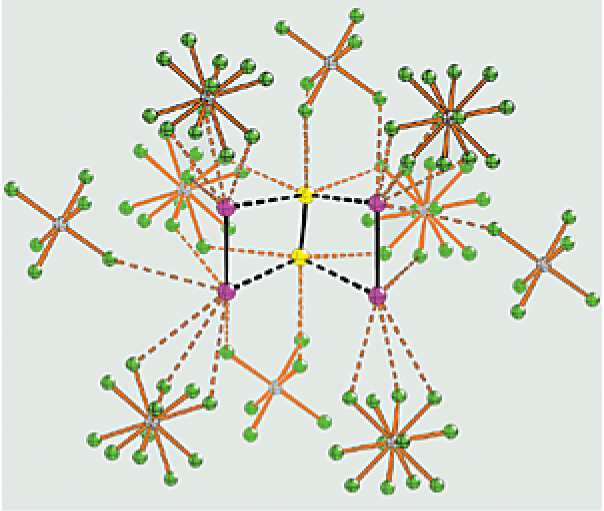
The alkyne analogs have decreasing bond overlap and increasing lone-pair character going from silicon to lead, Power says. This is observed in the bond angles of the substituents on the central atoms, which range from the slightly trans bent disilyne to a near right angle for the diplumbyne.

"The bond order for the carbon-carbon triple bond is 3.0, while for silicon it's about 2.5, germanium is 2.0, tin is 1.5, and lead is 1.0," Power explains. "You lose about half a bond order as you go deeper into the group. The disilyne is effectively a triple bond, while the lead compound effectively has a lead-lead single bond and a lone pair of electrons on each lead atom." There are a few compounds containing true triple bonds between the heavier group 14 elements and some transition metals, such as $Mo{\equiv}Ge$, which have a linear geometry and a bond order of 3.0, Power notes.

Passmore's $S_2I_4^{2+}$ compounds are prepared by reacting elemental iodine (I_2), elemental sulfur (S_8), and either arsenic pentafluoride or antimony pentafluoride, with sulfur dioxide as the solvent. Passmore first synthesized $S_2I_4(AsF_6)_2$ in 1980 and published a preliminary report on it (*Chem. Commun.* **1980,** 289). In 1992, his group reported the synthesis of the antimony salt and provided crystal structures for the two compounds (*Inorg. Chem.* **1992,** *31,* 273).

Attempts to obtain suitable spectra for the compounds were initially unsuccessful, Passmore says. The group has now obtained infrared and Raman spectra that are supported by density functional theory calculations. The team also redetermined the crystal structure of the arsenic salt.

Understanding the bonding in main-group chemistry is a careful business, Passmore says, which is why it has taken a long time to be certain about the multiple bonding in these sulfur compounds. "The details seem small when written in a paper, but the work was nontrivial," he adds. Even now, the group is conducting more extensive theoretical calculations on the sulfur iodide.



HIGH ORDER **The $S_2I_4^{2+}$cation consists of a central S_2 unit (bond order 2.4) weakly bound to an I_2 unit on either side, and it's supported by AsF_6^- counterions (S = yellow, I = purple, As = gray, F = green; brown dashed lines show closest fluorine contacts).**

PHOTO BY ROGER SMITH

THE NEW DATA confirm the initial thinking on the bonding in $S_2I_4^{2+}$, Passmore notes. The cation consists of a central sulfur-sulfur bond flanked by an I_2 unit on either side, overall resembling a triangular prism. The sulfur and iodine atoms are held together by a very weak bonding interaction.

The sulfur-sulfur bond lengths of the arsenic and antimony salts are 1.84 and 1.82 Å, respectively, corresponding to bond orders of 2.4 and 2.7. These data compare with S_2 and S_2^+, which in the gas phase have bond lengths of 1.89 and 1.82 Å, respectively, and bond orders of 2.0 and 2.5. Sulfur-sulfur single bond lengths are generally about 2.1 Å.

Even with the new experimental data in hand, Passmore faced an uphill battle to get the paper into print. He submitted the paper last July with the original claim that the $S_2I_4^{2+}$ salts have the highest bond order for any homonuclear main-group compounds, and the paper was accepted for publication. But just as it was in the final editing stage, the papers by Sekiguchi and Wiberg came out reporting the disilyne. This forced Passmore to revise his paper, which delayed its publication by nearly six months.

Passmore's new conclusion is that $S_2I_4^{2+}$ and the disilyne both clearly have a bond order greater than 2.0 and effectively tie for the position of the highest known bond order for isolated main-group compounds. The $S_2I_4^{2+}$ bond order "definitely should be recognized as one of the highest for bonding between main-group elements," Sekiguchi tells C&EN.

There's possibly one exception. A gallium-gallium triple bond in a compound was reported in 1997 by chemistry professor Gregory H. Robinson's group at the University of Georgia. Robinson's gallyne was immediately scrutinized by chemists working on multiple bonding, some of whom doubted it contained a true triple bond (C&EN, March 16, 1998, page 31). Part of the skepticism was that the gallium-gallium triple bond length was only slightly shorter than that for known single bonds. After further theoretical study, some chemists believe the triple bond description is justified, while others conclude that it is better described as a double bond.

Passmore makes note of Robinson's gallium compound in his *Inorganic Chemistry* paper, commenting that there is a lack of "general acceptance of a bond order greater than 2.0" for the gallyne. Robinson counters that his group has published theoretical results on two occasions in which bond orders of 2.79 and 3.02 were obtained for the gallyne, and he still defends his gallium triple bond. "Thus, I question the accuracy of the claim for the highest bond order," Robinson adds.

Bond length and bond order traditionally have gone hand in hand--the shorter the bond length, the higher the bond order. But Robinson and others believe that isn't necessarily a general relationship. Electronic structure, rather than bond length, determines the nature of multiple bonds, Robinson believes. "These compounds force us to examine fundamental issues of structure and bonding that we so often take for granted," he says.

Power agrees. This type of checking and rechecking each other's work serves to make the field stronger, he says. "It focuses people's thinking about the nature of bonding at the most fundamental level, whether you agree with other groups' ideas on bond order or not. In the end, you have to sort it out in your own mind."

By continuing to synthesize multiple-bond main-group compounds, chemists are opening up new and exciting areas of chemistry, Passmore concludes. "Clearly, we are still finding out what the facts are about the chemistry of these elements," he says.

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