

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Polyiodides and Polytellurides: Analogies and Differences

Maria C. Aragoni^a; Massimiliano Arca^a; Francesco A. Devillanova^a; Francesco Isaia^a; Vito Lippolis^a

^a Dipartimento di Chimica Inorganica ed Analitica, Università degli Studi di Cagliari, Monserrato, CA, Italy

To cite this Article Aragoni, Maria C. , Arca, Massimiliano , Devillanova, Francesco A. , Isaia, Francesco and Lippolis, Vito(2008) 'Polyiodides and Polytellurides: Analogies and Differences', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 183: 4, 1036 – 1045

To link to this Article: DOI: 10.1080/10426500801901061

URL: <http://dx.doi.org/10.1080/10426500801901061>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polyiodides and Polytellurides: Analogies and Differences

**Maria C. Aragoni, Massimiliano Arca,
Francesco A. Devillanova, Francesco Isaia,
and Vito Lippolis**

Università degli Studi di Cagliari, Dipartimento di Chimica Inorganica
ed Analitica, Monserrato (CA), Italy

Analogies and differences between polytellurides and polyiodides are discussed with the help of quantum chemical DFT calculations.

Keywords 3c-4e bond systems; DFT calculations; polyiodides; polytellurides

INTRODUCTION

It is well known that discrete and extended polyiodides derive from the interaction between the bases I^-/I_3^- and the acid I_2 and for this a structural relationship exists between these building blocks and I_2 -charge-transfer (CT) adducts. The reaction conditions (solvent, temperature, I^-/I_2 molar ratio) and the nature of the counter-cations (charge, shape, size, presence of donor/acceptor active sites) are responsible for the incredible variety of structural archetypes of polyiodides characterised in the solid state.^{1,2} The relatively flat potential energy surface for the 3c-4e bond system in I_3^- , and the wide modulation of the donor/ I_2 interaction strength on changing the donor atom (N, P, S, Se, ...), allow to freeze both I_3^- (Figure 1a) and I_2 in CT compounds (Figure 1b shows the case of the sulfur donors) in very different bond situations. Both scatter plots in Figures 1a and 1b indicate that the two bond lengths in $I-I-I^-$ and $D \cdots I-I$ systems are strictly correlated.³ Because of the structural analogy between these two systems (both having the central iodine in a hypervalent state 10-I-2), very asymmetric I_3^- 's can be alternatively described with the donor/acceptor charge-transfer model, whereas fairly balanced $D \cdots I_2$ adducts with the 3c-4e bond model.³ FT-Raman spectroscopy has played a crucial role in characterizing these systems: the analysis of the Raman spectra of numerous structurally

Address correspondence to F. A. Devillanova, Università degli Studi di Cagliari, Dipartimento di Chimica Inorganica ed Analitica, S.S. 554 Bivio per Sestu, I-09042 Monserrato (CA), Italy. E-mail: devilla@unica.it

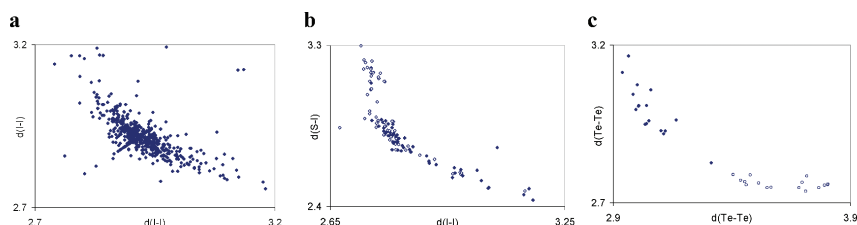


FIGURE 1 Scatter plots of the two bond distances (from CCDC database) within the linear (angle > 165°) fragments: a, (I–I–I)[–]; b, S–I–I; c, Te–Te–Te.

characterized polyiodides and CT adducts represented the experimental basis to confirm the analogy between these systems and to conclude that all polyiodides are combinations of I[–], I₂ and I₃[–], being the Raman response related only to the structural features of I₂ and I₃[–] building blocks.^{1,2}

Although the chemistry of polytellurides is less explored, their variety appears at least as rich as that of polyiodides for the tendency of tellurium, as well as of sulfur and selenium, to catenate.⁴ Due to the relatively strong Te–Te bond, the number of possible building blocks which can contribute to the formation of tellurium-based networks is higher than that of polyiodides. In fact, besides the species Te^{2–}, Te₂^{2–}, and Te₃^{4–}, which are isoelectronic with I[–], I₂ and I₃[–] respectively, other fundamental species [such as Te_n^{2–} chains or cyclic Te_n (n ≥ 3)] must be considered to explain the different structural archetypes of polytellurides observed. In addition, a substantial difference between polytellurides and polyiodides resides on the different charges associated to isoelectronic species, which are responsible for their different donor/acceptor ability and for their different stability. Differences and analogies between polytellurides and polyiodides will be discussed here with the help of DFT calculations, using selected examples from the literature.

Quantum-Chemical DFT Calculations

Quantum-chemical DFT calculations were carried out with the commercial suite Gaussian03.⁵ All calculations exploited the well-known three parameters hybrid functional Becke3LYP.⁶ For halogen and chalcogen atomic species the LanL2DZ basis set⁷ including diffuse and polarization functions⁸ and effective core potentials were used, while for C and H the double-zeta Shafer et al.⁹ basis sets were adopted.¹⁰ Force constants and the resulting vibrational IR- and Raman-active frequencies were computed by analytically determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates at the optimized

geometries. For all compounds, NBO populations¹¹ and Wiberg bond indexes¹² were also calculated at the optimized geometries.¹³ The programs Gabedit 2.0.7¹⁴ and Molden 4.6¹⁵ were used to investigate the charge distributions and MO's shapes.

DISCUSSION

Our discussion starts with the comparison between the isoelectronic species I^- and Te^{2-} , and I_2 and Te_2^{2-} . Te^{2-} and Te_2^{2-} are better donors than I^- and I_2 , while the acceptor ability of Te_2^{2-} is much lower than that of I_2 , since the negative charge prevents the approaching of nucleophilic species. In fact, while DFT calculations⁵ confirm the stability of the I_3^- species, they show that Te_3^{4-} is unstable with respect to the two Te^{2-} and Te_2^{2-} separate components (Figure 2a).

However, a search of the literature data on the linear Te–Te–Te arrangement shows that numerous examples of this linear three-body system have been structurally characterized and that, as found for I_3^- or for I_2 –CT adducts, the two bond distances are strictly correlated (see Figure 1c). In addition, the mean bond lengthening within the Te–Te–Te fragments is 11.5% with respect to the sum of the covalent radii (same entity of lengthening's found for I_3^- with respect to I_2) in good agreement with the 3c–4e description of the bond. It must be pointed out that, according to the relatively flat potential energy of the 3c–4e system, a

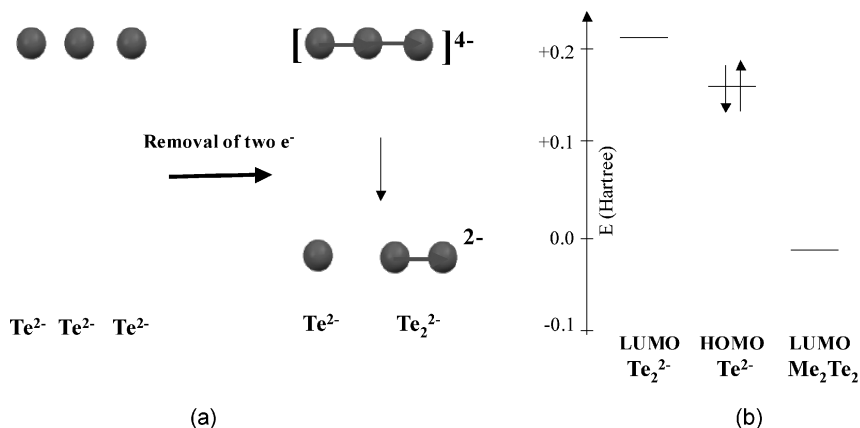


FIGURE 2 (a) The removal of two electrons from the system formed by three telluride anions leads to the Te_3^{4-} anion, which is unstable with respect to the two Te^{2-} and Te_2^{2-} separate components; and (b) calculated energies of the HOMO of Te_2^{2-} and of the LUMO of Te_2^{2-} and Me_2Te_2 .

wide variation of the Te–Te bond lengths is observed with several examples of very asymmetric situations, for which the use of the CT model for their description is fully justified. The energy (and consequently the accepting properties) of the empty σ^* orbital of the Te–Te fragment can be modulated by changing its electron population charge (which can assume all the formal values, including fractional ones, ranging between -2 in the ditelluride anion and $+2$ in the ditellurium dications). On the other hand, the energy of the tellurium atom, which acts as a donor is strictly dependent on its chemical surrounding. The case of Te_3^{4-} clarifies very well this aspect: in spite of the fact that the match of energy between the LUMO of Te_2^{2-} and the HOMO of Te^{2-} (Figure 2b) is appropriate for their interaction, the electrostatic repulsion due to the high charges on the two fragments prevents their approaching to give an effective donor/acceptor interaction, and consequently the existence of the Te_3^{4-} isolated linear anion. It is enough to consider the Me_2Te_2 neutral compound instead of the Te_2^{2-} species (Figure 2b) to verify that the decreased LUMO energy and the absence of charge allow the donor/acceptor interaction of Me_2Te_2 with Te^{2-} . Thus, the condition necessary to favour an increasing overlap between the two fragments is an increasing reduction of the total charge on the Te_2 species. This can be achieved by either attaching organic groups to the tellurium atoms or favouring the interactions of the telluride species with metal centres in transition metal complexes. The expected results are a very great variety of Te–Te–Te linear arrangements ranging from symmetric to very asymmetric bond situations, depending on the particular Te-donor/(Te–Te)-acceptor couple. Only few cases of linear Te_3 fragments with attached organic groups $[(\text{RTe})_3^-]$ ($\text{R}=\text{Ph}$, CF_3) are reported in literature;^{16–20} however, the case of $\text{Te}_3\text{Mes}_5^+$ reported by du Mont¹⁹ and that of $(\text{TeMe})_5^+$ by Seppelt²⁰ indicate how different can be the organic framework containing the 3c-4e Te–Te–Te system. A relatively higher number of linear Te–Te–Te fragments are found within transition metal complexes. In these cases the lowering of the charge in Te_2^{2-} by interaction with metal centres allows a wide modulation of $\text{np}(\text{Te}^{2-}) \rightarrow \sigma^*(\text{Te–Te})$ donor/acceptor interaction. The structural features of the two anionic complexes $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ and $[\text{Mo}(\text{CO})_5\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ shown in Figure 3 elucidate very well this aspect.^{21,22}

In $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$,²¹ the Te_2^{2-} is η^2 -bonded to the two iron atoms thus allowing a small but significant interaction (3.215 \AA) with the η^2 -coordinated Te^{2-} . In $[\text{Mo}(\text{CO})_5\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$, where the interaction of the terminal Te^- of the Te_2^{2-} ligand with a pentacarbonyl molybdenum fragment reduces the charge on Te_2^{2-} ligand, the donor/acceptor interaction is stronger as verified by the decrease in the $\text{Te}^{2-} \cdots \text{Te}_2^{2-}$ distance

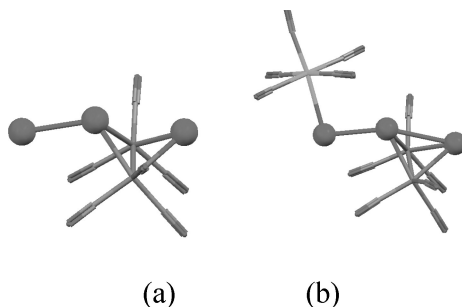


FIGURE 3 (a) $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ (from Ref. 21); and (b) $[\text{Mo}(\text{CO})_5\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ (from Ref. 22).

(3.157 Å) and the lengthening of the Te–Te one in Te_2^{2-} from 2.705 to 2.769 Å due to the increase of electron charge transferred from Te^{2-} to the σ^* MO of the η^2 -coordinated Te_2^{2-} .²² The lowering in the charge of Te_2^{2-} by interaction with metal ions represents the main way to obtain CT-type interaction not only with Te^{2-} but also with other donors. In this respect, the structural analogies of Te_7^{8-} , RTeTe_6^{7-} and ITe_6^{7-} fragments, found in some Mo/W trinuclear complexes,^{23–25} with the $\text{I}^- \cdot 3\text{I}_2$ (I_7^-) epta iodide²⁶ is very illustrative. In all these trinuclear complexes, the Te^{2-} , RTe^- and I^- donors interact with three Te_2^{2-} ligands η^4 attached to the metal centres.^{23–25}

The arrangement of three aligned tellurium atoms having a total distance of about 10% higher than the sum of the covalent radii represents one of the leitmotifs of tellurium chemistry. Examples of compounds containing this structural motif are found in numerous n -dimensional polymeric structures^{27–28} as well as in discrete polytellurides.^{28–33} Among these, the three anionic complexes $[\text{AgTe}_7]^{3-}$, $[\text{CuTe}_7]^{3-}$, and $[\text{HgTe}_7]^{2-}$ show similar structures: the Ag,²⁸ Cu³⁰ and one of the two Hg^{29b} reported complexes are characterized by very unbalanced Te–Te bonds, while in the other Hg^{II} complex, the Te–Te distances are quite similar [3.050(2)–2.997(2) Å].^{29a} The very unbalanced bonds suggest the origin of the Te_7^{4-} anion, which can be described as deriving from a $\text{np}(\text{Te}^-) \rightarrow \sigma^*(\text{Te}–\text{Te})$ donor/acceptor interaction between a monodentate Te_3^{2-} and a bidentate Te_4^{2-} ligand. Although the gold complex $[\text{AuTe}_7]^{3-}$ presents the same stoichiometry, its structure is different, being Au^{III} coordinated by a monodentate Te_2^{2-} and a tridentate Te_5^{4-} .³² This last polytelluride can be seen as formed by an $\text{np}(\text{Te}^-) \rightarrow \sigma^*(\text{Te}–\text{Te})$ donor-acceptor interaction between the lone pair

of the terminal tellurium atom of a bent $[\text{Au}^{\text{III}}(\eta^1 - \text{Te}_2^{-2})]^+$ moiety and one of the two Te–Te bonds of a Au^{III} -bicoordinated Te_3^{2-} ligand. In the dinuclear $[\text{Au}_2\text{Te}_{12}]^{4-}$ complex, two $[\text{AuTe}_5]^-$ fragments are held together by a Te_2^{2-} anion.³³

Another structural motif recognizable in many polytellurides is the square-planar Te_5^{6-} fragment, which is isoelectronic with ICl_4^- .³⁴ It can be seen as formed by two orthogonal 3c-4e bond systems, each obtained by removing two electrons from three aligned closed shell Te^{2-} for each direction. Strictly correlated to the Te_5^{6-} fragment, is also RTeTe_4^{5-} in which the central tellurium brings an organic group. As verified for Te_3^{4-} species, DFT calculations show that the high charges on these fragments prevent their existence as isolated anions. Also, in this case, a reduction of the charge is necessary to obtain the square-planar Te_5 fragment. In Cs_2Te_5 and Rb_2Te_5 ,^{35–36} a lowering of the charge from Te_5^{6-} to Te_5^{2-} is obtained by the formation of four 2c-2e bond systems with adjacent Te_5^{6-} fragments thus generating a $[\text{Te}_5^{2-}]_\infty$ polymeric ribbon. This occurs in different manners in the two salts: the four bonds are on the same side with respect the Te_5 plane in the case of caesium,³⁵ and two on one side and the other two on the opposite side in the case of Rb.³⁶ Alternatively, in both salts, the two orthogonal 3c-4e bond systems in each Te_5^{2-} unit can be considered as formed by five closed shell species: a central Te^{-2} surrounded by four Te^- of four Te_2^{2-} aligned perpendicularly to the Te_5 plane. The removal of two electrons from each direction produces the Te_5^{2-} unit. The remaining four free Te^- of each unit are engaged into the formation of adjacent Te_5^{2-} units to give a ${}^\infty_1 [\text{Te}_5^{2-}]$ ribbon. In the case of *catena*[bis(tetraethylammonium)(μ_4 -pentatelluro)-diarsenic],³⁷ the lowering of the charge of Te_5^{6-} is achieved by the interaction with the dumbbell As_2^{4+} cation thus generating the polymer $[\text{As}_2\text{Te}_5]^{2-}$.

A structural motif that makes the polytellurides chemistry quite different from that of polyiodides is the formation of cyclic Te_n fragments. For lack of space, only the case of cyclic Te_3 fragment^{38–42} will be discussed here. All the known compounds containing this cyclic arrangement are collected in Table 1.

In the $[\text{M}(\text{CO})_4\text{Te}_3]^{2+}$ complex cations^{38–39} ($\text{M} = \text{Mo}, \text{W}$) the three Te–Te distances correspond to single bonds, and each complex cation has been described as a Te_3^{2+} cyclic ligand coordinating the metal centre of an $\text{M}(\text{CO})_4$ fragment. DFT calculations carried out on the $[\text{MoTe}_3]^{2+}$ fragment confirm this description and give an optimized geometry with two equal Te–Te distances shorter than the third

TABLE I Experimental Bond Lengths Found in the Cyclic Te_3 Fragment for all the Reported Species, Together with the Calculated Values for $[\text{MoTe}_3]^{2+}$, $[\text{NbTe}_3]^{5+}$, and Te_3^n ($n = 0, +2, -2$)

Compound	d_1	d_2	d_3	Ref.
$[\text{W}(\text{CO})_4\text{Te}_3]^{2+}$	2.708	2.728	2.708	38
$[\text{Mo}(\text{CO})_4\text{Te}_3]^{2+}$	2.718	2.736	2.718	39
$[\text{Cr}(\text{en})_3]^{3+}[\text{Te}_6]^{3-}$	3.138	3.138	3.138	40
$[\text{NbTe}_{10}]^{3-}$	3.132	3.154	3.161	41
$[\text{TaTe}_{10}]^{3-}$	3.171	3.146	3.171	42
$[\text{MoTe}_3]^{2+}$ fragment	2.770	2.859	2.770	Calcd.
$[\text{NbTe}_3]^{5+}$ fragment	2.949	2.949	2.949	Calcd.
Cyclic Te_3	2.782	2.782	2.782	Calcd.
Cyclic Te_3^{2+}	2.645	2.645	3.011	Calcd.
Cyclic Te_3^{2-}	3.165	3.165	3.165	Calcd.

distance and fairly close to those corresponding to a single bond (Table 1). The other three compounds containing such a fragment are the two complexes $[\text{MTe}_{10}]^{3-}$ ($\text{M} = \text{Nb}, \text{Ta}$),^{41,42} and the polymeric 2D-network described as formed by interacting $[\text{Te}_6]^{3-}$ anions.⁴⁰ In all these compounds, the endocyclic Te–Te distances are much longer than that found in the Mo and W complexes and than that calculated for the cyclic neutral Te_3 . The sketches of the MO's of cyclic Te_3 (Figure 4) show that the LUMO is a σ^* -orbital (c) in the molecular plane which can accept electron density from the π^* MO of the Te_2^{2-} ligands.

The difference between the $[\text{MTe}_{10}]^{3-}$ complexes and the $[\text{Te}_6]^{3-}$ anion is that in the complexes three Te_2^{2-} ligands coordinate the metal centre with one tellurium, the second tellurium acting as a donor towards the LUMO of the Te_3 cyclic fragment, while in $[\text{Cr}(\text{en})_3]^{3+}[\text{Te}_6]^{3-}$, the polytellurides network is formed by combination of one cyclic Te_3 with three Te_2^{2-} anions: one tellurium of each Te_2^{2-} has a donor/acceptor interaction with the cyclic Te_3 fragment, while the second tellurium of each Te_2^{2-} anion interacts with different Te_3 cycles. These three interactions pour electron charge on the σ^* MO of Te_3 thus increasing the Te–Te bond distance. With the aim of confirming this, we have carried out DFT calculations on the cyclic Te_3^{2-} anion. Although this anion is less stable with respect to the open structure by 51.25 Kcal/mole, its optimized geometry, which represents a transition state, has three equal, very elongated bond distances (3.165 Å) which are comparable with the experimental distances found in the examined compounds.

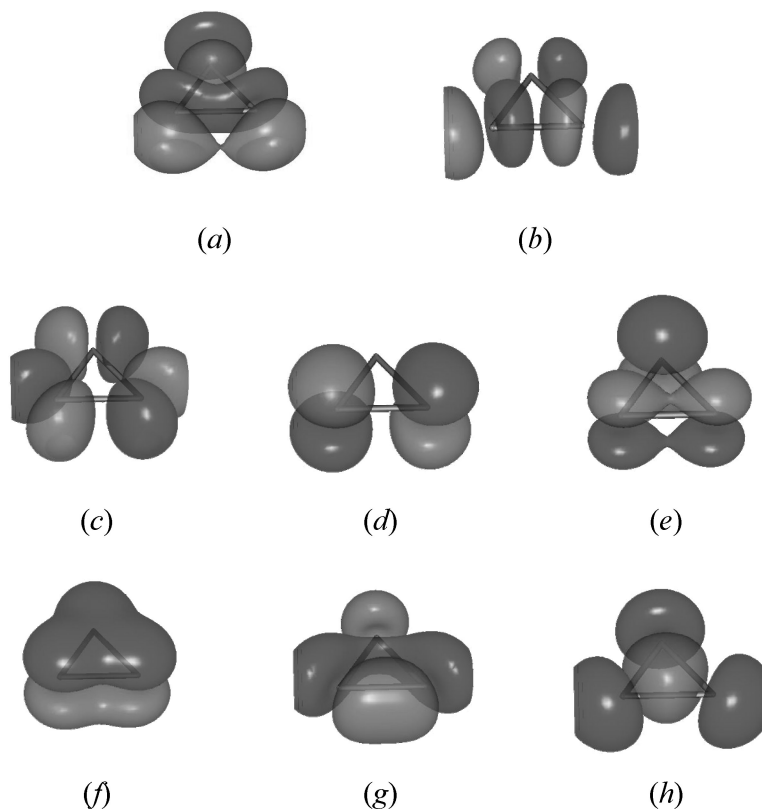


FIGURE 4 Sketches of the MO's of cyclic Te_3 . The couple of degenerate MO's d and e are the HOMO and c is the LUMO.

CONCLUSIONS

Summarily, the chemistry of polytellurides, still widely unexplored, certainly should reserve a lot of new structural archetypes of compounds in combination with the great variety of coordination compounds necessary to lower their electron population and hence their charges, favouring the freezing of $\text{Te} \cdots \text{Te}$ contacts in a practically continuous manner. In the case of polyiodides, FT-Raman spectroscopy has supplied an experimental basis for the conclusion that all the polyiodides are built up by the combinations of only three building blocks. For the polytellurides, no systematic characterization by vibrational spectroscopy has been carried out to ascertain possible correlations between the structural features of basic polytellurides and their vibrational properties. These

correlations could be of help in the identification of the products in absence of X-ray crystal structure determination.

REFERENCES

- [1] P. H. Svensson, and L. Kloo, *Chem. Rev.*, **103**, 1649 (2003).
- [2] A. J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek, and M. Schröder, *Chem. Soc. Rev.*, **27**, 195 (1998).
- [3] M. C. Aragoni, M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, and A. Mancini, *Bioinorganic Chemistry and Applications* (2007) Article ID 17416.
- [4] I. Krossing, In *Handbook of Chalcogen Chemistry*, F. A. Devillanova, Ed. (RSC, Cambridge, UK, 2006), Chapter 7.1, p. 381–416.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian03*, Revisions B02-05 (Gaussian, Inc., Wallingford, CT, 2004).
- [6] (a) A. D. Becke, *J. Chem. Phys.*, **98**, 5648–5648 (1993); (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988); (c) S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, **58**, 1200–1211 (1980); (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.*, **98**, 11, 623–11,627 (1994).
- [7] (a) T. H. Dunning Jr., and P. J. Hay, In *Methods of Electronic Structure Theory*, Vol. 2, H. F. Schaefer III, Ed. (Plenum Press, New York, 1977); (b) P. J. Hay, and W. R. Wadt *J. Chem. Phys.*, **82**, 270–283 (1985); (c) P. J. Hay, and W. R. Wadt, *J. Chem. Phys.*, **82**, 284–298 (1985).
- [8] C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert, and L. S. Sunderlin, *J. Phys. Chem. A* **105**, 8111–8116 (2001).
- [9] A. Schafer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.*, **97**, 2571–2577 (1992).
- [10] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/02/06, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information.
- [11] (a) A. E. Reed, and F. Weinhold, *J. Chem. Phys.*, **78**, 4066–4073 (1983); (b) A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.*, **83**, 735–746 (1985); (c) A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, **88**, 899–926 (1988).
- [12] K. Wiberg, *Tetrahedron*, **24**, 1083–1096 (1968).
- [13] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

- [14] Gabedit is a free Graphical User Interface (GUI) for computational chemistry packages. It is written by Abdul-Rahman Allouche. Gabedit is available from <http://lasim.univ-lyon1.fr/allouche/gabeditb> (accessed) (2007).
- [15] G. Schaftenaar, and J. H. Noordik, *J. Comput.-Aided Mol. Design*, **14**, 123–134 (2000).
- [16] D. Witthaut, K. Kirschbaum, O. Conrad, and D. M. Giolando, *Organometallics*, **19**, 5238 (2000).
- [17] A. C. Hillier, S. Y. Liu, A. Sella, and M. R. J. Elsegood, *Angew. Chem., Int. Ed.*, **38**, 2745 (1999).
- [18] H. T. M. Fischer, D. Naumann, and W. Tyrra, *Chem.-Eur. J.*, **12**, 2515 (2006).
- [19] J. Jeske, W. -W. du Mont, and P. G. Jones, *Angew. Chem., Int. Ed.*, **36**, 2219 (1997).
- [20] B. Müller, H. Poleschner, and K. Seppelt, Tenth International Conference on the Chemistry of Selenium and Tellurium, Łódź (Poland), 22–27 June, p. 23, (2007).
- [21] B. K. Das, and M. G. Kanatzidis, *Inorg. Chem.*, **34**, 5721 (1995).
- [22] B. W. Eichhorn, R. C. Haushalter, and J. S. Merola, *Inorg. Chem.*, **29**, 728 (1990).
- [23] X. Lin, H. -Y. Chen, L. -S. Chi, and H. -H. Zhuang, *Polyhedron*, **18**, 217 (1999).
- [24] J. Li, Z. Chen, T. J. Emge, and M. Proserpio, *Inorg. Chem.*, **36**, 1437 (1997).
- [25] D. Freedman, T. J. Emge, and J. G. Brennan, *Inorg. Chem.*, **41**, 2202 (2002).
- [26] F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis, and G. Verani, *Inorg. Chem.*, **32**, 3694 (1993).
- [27] K. W. Kinkhammer, and P. Böttcher, *Z. Naturforsch., B. Chem. Sci.*, **45**, 141 (1990).
- [28] D. M. Smith, and J. A. Ibers, *Coord. Chem. Rev.*, **200**, 187 (2000).
- [29] (a) J. M. McConnachie, M. A. Ansari, J. C. Bollinger, R. J. Salm, and J. A. Ibers, *Inorg. Chem.*, **32**, 3201 (1993); (b) U. Müller, G. Grebe, B. Neumüller, B. Schreiner, and K. Dehnicke, *Z. anorg. Allg. Chem.*, **619**, 500 (1993).
- [30] D. M. Smith, L. C. Roof, M. A. Ansari, J. M. McConnachie, J. C. Bollinger, M. A. Pell, R. J. Salm, and J. A. Ibers, *Inorg. Chem.*, **35**, 4999 (1996).
- [31] P. Sekar, P. F. Arnold Junior, and J. A. Ibers, *Inorg. Chem.*, **41**, 577 (2002).
- [32] M. A. Ansari, J. C. Bollingerand, and J. A. Ibers, *J. Am. Chem. Soc.*, **115**, 3838 (1993).
- [33] S. S. Dhingra, and R. C. Haushalter, *Inorg. Chem.*, **33**, 2735 (1994).
- [34] W. S. Sheldrick, In *Handbook of Chalcogen Chemistry*, F. A. Devillanova, Ed. (RSC, Cambridge, UK, 2006), Chapter 9.2, p. 553.
- [35] Von P. Böttcher, and U. Kretschmann, *Z. anorg.allg. Chem.*, **491**, 39–47 (1982).
- [36] Von P. Böttcher, and U. Kretschmann, *J. Less-Common Metals*, **95**, 81–91 (1983).
- [37] C. J. Warren, R. C. Haushalter- A. B. Bocarsly, *Chem. Mater.*, **6**, 780–783 (1994).
- [38] R. Faggiani, R. J. Gillespie, C. Campana, and J. W. Kolis, *J. Chem. Soc., Chem. Commun.*, 485 (1987).
- [39] A. Seigneurin, T. Makani, D. J. Jones, and J. Roziere, *J. Chem. Soc., Dalton Trans.*, 2111 (1987).
- [40] C. Reisner, and W. Tremel, *Chem. Commun.*, 387 (1997).
- [41] W. A. Flomer, and J. W. Kolis, *J. Am. Chem. Soc.*, **110**, 3682 (1988).
- [42] W. A. Flomer, J. W. Kolis, and W. T. Pennington, *Acta Crystallogr., Sect.C: Cryst. Struct. Commun.*, **52**, 2445 (1996).