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Unusually Short Distances between the Carbonyl Oxygen and the Tin Atom in $RCOSMR'_3$ (M = Ge, Sn, Pb): The Importance of Intramolecular $n_O \rightarrow \sigma^*_{MS}$ Orbital Interactions

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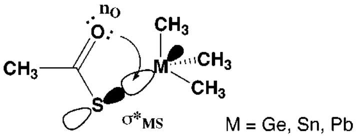
ABSTRACT



We found that the C═O···Sn distance in $RCOSSnR'_3$ was shorter than the C═O···Ge distance in $RCOSGeR'_3$ and theoretically confirmed that the orbital interactions between the nonbonding orbitals on the carbonyl oxygen (n_O) and the σ^*_{SnS} orbitals were important in regard to the shortness.

The effects of nonbonded intramolecular as well as intermolecular interactions on the structures of molecules are a growing field of study.[1] Inter- and intramolecular interactions may reflect the affinity between elements. The strong affinity of silicon to an oxygen atom is well documented.[2] However, little is known about the magnitude of the interactions (affinity) between other Group 14 metals and oxygen or chalcogen atoms such as sulfur and selenium. We report here the unusually short distances between the carbonyl oxygen and tin atoms in Group 14 metal derivatives of thiocarboxylic acids ($RCOSMR'_3$, M = Ge, Sn, Pb) and the nature of this nonbonded interaction between the carbonyl oxygen and Group 14 metals: the interactions between the nonbonding orbitals on the carbonyl oxygen (n_O) and the σ^*_{MS} orbitals are very important.

Triphenylgermanium (**1**), -tin (**2**), and -lead (**3**) 4-methylbenzenecarbothioates were synthesized by reacting the corresponding potassium carbothioate with Ph_3GeCl, Ph_3SnCl, and Ph_3PbCl, respectively.[2b] The structures of **1**−**3** determined by X-ray analysis were isomorphous, a distorted tetrahedron in which the lengths of the C(11)−O(11), C(11)−S(11), and M(1)−S(11) bonds in $RCOSMPh_3$ (M = Ge, Sn, Pb) are comparable to C═O double and C−S and M−S single bonds, respectively (Table 1).[3−4]

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[1] Rosenfield, R. E.; Parthsarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 486. Row, T. N. G.; Parthsarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477. Wei, Y.; Hendricksen, W. A.; Crouch, R. J.; Satow, Y. *Science* **1990**, *249*, 1398. Hendricksen, W. A. *Science* **1990**, *254*, 51. Wei, Y.; Kahn, R.; Fourma, R.; Drickamer, K.; Hendricksen, W. A. *Science* **1990**, *254*, 1608. Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. I.; Reibenspies, J. *J. Am. Chem. Soc.* **1993**, *115*, 5056. Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077. Mnyeav, R. M.; Minkin, V. I. *Can. J. Chem.* **1998**, *76*, 776. Komatsu, H.; Iwaoka, M.; Tomoda, S. *Chem. Commun.* **1999**, 205. Inagaki, S.; Ohashi, S.; Kawashima, T. *Org. Lett.* **1999**, *1*, 1145. Niyomura, O.; Kato, S.; Inagaki, S. *J. Am. Chem. Soc.* **2000**, *122*, 2132.

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[4] Covalent bond radii (Å): C−S 1.81, Ge−O 1.88, Ge−S 2.26, Sn−O 2.06, Sn−S 2.44, Pb−O 2.28, Pb−S 2.58: Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, NY, 1976; pp 146−155.

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Table 1. X-ray Data for 4-$CH_3C_6H_4COSMPh_3$ and CH_3SMPh_3 (M = Ge, Sn, Pb)

	Ge	Sn	Pb
	4-$CH_3C_6H_4COSMPh_3$		
C═O···M	3.003(2)	2.907(2)	2.990(4)
M(1)−S(11)	2.2547(8)	2.4453(9)	2.539(2)
C(11)−O(11)	1.209(3)	1.208(2)	1.222(7)
C(11)−S(11)	1.790(3)	1.775(3)	1.770(6)
C(11)−C(21)	1.944(3)	2.131(3)	2.205(5)
M(1)−C(31)	1.942(3)	2.141(3)	2.213(5)
M(1)−C(41)	1.934(3)	2.123(3)	2.202(5)
M(1)−S(11)−C(11)	98.25(10)	93.5(1)	94.1(2)
	CH_3SMPh_3[a]		
M−S	2.224(1)	2.391(2)	2.489(6)
M−C_{ipso}	1.931(1)	2.135(7)	2.201(13)
M−C_{ipso}	1.930(2)	2.139(7)	2.185(18)
M−C_{ipso}	1.932(1)	2.115(7)	2.186(16)
M−S−CH_3	101.4(3)	102.6(8)	100.5(12)

[a] Reference 6.

The distances between the carbonyl oxygen and the central Group 14 metals are all within the sum of the van der Waals radii of both atoms,[5] respectively, indicating intramolecular attraction between the two atoms (Figure 1). Interestingly, despite the large atomic radius of tin compared with that of germanium, the C═O···Sn distance [2.907(2) Å] in **2** is about 0.1 Å shorter than C═O···Ge distance [3.003(2) Å] in **1**. The C═O···Pb distance [2.990(4) Å] in **3** is longer than that in **2**. The M(1)−S(11)−C(11) angles and the M(1)−S(11) distances in **1**, **2**, and **3** are 3−9° narrow and 0.03−0.05 Å longer, respectively, compared with those in CH_3SMPh_3 (M = Ge, Sn, Pb)[6] having no carbonyl group (Table 1).

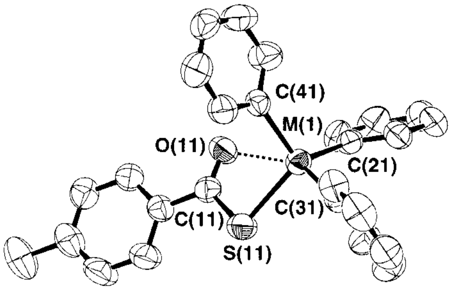

Figure 1. Molecular structures of 4-$CH_3C_6H_4COSMPh_3$ (**1**, M = Ge; **2**, M = Sn; **3**, M = Pb).

To elucidate the nature of this unusual nonbonded attraction, ab initio geometry optimizations at the B3LYP/LANL2DZ+p level[7] with the Gaussian 98 program[8] were performed on the model compounds trimethylgermanium (**1′**), -tin (**2′**), and -lead (**3′**) ethanecarbothioates. The calculations for **1′**, **2′**, and **3′** indicated that the C═O···Sn distance (3.058 Å) in **2′** is 0.1 Å shorter than that in **1′**, while the M−S distances increase in the order **1′** > **2′** > **3′** (Table 2).

Table 2. Calculated Geometrical Parameter for $CH_3COSM(CH_3)_3$ (M = Ge, Sn, Pb) at B3LYP/LANL2DZ+p Level

	M		
	Ge (**1′**)	Sn (**2′**)	Pb (**3′**)
M(1)···O(3)	3.147 Å	3.058 Å	3.113 Å
M(1)−S(2)	2.313 Å	2.496 Å	2.568 Å
C(4)−O(3)	1.217 Å	1.222 Å	1.223 Å
M(1)−S(2)−C(4)	99.8°	95.2°	95.3°

The bond angle Sn−S−C (95.2°) in **2′** also is narrow compared with that in **1′** (99.8°). These results are consistent with the results obtained by X-ray structural analyses of **1**−**3**. To obtain further information regarding the electronic structures of **1**−**3**, NBO (natural bond orbital) analyses were carried out. The NBO analysis showed that the orbital interactions between the n orbital (n_O) on the carbonyl oxygen and the σ^*_{MC} orbitals (Figure 2a) are present, but their values are close to each other (Table 3). On the other hand, the interactions between the n_O and σ^*_{MS} orbitals (Figure 2b) are also appreciable, and interestingly the stabilization energies of the $n_O \rightarrow \sigma^*_{MS}$ in **2′** and **3′** are ca.

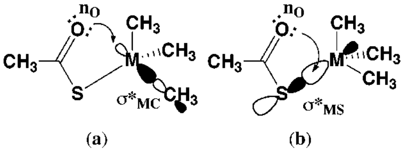

Figure 2. Nonbonded attraction due to (a) the $n_O \rightarrow \sigma^*_{MC}$ and (b) $n_O \rightarrow \sigma^*_{MS}$.

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(5) Sum of the van der Waals radii (Å): Ge···O 3.40, Sn···O 3.58, Pb···O 3.44: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

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(7) The three-parameter exchange of Becke in conjunction with the Lee−Yang−Parr correlation functional (B3LYP) was applied in our calculations. The effective core potentials (ECPs) LANL2DZ+p were used for C, O, S, Ge, Sn, Pb. The d-polarization function for ECP basis set of all atoms except for H are taken from Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, Y.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam; 1984.

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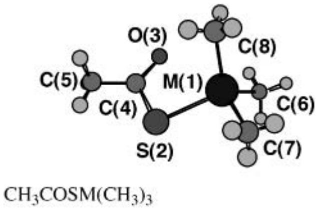
Table 3. NBO Analysis of $CH_3COSM(CH_3)_3$ at B3LYP/LAN2DZ+p Level



$CH_3COSM(CH_3)_3$

	ΔE (kcal mol^{-1})[a]	
M	$n_O \rightarrow \sigma^*_{MC(7)}$	$n_O \rightarrow \sigma^*_{MS}$
Ge	1.82	0.64
Sn	2.46	2.25
Pb	2.44	2.05

[a] ΔE = stabilization energies associated with delocalization.

3.5 times that in **1′**. The contour maps of the n_O and σ^*_{MS} orbitals in the molecular plane M(1)−S(2)−C(4) for the model compounds were depicted by using the MOLDEN 3.6 program.[9] As shown in Figure 3, the overlaps (overlap integral, 0.0271) between the n_O and the part on M in the σ^*_{MS} orbitals in the tin **2′** are larger than that (overlap integral, 0.0253) in the germanium compound **1′**. Thus, the magnitude of such interactions agrees with the order of the shortness of the C═O···M distances. This may substantially contribute to the structure of such organo Group 14 metal derivatives of chalcogenocarboxylic acids and may also result in shortening the distance in C═O···Sn, as has been observed by X-ray molecular structural analysis. The atomic charge (1.06) of the tin in **2′** is clearly larger than that in **1′** (0.76), while those of the carbonyl oxygens show similar values (−0.21 to −0.23), suggesting that the electrostatic interactions may also contribute to the short C═O···Sn distances. The longer C═O···Pb distance compared with the C═O···Sn distance may arise from the corresponding M−S bond lengths, although the magnitude of the overlaps between the n_O and σ^*_{MS} orbitals in **3′** is close to that in **2′**.

In summary, the crystal structure in **2** showed unusual intramolecular C═O···Sn attractions compared with those in **1** and **3**. The short distance results from the interactions between the n_O and σ^*_{MS} orbitals rather than those between n_O and σ^*_{MC} orbitals. These findings may help us to understand not only organic synthesis using organotin compounds but also the biological activities of various organotin compounds.

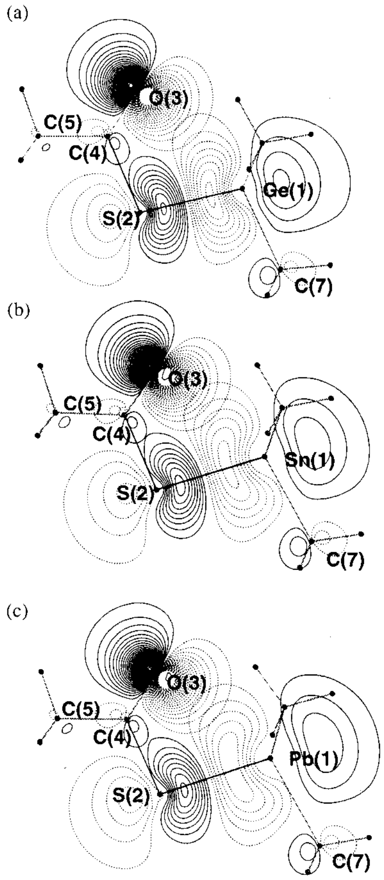


Figure 3. The overlapping between n_O (p-type lone pair) and σ^*_{MS} orbitals in the molecular plane M(1)−S(2)−C(4) of (a) **1′**, (b) **2′**, and (c) **3′** calculated at the B3LYP/LANL2DZ+p level.

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Supporting Information Available: Spectroscopic and X-ray crystal data for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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