The First Theoretical and Experimental Proof of Polythiocarbamatozinc(II) Complexes, Catalysts for Sulfur Vulcanization

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Abstract: The existence of polythiocarbamatozinc complexes, species presumed to be involved in catalyzing sulfur vulcanization, has been studied by computational and mass-spectrometric techniques. Density functional calculations reveal that the sulfuration energy of bis(trithiocarbamato)zinc(II) is comparable to that of bis(phenyltrithiolato)zinc(II), a stable sulfurated complex. Interestingly, the analogous nonsymmetrically sulfurated complex (dithiocarbamato)(tetrathiocarbamato)zinc(II) is energetically slightly more favorable. The calculations indicate that polythiocarbamatozinc complexes may indeed be involved in the sulfur vulcanization cascade, a conclusion corroborated by ensuing laser-desorption ionization (LDI) mass-spectrometric measurements on mixtures of dithiocarbamatozinc(II) complexes and elemental sulfur. These demonstrate the presence of polythiocarbamatozinc ions that are sulfurated with up to eight additional sulfur atoms.

Keywords: density functional calculations · mass spectrometry · S ligands · vulcanization · zinc

Introduction

Accelerated sulfur vulcanization is the key technology of a vast industry that produces a wide range of useful rubber materials. Despite decades of extensive fundamental and applied research, essential aspects about the mechanism of accelerated vulcanization are still unknown.[1] This is particularly true for what are called sulfur-rich or polythiocarbamatozinc(II) complexes. Polythiocarbamatozinc(II) complexes are inferred to be important catalytic intermediates in the accelerated sulfur-vulcanization of rubber,[1, 2] and have been suggested to form when zinc dithiocarbamates **1**, present in the vulcanization mixture, incorporate one or more sulfur atoms in the dithiocarbamate chelate ring.[3]

The possible involvement of polythiozinc(II) complexes in the vulcanization process was proposed as early as 1921.[4, 5] To

Zn(dmtc)₂, **1**

Bis(dimethylpolythiocarbamato)zinc(II)
(x or y > 0)
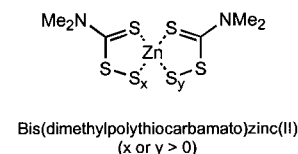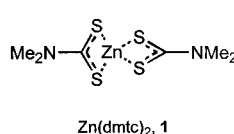
date such intermediates occupy a central position in many of the proposed vulcanization schemes.[1, 2] They are, for example, claimed to activate elemental sulfur,[2, 6, 7] to assist in the exchange and transport of sulfur atoms in the vulcanizing rubber,[8, 9] and also to catalyze the formation of sulfur crosslinks.[10] Nevertheless, proof for their existence is lacking. Although X-ray crystal structures of related bis(phenyltrithiolato)zinc(II) complexes,[11, 12] as well as of rhenium(III)[13] and osmium(III) trithiocarbamate[14] complexes may suggest the existence of polythiocarbamatozinc(II) complexes, such complexes have not been synthesized, and have not even been detected spectroscopically.[15-17] The proposed reaction schemes are therefore only based on hypotheses and indirect indications. We felt that computational techniques would furnish desirable new evidence about the (in)ability to form polythiocarbamatozinc complexes from **1** and sulfur.

In the past few years computational techniques have become increasingly powerful and reliable, and are now able to handle large systems containing transition metals.[18, 19] Their application has been particularly important in evaluating the structure and reactivity of transient transition-metal intermediates that occur in catalytic processes.[19] Therefore, and for the first time in the field of sulfur vulcanization,

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density functional theory (DFT)–based calculations were applied to investigate the possible involvement of polythiocarbamatozinc(II) complexes as catalysts in sulfur vulcanization. Herein we report state-of-the-art DFT calculations which reveal that polythiocarbamatozinc complexes are likely to form during vulcanization, as their sulfuration energies are comparable to those of stable polythiolatozinc complexes. This result prompted us to seek additional experimental evidence by means of mass spectrometry. Consequently we report laser-desorption ionization (LDI) mass-spectrometric (MS) data, which constitutes the first direct experimental proof for polythiocarbamatozinc(II) complexes.

Results and Discussion

Structure of polythiocarbamatozinc(II) complexes: The inability to prove the existence of polythiocarbamatozinc(II) has been an important disadvantage of theories claiming their involvement as vulcanization catalysts. However, some indication has been obtained because certain related trithiolatozinc(II) complexes do exist. Bis(phenyltrithiolato)zinc(II) complexes **2** have been synthesized, and their X-ray crystal structures have been solved.[11, 12] By density functional calculation of the energy of the sulfurated bis(phenyltrithiolato)zinc complex (3/3) **2** (Scheme 1), as well as that of the

Scheme 1. Sulfuration of zinc complexes **1** and **2**.

Abstract in Dutch: *Het bestaan van polythiocarbamatozinkcomplexen, verbindingen waarvan wordt aangenomen dat ze betrokken zijn bij het katalyseren van zwavelvulkanisatie, is onderzocht met behulp van berekeningen en massaspectrometrische technieken. Quantumchemische berekeningen tonen aan dat het complex bis(trithiocarbamato)zink(II) een sulfureringsenergie heeft die vergelijkbaar is met de energie van bis(fenyltrithiolato)zink(II), een stabiel zwavelrijk complex. Het analoge niet-symmetrische zwavelrijke complex (dithiocarbamato)(tetrathiocarbamato)zink(II) is energetisch iets gunstiger. Deze berekeningen geven aan dat polythiocarbamatozinkcomplexen inderdaad betrokken kunnen zijn in de zwavelvulkanisatie-cascade, een conclusie die bovendien wordt bevestigd door Laser-Desorptie Ionizatie (LDI)-massa-spectrometrische metingen, uitgevoerd aan mengsels van dithiocarbamato-zinkcomplexen en zwavel. Daarbij worden polythiocarbamato-zink-ionen waargenomen die zijn verrijkt met één tot acht extra zwavelatomen.*

non-sulfurated bis(phenyldithiolato)zinc(II) complex (2/2) **2**,[20] an energy value $\Delta E_{\text{sulfuration,2}}$ for an experimentally-observed sulfuration can be obtained (Scheme 1). Similarly, an energy value $\Delta E_{\text{sulfuration,1}}$ for the hypothesized sulfuration of bis(dimethyldithiocarbamato)zinc(II) **1** may be calculated. Comparison of these values would yield information about the thermodynamics of the latter process. This methodology requires correct calculation and optimization of the four zinc complexes depicted in Scheme 1, whereas the reported X-ray crystal structures of (2/2) and (3/3) **2** are used for comparison and validation.

First the structures of (2/2) **2** and (3/3) **2** were calculated by DF methods. Table 1 lists the most relevant calculated and observed bond lengths and angles. As can be seen these are in good agreement. The average deviation for all bond lengths and angles of (2/2) or (3/3) **2** is about 3%.
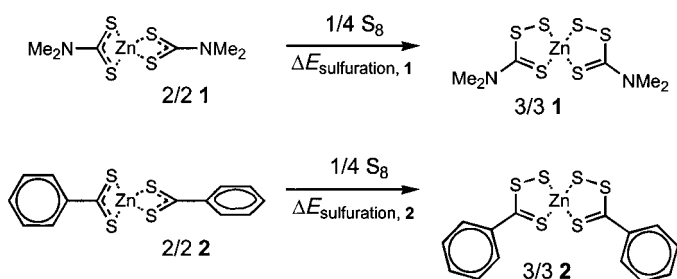
Table 1. Selected bond lengths [Å] and angles [°] of (sulfurated) complexes **1** and **2**.

Complex		Calculated **1**	Calculated **2**	Observed **2**
(2/2)	Zn–S1	2.400	2.397	2.355(4)[a]
	C1–S1	1.754	1.729	1.70(1)[b]
	C1–R1	1.347[c]	1.469[d]	1.46(2)[d]
	Zn-S1-C1	82.1	81.8	82.0(4)
	S1-C1-R1	120.9[c]	120.3[d]	120.2(8)[d]
(3/3)	Zn–S1	2.346	2.370	2.328(3)
	Zn–S3	2.417	2.395	2.335(3)
	C1–S2	1.783	1.732	1.70(1)
	C1–S3	1.721	1.705	1.68(1)
	S1–S2	2.088	2.063	2.007(3)
	C1–R1	1.354[c]	1.476[d]	1.46(1)[d]
	Zn-S3-C1	101.9	102.4	104.3(3)
	Zn-S1-S2	99.3	100.4	102.1(1)
	S1-S2-C1	109.7	111.4	111.4(3)
	S1-Zn-S2	96.1	96.9	95.8(1)
	Zn1-S1-S2-R1	24.3[c]	− 10.9[d]	− 4.2[d]
	S3-R1-C2-C3	9.7[c]	39.9[d]	38.8[d]

[a] Average value for Zn1–S1 and Zn1–S2. [b] Average value for C1–S1 and C1–S2. [c] R1 = N1. [d] R1 = C1.

The calculated structures of (2/2) **1** and (3/3) **1** are depicted in Figure 1. The tetrahedrally coordinated structure calculated for (2/2) **1** could not be compared to an X-ray crystal structure, since in the crystal lattice **1** is dinuclear.[21] In this case the applied methodology was nevertheless validated by calculating the structure of the analogous anionic complex tris(dimethyldithiocarbamato)zincate, [Zn(dmtc)₃]⁻. An X-ray crystal structure is available of this complex.[22] Again good agreement was obtained between calculated and observed bond lengths and angles, demonstrating that the density functional methodology provides rapid access to reliable molecular information about zinc–thiolate complexes. Finally, the inferred structure of (3/3) **1** was obtained by insertion of two sulfur atoms in the Zn–S bond of (2/2) **1**, and optimization.

One striking feature about (3/3) **1** is the puckering of the five-membered zinc–trithiocarbamate rings. The additional sulfur atoms are slightly below, and the zinc ion substantially above the chelate plane, defined by the original dithiocarbamate ligand ($\tau_{\text{Zn1-S1-S2-C1}} = 25°$). In contrast, for (3/3) **2** the five-
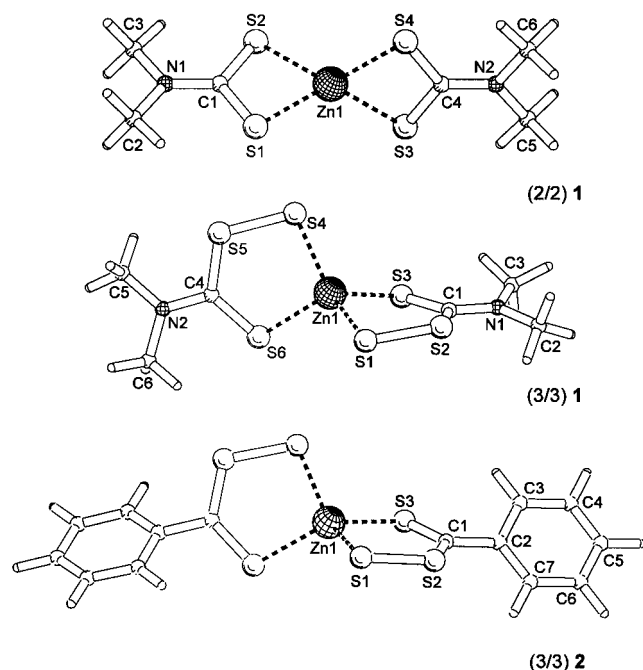
Figure 1. DF-calculated structure of (2/2) **1** and (3/3) **1**, and X-ray crystal structure of (3/3) **2**.

membered chelate ring is relatively planar ($\tau_{Zn1\text{-}S1\text{-}S2\text{-}C1} = -11°$). Another feature is that, upon going from (2/2) **2** to (3/3) **2**, the aromatic ring rotates out of the plane with the chelate ring to as much as 38°. In (3/3) **1**, on the other hand, the orientation of nitrogen atoms is trigonal planar, just as for (2/2) **1**, and the rotation relative to the chelate ring is only 8°. This implies that in (3/3) **1** π donation by the substituent NMe$_2$ is stronger than by the phenyl substituent in (3/3) **2**. This results in somewhat longer C–S distances for (3/3) **1** than for (3/3) **2**. Nevertheless, the most important outcome of the calculations is the substantial overall similarity between the optimized structures of the sulfur-rich complexes (3/3) **1** and (3/3) **2**. Thus, from the structural data no evidence is obtained that indicates that sulfuration of bis(dimethyldithiocarbamato)zinc(II) would be less favorable than sulfuration of bis(phenyldithiolato)zinc(II).

Instead of symmetrical sulfur insertion, leading to (3/3) **1** or **2**, two sulfur atoms may also be inserted in the same dithiocarbamate ligand. This is depicted for **1** in Figure 2, but was also calculated for **2**. In (2/4) **1** the sulfur atoms are inserted on the same side of the ligand, whereas in (2/4′) **1**, the two atoms are inserted on opposite sides of the ligand. Finally, Figure 2 shows the structure of (4/4) **1**, in which four sulfur atoms are inserted symmetrically. The geometries of the complexes (2/3) **1** and (3/4) **1** were also optimized, yet their structures are very similar to those presented above and are therefore not discussed here.

The geometrical changes brought about by sulfuration are quite small. This is evident when (2/2), (3/3) and (4/4) **1** are compared (Table 2). It is observed that one thione C–S bond shortens from 1.754 Å in dithiocarbamate, through 1.721 Å, and finally to 1.707 Å in the tetrathiocarbamate ligand, that is it attains slightly more double-bonded character. At the same time the other C–S bond becomes more single-bonded,
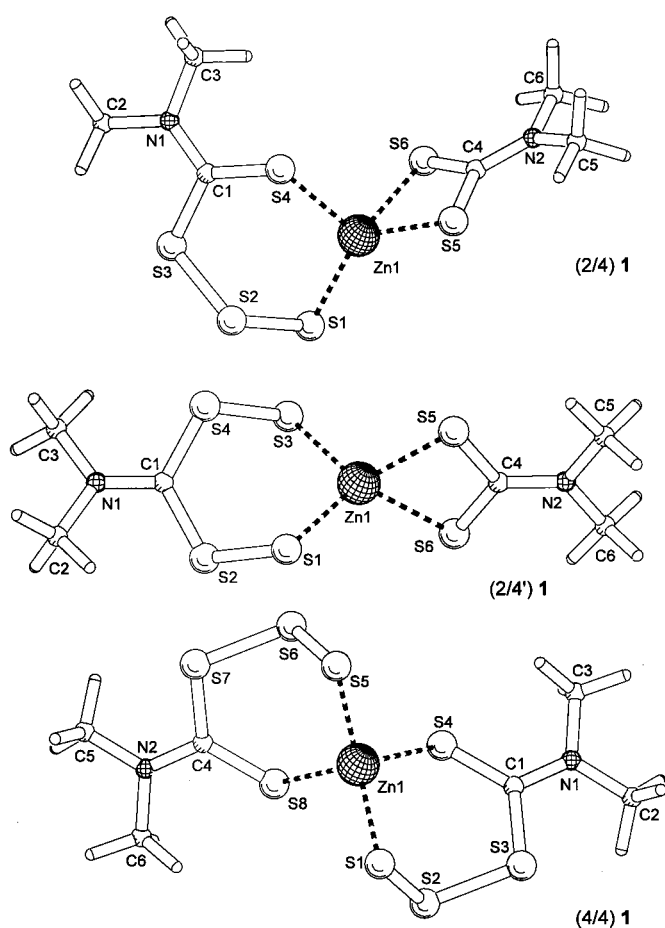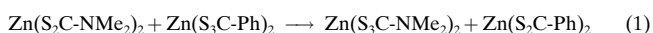

Figure 2. DF-calculated structures of (2/4) **1**, (2/4′) **1** and (4/4) **1**.

Table 2. Selected bond lengths [Å] of thiocarbamato complexes of **1**.

Complex	Zn–S=	Zn–S-S	S=C	S–C
(2/2)	2.400	–	1.754	1.754
(3/3)	2.417	2.346	1.721	1.783
(4/4)	2.524	2.320	1.707	1.813

increasing slightly to 1.783 Å in the trithiocarbamate and to 1.813 Å in the tetrathiocarbamate. The Zn–thione bond lengthens from 2.400 Å over 2.417 Å to 2.524 Å. Finally, the extra sulfur atoms become more firmly bound, as reflected by the distances of 2.400, 2.346 and 2.320 Å, respectively.

Calculation of sulfuration energies: By calculating the energies of the optimized structures, it is possible to predict the energy difference for sulfuration of the various complexes. Such sulfuration energies may be expressed as isodesmic reactions,[23] which yields very accurate reaction enthalpies because the number of bonds of each formal type is retained. Equation 1 depicts isodesmic sulfur transfer from (3/3) **2** to (2/2) **1**. For this sulfur-exchange reaction an energy difference of only 58.6 kJ mol^{-1} was calculated. Thus, insertion of two sulfur atoms in (2/2) **1** is just slightly less favorable than insertion in (2/2) **2**, implying that this reaction should be practically feasible.

$$\text{Zn}(\text{S}_2\text{C-NMe}_2)_2 + \text{Zn}(\text{S}_3\text{C-Ph})_2 \longrightarrow \text{Zn}(\text{S}_3\text{C-NMe}_2)_2 + \text{Zn}(\text{S}_2\text{C-Ph})_2 \quad (1)$$
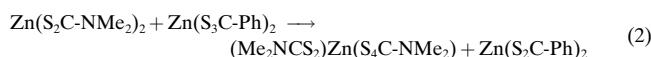
The sulfuration energies for the various polythio complexes may also be expressed relative to the energy of the unsulfurated complex and the ground-state energy of the sulfur atoms.[24] The values for sulfuration of **1** and **2** are listed in Table 3.

Entry	Reactants	Products	**1**	**2**
1	(2/2) + S	(2/3)	− 246.7	–
2	(2/3) + S	(3/3)	− 247.4	–
3	(2/2) + 2 S	(3/3)	− 494.1	− 552.7
4	(2/2) + 2 S	(2/4)	− 503.7	− 500.4
5	(2/2) + 2 S	(2/4′)	− 456.1	–
6	(3/3) + S	(3/4)	− 248.0	–
7	(3/4) + S	(4/4)	− 263.3	–
8	(3/3) + 2 S	(4/4)	− 511.3	− 466.8
9	(2/2) + 4 S	(4/4)	− 1005.4	− 1019.5

The observed[20] insertion of two sulfur atoms into (2/2) **2**, which yields (3/3) **2**, is calculated to be exothermic by 552.7 kJ mol⁻¹. The reaction of interest, that is sulfur insertion into **1** (Table 3, entry 3) is slightly less exothermic, namely by 494.1 kJ mol⁻¹.

As expected, insertion of only one sulfur atom into **1** provides just half the energy, 246.7 kJ mol⁻¹ and 247.4 kJ mol⁻¹, respectively, upon going from (2/2) **1** via (2/3) **1** to (3/3) **1**. Table 2 shows that when the second sulfur atom is inserted in the ring already containing an additional sulfur atom (resulting in the nonsymmetrical complex (2/4) **1**, shown in Figure 2), the energy gain is 257.0 kJ mol⁻¹, totalling to 503.7 kJ mol⁻¹ for nonsymmetric insertion of two sulfur atoms into one zinc–dithiocarbamate ring (entry 4). This energy gain implies that (2/4) **1** is energetically favored over (3/3) **1** by about 10 kJ mol⁻¹. Thus, when Equation (1) is reformulated into Equation (2), the energy difference for sulfur exchange reduces to 49.0 kJ mol⁻¹.

$$Zn(S_2C\text{-}NMe_2)_2 + Zn(S_3C\text{-}Ph)_2 \longrightarrow$$
$$(Me_2NCS_2)Zn(S_4C\text{-}NMe_2) + Zn(S_2C\text{-}Ph)_2 \qquad (2)$$

In contrast, for **2** the symmetrical (3/3) complex is favored over the (2/4) complex by 52.3 kJ mol⁻¹, which is in agreement with the fact that (3/3) **2** is found experimentally. This striking difference between complexes that are otherwise so similar may in fact be related to the larger participation of the NMe₂ substituent of **1** in the π-bonding system of the sulfur atoms, compared to the phenyl group in **2**.

Table 3 also shows that formation (2/4′) **1** is relatively unfavorable, but, interestingly, that insertion of two additional sulfur atoms in (2/4) **1**, furnishing (4/4) **1**, is energetically more exothermic than insertion of the first two sulfur atoms. This implies that if sulfuration of **1** with two sulfur atoms would occur, perpetuating sulfuration to (4/4) **1** would be quite likely. In contrast, the sulfuration energy of **2** decreases when going from (2/2) via (3/3) to (4/4) from 552.7 kJ mol⁻¹ to 466.8 kJ mol⁻¹, respectively. However, incorporation of four sulfur atoms into **2** still yields about 15 kJ mol⁻¹ more energy than incorporation into **1**.

The theoretically predicted energies for sulfuration of **1** and **2** are quite large, and have values of about − 250 kJ mol⁻¹ per sulfur atom. However, in practice the required sulfur atoms are derived from octatomic elemental sulfur, which has to be broken up first. This involves a substantial amount of endothermic energy too. The calculated atomization energy values of S_8 lie in the same order of magnitude as the predicted sulfuration energies. It should be remembered, however, that sulfur vulcanization is usually performed at high temperatures, which may furnish part of the energy required to break up the sulfur ring.

The important outcome is that the theoretical data indicate that a (3/3) or a (2/4) tetrathiocarbamatozinc(II) complex has an energy comparable to that of the bis(trithiobenzoato)-zinc(II) complexes. The latter are stable compounds at ambient temperature.[11, 12] As a consequence the sulfuration energy of **1** will be quite balanced, or slightly endothermic, furnishing evidence that **1** is likely to be sulfurated in the presence of elemental sulfur, and especially at elevated temperatures, for example during vulcanization. This is endorsed by the observation that the solubility of elemental sulfur in benzene increases proportionally with the amount of **1** added,[25] which may indeed be explained by incorporation of sulfur in the zinc–dithiocarbamate ring. Interestingly, and hitherto unnoticed, the density functional calculations point out that incorporation of more than two sulfur atoms into **2** would be feasible, whereas insertion of two additional sulfur atoms into (2/2) **1** is energetically as likely as insertion of the first two. It is this characteristic which may even explain why **1** is so effective as vulcanization catalyst.

LDI-MS on zinc–dithiocarbamate/sulfur mixtures: The outcome of the calculations provided the stimulus to continue our search for experimental techniques that could confirm the theoretical predictions regarding involvement of polythiocarbamatozinc(II) catalysts. In view of the apparent instability of polythiocarbamatozinc complexes, efforts were directed at mass-spectrometric techniques. These deal with isolated complexes in vacuum, which would prevent undesired transfer or loss of the additional sulfur atoms. Unfortunately, direct heating probe-MS, in which a sample of **1** mixed with sulfur was heated to vulcanization temperatures (140 °C) was unsuccessful. At these temperatures no zinc-containing species were shown to evaporate from the probe. Heating the probe from room temperature up to 350 °C was equally unsuccessful as elemental sulfur evaporated completely at the low pressures required in the probe chamber, prior to reaching a temperature where **1** desorbs. Thus it appeared necessary to activate either elemental sulfur or **1**, whilst maintaining a mixture at the same time. As heat activation was excluded, the principles of (matrix-assisted) laser-desorption ionization (MA)LDI-MS proved to be extremely useful. This technique uses laser excitation to desorb and ionize sample molecules, in an indirect way,[26] after which they desorb from the probe and may be detected.

LDI-MS in positive-ion mode of a mixture of bis(dimethyldithiocarbamato)zinc(II), Zn(dmtc)₂, and elemental sulfur produces a multitude of signals. Part of the spectrum in the positive-ion mode is depicted in Figure 3.
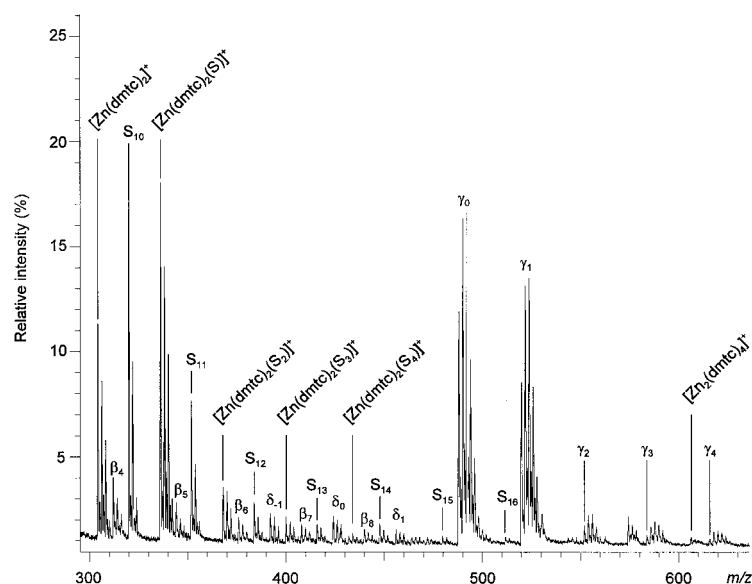
Figure 3. Summed LDI-ToF mass spectrum of a mixture of **1** and elemental sulfur ($\beta_x = [Zn\text{-}S_x\text{-}dmtc]^+$; $\gamma_x = [Zn_2(dmtc)_3(S_x)]^+$; $\delta_x = [Zn(dmtc)_3(S)_x]^+$).

The low-mass region of the spectrum (not shown) displays a variety of ions derived from elemental sulfur, that is S_2^+ up to S_8^+. It is believed that these ions result from direct ionization of (fragments of) elemental sulfur. Alternatively such ions may combine with nonionized sulfur. This would explain the ions S_9^+ up to S_{16}^+, which can be observed in the high-mass part of the MS spectrum. However, and more important for the current investigation, the sulfur ions may also react with **1** (prior to desorption and/or time-of-flight detection), which would account for the multitude of zinc-derived ions observed in the spectrum. Indeed this appears to be the case, as when no elemental sulfur is added, no positive LDI mass spectrum can be obtained for **1**. Thus sulfur acts as a pseudo-MALDI matrix and provides indirect ionization of the zinc complex. In the present study this phenomenon proved to be essential.

The zinc ions observed in Figure 3 may be divided in three subsets, and are listed together with their assignment in Table 4. The first and most relevant subset commences with signals at $m/z = 304$, 306, and 308 Da, the isotope pattern of intact $[Zn(dmtc)_2]^+$. Then, at repeating mass increments of 32 Da, and with decreasing intensities, corresponding ions are detected indicating incorporation of one up to four additional sulfur atoms.

Table 4. Assignment of zinc-derived signals in the LDI-MS spectrum of **1** and sulfur.

m/z	Desig-nation	Assignment	m/z	Desig-nation	Assignment
304.3	–	$[Zn(dmtc)_2]^+$	432.1	–	$[Zn(dmtc)_2(S_4)]^+$
312.0	β_4	$[Zn\text{-}S_4\text{-}dmtc]^+$	440.1	β_8	$[Zn\text{-}S_8\text{-}dmtc]^+$
336.2	–	$[Zn(dmtc)_2(S)]^+$	456.1	δ_1	$[Zn(dmtc)_3(S)]^+$
344.1	β_5	$[Zn\text{-}S_5\text{-}dmtc]^+$	488.0	γ_0	$[Zn_2(dmtc)_3]^+$
368.1	–	$[Zn(dmtc)_2(S_2)]^+$	520.1	γ_1	$[Zn_2(dmtc)_3(S)]^+$
376.0	β_6	$[Zn\text{-}S_6\text{-}dmtc]^+$	552.0	γ_2	$[Zn_2(dmtc)_3(S_2)]^+$
392.1	δ_{-1}	$[Zn(dmtc)_2(SCNMe_2)]^+$	583.8	γ_3	$[Zn_2(dmtc)_3(S_3)]^+$
400.0	–	$[Zn(dmtc)_2(S_3)]^+$	607.4	–	$[Zn_2(dmtc)_4]^+$
407.9	β_7	$[Zn\text{-}S_7\text{-}dmtc]^+$	615.8	γ_4	$[Zn_2(dmtc)_3(S_4)]^+$
424.0	δ_0	$[Zn(dmtc)_3]^+$			

These results support the above-mentioned density functional calculations, which indicate that it is energetically feasible to incorporate more than one sulfur atom into the zinc–dithiocarbamate chelate ring (that is, more than two per complex). However, no statement can be made about the actual structure, for example (3/3) or (2/4) **1** for a disulfurated zinc complex. The (additional) involvement of metallasulfur rings as reported,[13] for example, for $Os_2(S_5)(S_3CNMe_2)$-$(S_2CNMe_2)_3$ is considered less likely. It is clear from the MS spectra that the polythiocarbamato-zinc(II) complexes display no preference for one particular number of sulfur atoms, which would obviously be required for discrete metallasulfur ring formation. Instead, the decreasing intensity with increasing number of sulfur atoms might point to a statistical phenomenon, in which the favorable enthalpy of sulfur insertion is offset by unfavorable entropy. However, this conclusion should be handled with care due to the unknown ionization efficiencies of these species.

The second subset also corroborates that **1** is able to incorporate more than one sulfur atom in the zinc–dithiocarbamate ring. This subset (indicated with β) commences with a large (relative intensity 85%) signal at $m/z = 186$ Da (not shown in Figure 3), which can be attributed to [Zn-dmtc]$^+$ in view of the zinc isotope pattern. Again, at repeating mass increments of 32 Da, corresponding ions show that up to eight sulfur atoms are incorporated. The ions that contain more sulfur atoms have successively lower intensities, with the exception of [Zn-S_2-dmtc]$^+$, of which the intensity is two–three times higher than that of the neighboring [Zn-S-dmtc]$^+$ and [Zn-S_3-dmtc]$^+$ ions. This may be associated with the additional stability that arises from the involvement of a six-membered ring (that is, as in (4/4) **1** in Figure 2).

The third subset of species (γ) is observed at m/z 488 and is characterized by the isotope pattern of a Zn_2 compound. In the crystal lattice, **1** is indeed dinuclear.[21] The ion with m/z 488 must be $[Zn_2(dmtc)_3]^+$, that is the dimer minus one dmtc group. Again incorporation of up to four additional sulfur atoms is evident ($m/z = 520$, 552, 584, and 616). The ion of the parent compound, $[Zn_2(dmtc)_4]^+$ ($m/z = 608$), can hardly be discerned.

Smaller zinc-derived signals at $m/z = 392$, 424, and 456 Da are assigned to $[Zn(dmtc)_2(SCNMe_2)]^+$, $[Zn(dmtc)_3]^+$, and $[Zn(dmtc)_3(S)]^+$ (designated δ). The low-mass region further-more displays various fragments of complexes, such as a signal at $m/z = 152$ (relative intensity 56%), which can be attributed to $[Me_2NCS_3]^+$.

Formation of polythiocarbamatozinc complexes is not restricted to **1**. The LDI-MS spectrum of the ethyl-derivative of **1**, bis(diethyldithiocarbamato)zinc(II) was also measured, and displayed similar ions. This indicates, not unexpectedly, that sulfur incorporation is a general feature of the class of zinc–dithiocarbamates.

Hitherto only zinc-dithio acids have been observed that were enriched with up to two sulfur atoms. Now LDI-MS provides the first experimental evidence for the existence of

polythiocarbamatozinc complexes. These measurements confirm the outcome of the density functional calculations; the formation of disulfurated dithiocarbamatozinc complexes is possible, but larger numbers of sulfur atoms may be incorporated in the zinc–dithiocarbamate chelate ring as well.

Conclusion

The first density functional study in the field of sulfur vulcanization has revealed that polythiocarbamatozinc complexes may indeed be involved as catalytic intermediates in the vulcanization cascade. It has been calculated that their formation energy is comparable to that of bis(phenyltrithiolato)zinc(II), an experimentally observed sulfurated zinc complex. This theoretical prediction is confirmed by laser-desorption ionization mass-spectrometric measurements, which prove the presence of the inferred bisulfurated zinc(II) complexes. Moreover, the MS data also display the formation of polythiocarbamato complexes with more than one sulfur atom inserted in the zinc–dithiocarbamate ring, which had been predicted by the density functional calculations. The combined theoretical and mass-spectrometric evidence constitutes the first direct proof for the existence of these hitherto undetected polythiocarbamatozinc complexes.

Experimental Section

Density functional calculations: The calculations were carried out using the Amsterdam-Density-Functional (ADF) programme developed by Baerends et al.[27] The MOs were expanded in an uncontracted set of Slater type orbitals (STOs) containing diffuse functions. The basis sets of the main-group atoms are of double-ζ quality and have been augmented with one set of polarisation functions on each element (2p on H, 3d on C, N and S).[28, 29] The zinc basis set is of triple-ζ quality and has been augmented with a 4p polarisation function. The 1s core shell of carbon, nitrogen and the 1s2s2p core shells of zinc and sulfur were treated by the frozen-core (FC) approximation.[30] An auxiliary set of s, p, d, f and g STOs, centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.[31] The numerical integration was done using the scheme developed by te Velde et al.[32] All calculations were performed at the NL-SCF level, using the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrisation[33] with nonlocal corrections for exchange (Becke88)[34] and correlation (Perdew86).[35] Geometries were optimized by using the analytical gradient method implemented by Versluis[36] and Ziegler.[37]

LDI-MS: (Matrix-assisted) laser-desorption ionisation time-of-flight mass spectrometry, (MA)LDI-ToF-MS, was performed on a Bruker Biflex II using a nitrogen laser at 337 nm, an accelerating voltage of 19.5 kV, a reflector voltage of 20 kV and an extraction pulse height of 5.5 kV with a delay time of 400 ns with respect to the laser pulse. The mass spectra obtained for 110 shots were summed. Bis(dimethyldithiocarbamato)zinc(II) **1** (97%, Aldrich) and bis(diethyldithiocarbamato)zinc(II) (98%, Aldrich) were recrystallized from chloroform and mixed with two molar equivalents of elemental sulfur (S_8). Samples were suspended in acetone and 0.5 μL spots were pipetted on the target.

[1] P. J. Nieuwenhuizen, J. Reedijk, M. van Duin, W. J. McGill, *Rubber Chem. Technol. Rubber Rev.* **1997**, *70*, 368.
[2] L. Bateman, C. G. Moore, M. Porter, B. Saville in *The Chemistry and Physics of Rubber-like Substances* (Ed.: L. Bateman), Maclaren & Sons Ltd., London, **1963**, pp. 449.
[3] An alternative class of zinc(II) catalysts for vulcanization are the bis(mercaptobenzothiazolato)zinc(II) complexes. They are likely to form similar polythio complexes.
[4] C. W. Bedford, L. B. Sebrell, *Ind. Eng. Chem.* **1922**, *14*, 25.
[5] W. Scott, C. W. Bedford, *Ind. Eng. Chem.* **1921**, *13*, 125.
[6] M. Porter in *The Chemistry of Sulfides* (Ed.: A. V. Tobolsky), Wiley, New York, **1968**, p. 165.
[7] J. A. Brydson in *Rubber Chemistry*, Applied Science, London, **1978**, Ch. 8.
[8] R. W. Layer, *Rubber Chem. Technol.* **1992**, *65*, 211.
[9] R. W. Layer, *Rubber Chem. Technol.* **1992**, *65*, 822.
[10] P. J. Nieuwenhuizen, S. Timal, J. G. Haasnoot, A. L. Spek, J. Reedijk, *Chem. Eur. J.* **1997**, *3*, 1846.
[11] M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc. (A)* **1971**, 3191.
[12] J. P. Fackler, Jr., J. A. Fetchin, D. C. Fries, *J. Am. Chem. Soc.* **1972**, *94*, 7323.
[13] L. J. Maheu, L. H. Pignolet, *J. Am. Chem. Soc.* **1980**, *102*, 6346.
[14] H. H. Murray, W. Liwen, S. E. Sherman, M. A. Greaney, K. A. Eriksen, B. Carstensen, T. R. Halbert, E. I. Stiefel, *Inorg. Chem.* **1995**, *34*, 841.
[15] D. Craig, W. L. Davidson, A. E. Juve, I. E. Geib, *J. Polym. Sci.* **1951**, *6*, 1.
[16] M. M. Coleman, J. R. Shelton, J. L. Koenig, *Rubber Chem. Technol.* **1973**, *46*, 957.
[17] M. Geyser, W. J. McGill, *J. Appl. Polym. Sci.* **1996**, *60*, 425.
[18] T. Ziegler, *Chem. Rev.* **1991**, *91*, 651.
[19] T. Ziegler, *Can. J. Chem.* **1995**, *73*, 743.
[20] M. Bonamico, G. Dessy, V. Fares, L. Scaramuzza, *J. Chem. Soc. Dalton Trans.* **1972**, 2515.
[21] H. P. Klug, *Acta Crystallogr.* **1966**, *21*, 536.
[22] J. A. McCleverty, N. J. Morrison, N. Spencer, C. C. Ashworth, N. A. Bailey, M. R. Johnson, J. M. A. Smith, B. A. Tabbiner, C. R. Taylor, *J. C. S., Dalton* **1980**, 1945.
[23] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
[24] E. J. Baerends, V. Branchadell, M. Sodupe, *Chem. Phys. Lett.* **1997**, *265*, 481.
[25] D. Coucouvanis in *Progr. Inorg. Chem. Vol. 11* (Ed.: S. J. Lippard), Wiley, New York, **1970**, p. 233 ff.
[26] M. Karas, F. Hillenkamp, *Anal. Chem.* **1988**, *60*, 2299.
[27] C. Fonseca-Guerra, O. Visser, J. G. Snijders, G. te Velde, E. J. Baerends in *METECC-95* (Eds.: E. Clementi and C. Corongiu), Cagliari, **1995**, pp. 307.
[28] J. G. Snijders, P. Vernooijs, E. J. Baerends, Internal Report, Vrije Universteit Amsterdam, The Netherlands, **1981**.
[29] J. G. Snijders, E. J. Baerends, P. Vernooijs, *At. Nucl. Data Tables* **1982**, *99*, 84.
[30] E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41.
[31] K. Krijn, E. J. Baerends, Internal Report, Vrije Universiteit Amsterdam, The Netherlands, **1984**.
[32] E. J. Baerends, G. te Velde, *J. Comp. Phys.* **1992**, 84.
[33] S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
[34] A. D. Becke, *Phys. Rev. A.* **1988**, *38*, 3098.
[35] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[36] L. Versluis, T. Ziegler, *J. Chem. Phys.* **1988**, *322*, 88.
[37] L. Fan, L. Versluis, T. Ziegler, E. J. Baerends, W. Raveneck, *Int. J. Quantum. Chem.; Quantum. Chem. Symp.* **1988**, *S22*, 173.