DOI: 10.1002/chem.200701089

Complexation of the Vulcanization Accelerator Tetramethylthiuram Disulfide and Related Molecules with Zinc Compounds Including Zinc Oxide Clusters (Zn_4O_4)

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Abstract: Zinc chemicals are used as activators in the vulcanization of organic polymers with sulfur to produce elastic rubbers. In this work, the reactions of Zn^{2+}, $ZnMe_2$, $Zn(OMe)_2$, $Zn(OOCMe)_2$, and the heterocubane cluster Zn_4O_4 with the vulcanization accelerator tetramethylthiuram disulfide (TMTD) and with the related radicals and anions $Me_2NCS_2^{\bullet}$, $Me_2NCS_3^{\bullet}$, $Me_2NCS_2^-$, and $Me_2NCS_3^-$ have been studied by quantum chemical methods at the MP2/6-31+G(2df,p)//B3LYP/6-31+G* level of theory. More than 35 zinc complexes have been structurally characterized and the energies of formation from their components calculated for the first time. The binding energy of TMTD as a bidendate ligand increases in the order $ZnMe_2 < Zn(OOCMe)_2 < Zn(OMe)_2 < Zn_4O_4 < Zn^{2+}$. The last two zinc species also form very stable complexes with the radicals $Me_2NCS_2^{\bullet}$ and $Me_2NCS_3^{\bullet}$. Dissociation of the TMTD molecule at the S–S bond on reaction with the Zn_4O_4 cluster is predicted to be strongly exothermic, in sharp contrast to the endothermic S–S bond dissociation of the free molecule. The same holds for tetramethylthiuram trisulfide (TMTT). Surprisingly, the resulting complexes contain Zn–S as well as S–O bonds. The Zn_4O_4 nanocluster serves here as a model for bulk zinc oxide used as an activator in rubber vulcanization by sulfur. The further uptake of sulfur atoms by the various complexes from S_8 or TMTD with formation of species derived from the radical $Me_2NCS_3^{\bullet}$ or the trithiocarbamate anion $Me_2NCS_3^-$ is endothermic for mono- and dinuclear zinc dithiocarbamate (dtc) complexes such as $[Zn(dtc)_2]$ and $[Zn_2(dtc)_4]$, but exothermic in the case of polynuclear zinc oxide species containing bridging ligands as in $[Zn_4O_4(\mu\text{-}S_2CNMe_2)]$ and $[Zn_4O_4(\mu\text{-dtc})]$. Therefore, zinc oxide as a polynuclear species is predicted to promote the formation of trisulfido complexes, which are generally assumed to serve as catalysts for the transfer of sulfur atoms during rubber vulcanization. This prediction is in accord with the empirical knowledge that ZnO is a better activator in TMTD-accelerated rubber vulcanization than zinc dithiocarbamate.

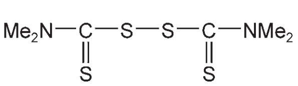
Keywords: ab initio calculations · density functional calculations · S ligands · vulcanization · zinc

Introduction

Vulcanization of unsaturated organic polymers to produce rubber is one of the key technologies of modern society. The annual production of rubber exceeds 17 million tons worldwide. In this process, natural or synthetic polyolefins react with sulfur compounds to generate sulfidic and polysulfidic cross-links between the carbon chains and give an elastic material. Tetramethylthiuram disulfide (TMTD) is one of the most important accelerators for this type of sulfur vulcanization.

Tetramethylthiuram disulfide is usually applied together with zinc oxide,[1] and the function of the latter in this con-

TMTD:



$Me_2N{-}C({=}S){-}S{-}S{-}C({=}S){-}NMe_2$

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text has recently been studied extensively.[2] The formation of zinc thiolate complexes such as bis-dithiocarbamato zinc $[Zn(S_2CNMe_2)_2]$ has been postulated, which are believed to take up more sulfur atoms from TMTD or from added elemental sulfur. The resulting polysulfido complexes are assumed to attack the natural or synthetic polyolefins with eventual generation of cross-links between the polymeric chain molecules and formation of a useful rubber material.[3] However, a detailed and realistic reaction mechanism is not known and, in particular, the fate of the oxygen atoms of ZnO in the rubber mixture is unclear. A recent review stated “even today, a clear notation of the exact mechanism in accelerated sulfur vulcanization is still absent and the role of zinc oxide or zinc complexes is rather ill-understood”.[2]

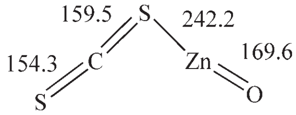
Typically, a vulcanization mixture consists of a natural or synthetic polyolefin (100), carbon black (50), elemental sulfur (0.5–4), zinc oxide (2–4), stearic acid (1–4), organic accelerators (0.5–2), and small amounts of antioxidants, retarders, and other chemicals (quantities given in parts per hundred of rubber).[4] The vulcanization reaction takes place between 130 and 160 °C. Thus, in the case of TMTD acceleration the first step may be homolytic dissociation of the TMTD molecule. Previously, we have shown that the dissociation of TMTD at the sulfur–sulfur bond requires an enthalpy of only 150 $kJ\,mol^{-1}$.[5] This rather low value is explained by resonance stabilization of the formed thiuram radicals $Me_2NCS_2^{\bullet}$, which are of C_{2v} symmetry. In other words, TMTD-accelerated vulcanization may be a radical chain reaction. However, in the presence of lithium cations TMTD dissociates with formation of lithium complexes with the thiuram radicals as ligands. The reaction enthalpy of this process is even lower than 150 $kJ\,mol^{-1}$.[5] Zinc ions as present in zinc oxide may have a similar effect.

The reaction of TMTD with bulk ZnO has been studied several times experimentally but with conflicting results.[6] The most recent and most reliable study showed that heating of a TMTD/ZnO (2/1) mixture for 16 h to 140 °C results in the following main products: zinc dithiocarbamate [Zn(dtc)$_2$], $ZnSO_4$, tetramethylthiourea $(Me_2N)_2CS$, S_8, CS_2, and COS.[7] Evidently, the products $(Me_2N)_2CS$, S_8, and CS_2 result from simple thermal decomposition of TMTD. However, formation of the dithiocarbamate (dtc) anions requires two-electron reduction of TMTD.[8,9] Since both the original mixture and conventional vulcanization mixtures do not contain any common reductant, the formation of [Zn(dtc)$_2$] in the TMTD/ZnO reaction has been explained by simultaneous oxidation of sulfur to sulfate, recovered as $ZnSO_4$.[10] Note that the actual vulcanization reaction starts at temperatures well below 100 °C, is usually performed at 140 °C, and is completed in much less than the 16 h used in the above experiments. Therefore, the question arises which are the primary products of the reaction of the Lewis base TMTD with the Lewis acidic atoms on the surface of ZnO crystals and whether these products are able to initiate the cross-linking reaction. It has long been suspected that such intermediates of unknown structure exist.[11]

In the present work, we have studied the interaction of TMTD with a number of zinc species such as Zn^{2+}, $ZnMe_2$, $Zn(OMe)_2$, $Zn(OOCMe)_2$, and the cubelike cluster Zn_4O_4 using quantum chemical methods. The last-named species is a model for the surface atoms of bulk zinc oxide since it contains only three-coordinate atoms. In the bulk material the coordination number of the zinc atoms is four. The reactions of the Zn_4O_4 cluster with a number of small molecules have already been studied by a similar theoretical approach.[12] Since vulcanization is often performed with addition of elemental sulfur, we have also investigated a number of more sulfur-rich complexes formally derived by uptake of single sulfur atoms from elemental sulfur or from TMTD.

Results and Discussion

Reference calculations: We describe below a number of hypothetical gas-phase reactions of the zinc species Zn^{2+}, $ZnMe_2$, $Zn(OMe)_2$, $Zn(OOCMe)_2$, and Zn_4O_4 with TMTD and derivatives of TMTD such as the radicals $Me_2NCS_2^{\bullet}$ and $Me_2NCS_3^{\bullet}$ and the anions $Me_2NCS_2^-$ and $Me_2NCS_3^-$. The binding energies of these S-donor ligands to the zinc species were calculated at the MP2/6-31+G(2df,p)//B3LYP/6-31+G* level of theory without any further corrections. This method was chosen on the basis of two sets of benchmark calculations with a hierarchy of basis sets, namely, 6-31+G*, 6-311+G**, 6-31+(2df,p) and 6-311+G(3df,2p). To simulate the coordination of a thione sulfur atom to a positively charged zinc center, the binding energy of the hypothetical model complex [$(CS_2)ZnO$], shown in Scheme 1, was calculated at various levels of theory. At the B3LYP/6-31+G* level of theory, this molecule is planar and has a Zn–S bond of length 242.2 pm (C_s symmetry); the bond angles are C-S-Zn 98.1, S-C-S 178.9, and S-Zn-O 175.7° (dipole moment: 9.66 D).



Scheme 1. Hypothetical model complex [$(CS_2)ZnO$].

From this geometry it can be concluded that the positively charged zinc atom (+1.16) is coordinated to one of the sulfur 3p lone pairs. The results of the various single-point energy calculations in Table 1 demonstrate that the convergence of Møller–Plesset perturbation theory, that is, HF, MP2, MP3, to MP4, is somewhat unsatisfactory. Both B3LYP and MP2 yield comparable results. Our best level of theory corresponds to the CCSD(T) method. The B3LYP method underestimates the binding energy compared to the best CCSD(T) result, while the MP2 theory overestimates it.

The homolytic dissociation energy of sulfur–sulfur bonds as in TMTD is an important factor to consider in this work.

Table 1. Calculated reaction energies [kJ mol^{-1}] for the coordination of CS_2 to monomeric ZnO in [$(CS_2)ZnO$], based on the B3LYP/6-31+G* geometry.

Level	6-31+G*	6-311+G**	6-31+G(2df,p)	6-311+G(3df,2p)
B3LYP	−51.0	−50.8	−56.3	−55.7
HF	−32.0	−30.5	−37.0	−35.3
MP2	−77.9	−70.3	−72.7	−67.9
MP3	−53.4	−43.2	−47.3	
MP4SDQ	−82.2	−73.3	−76.2	
MP4SDTQ	−99.3	−91.5	−94.0	
CCSD	−61.1	−52.4	−56.0	
CCSD(T)	−66.5	−58.2	−61.7	

To study the dependence of this energy on the theoretical method chosen, the hypothetical model disulfide HC(=S)S–SC(=S)H was calculated at several levels of theory. The data in Table 2 clearly demonstrate that the B3LYP method considerably underestimates the S–S bond dissociation energy, while the MP2 results are in closer agreement with the CCSD(T) values. The effect of the basis set is rather small in this case. In both sets of benchmark calculations, the 6-31+G(2df,p) results are close to those with the larger 6-311+G(3df,2p) basis. Hence, the affordable MP2/6-31+G-(2df,p)//B3LYP/6-31+G* level of theory was eventually chosen as a compromise for all zinc complexes examined in this work. At this level of theory, the S–S bond dissociation energy of TMTD (157 kJ mol^{-1}) is in very good agreement with the higher level G3X(MP2) value of 150 kJ mol^{-1}.[5] The absolute energies and dipole moments of all investigated species are presented in Table S1 in the Supporting Information.

Table 2. Calculated S–S bond dissociation energies [kJ mol^{-1}] of HC(=S)S–SC(=S)H at various levels of theory, based on the B3LYP/6-31+G* geometry.

Level	6-31+G*	6-311+G**	6-31+G(2df,p)	6-311+G(3df,2p)
B3LYP	150.3	147.0	165.4	165.5
HF	175.5	175.3	188.7	186.7
MP2	202.9	207.3	236.6	235.7
MP3	199.3	202.9	223.7	
MP4SDQ	198.6	201.3	225.4	
MP4SDTQ	186.9	190.0	216.3	
CCSD	197.4	200.0	223.5	
CCSD(T)	184.3	187.0	211.5	

Reactions of TMTD with Zn^{2+}: Tetraalkylthiuram disulfides $R_2NC(=S)S-SC(=S)NR_2$ are excellent bidentate ligands towards metal ions[5,13] since the thione sulfur atoms are negatively charged and act as strong Lewis basic centers.[5] Accordingly, the interaction energy of TMTD with Zn^{2+} cations is quite large [Eq. (1)].

$$Zn^{2+} + \text{TMTD} \rightarrow [\text{Zn(TMTD)}]^{2+}\ (\mathbf{1}) \qquad \Delta E = -1230.8\ \text{kJ mol}^{-1} \tag{1}$$

Due to the higher negative charge on the thione sulfur atoms, the reaction energy is much larger than in the case of the related complex between H_2S and Zn^{2+} (−525.1 kJ mol^{-1}, calculated at the B3LYP/6-311+G(d,p) level).[14] The complex cation **1** is of C_2 symmetry with ZnS bonds of length 222.4 pm and an S-Zn-S bond angle of 159.5° (Figure 1). On complex formation, the CSSC torsion angle of TMTD changes from ±88.0° in the free ligand to −120.7° in **1**, and the S–S bond length increases from 203.9 pm in TMTD to 212.2 pm in **1**. Therefore, one would expect the homolytic dissociation energy of this bond to be smaller than that in the free TMTD molecule (see below). The largest structural changes on complex formation occur at the C=S bonds, which increase in length from 165.7 pm in TMTD to 174.4 pm in **1**. The structure of **1** differs from that of the analogous complex [Li(TMTD)]$^+$ insofar as the metal atom in the latter is coordinated to three sulfur atoms,[5] while in **1** the larger zinc atom is two-coordinate.

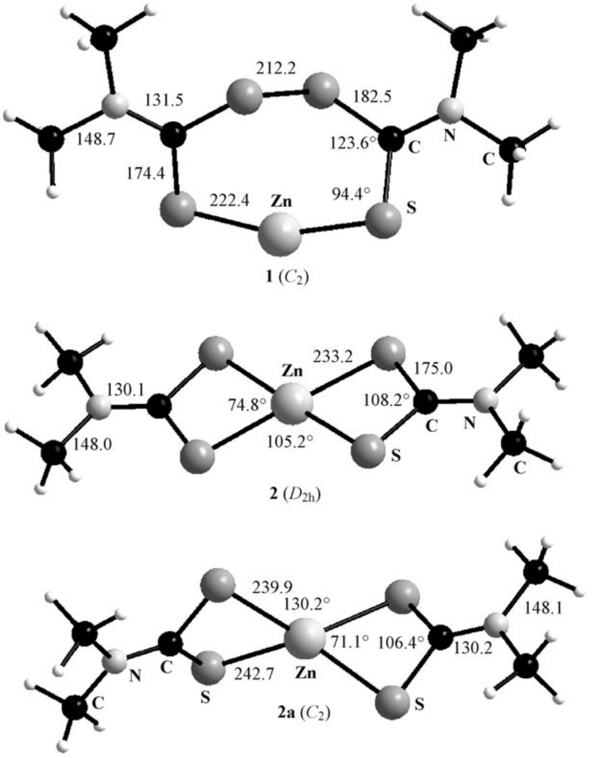


Figure 1. Structures of the complexes [Zn(TMTD)]$^{2+}$ (**1**), singlet [Zn-$(S_2CNMe_2)_2$]$^{2+}$ (**2**), and triplet [Zn$(S_2CNMe_2)_2$]$^{2+}$ (**2a**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

The energy liberated in the reaction shown in Equation (1) is substantially larger than that required for dissociation of TMTD with homolytic cleavage of the sulfur–sulfur bond, calculated at the same level of theory [Eq. (2)].

$$\text{TMTD} \rightarrow 2\,\text{Me}_2\text{NCS}_2^{\cdot} \quad \Delta E = +156.6\ \text{kJ mol}^{-1} \tag{2}$$

Therefore, the question arises whether complex **1** immediately rearranges to four-coordinate species **2** containing two thiuram radical ligands $Me_2NCS_2^{\bullet}$. Due to its large dipole moment of 5.07 D (see Table S1 in the Supporting Information) this radical should be a good ligand. The corresponding reaction is in fact strongly exothermic regardless of whether the novel complex is formed in the singlet ground state (**2**) or in the sligthly less stable triplet state (**2a**); see Equation (3).

$$\begin{aligned} &Zn^{2+} + TMTD \rightarrow [Zn(S_2CNMe_2)_2]^{2+}\ (\mathbf{2}) \\ &\Delta E = -1157.0\ kJ\,mol^{-1} \end{aligned} \tag{3}$$

The energy difference between **2** and **2a** is 22.6 kJ mol^{-1}. The structures of these two complexes are presented in Figure 1. They differ mainly by the coordination geometry at the zinc atom. The more stable species **2** is of D_{2h} symmetry with a planar ZnS_4 skeleton, while **2a**, containing a distorted tetrahedral ZnS_4 unit, is of C_2 symmetry.

The results given in Equations (1)–(3) are of considerable significance for the vulcanization process, since they show that zinc atoms bearing a sufficiently high positive charge facilitate cleavage of the S–S bond of the accelerator molecule TMTD on heating, as the isomerization reaction **1**→**2** requires only 73.8 kJ mol^{-1}, as opposed to the 156.6 kJ mol^{-1} needed to dissociate the free TMTD molecule.[5]

From the above data it follows that the addition of thiuram radicals to Zn^{2+} is strongly exothermic [Eq. (4)].

$$\begin{aligned} &Zn^{2+} + 2\,Me_2NCS_2^{\cdot} \rightarrow [Zn(S_2CNMe_2)_2]^{2+}\ (\mathbf{2}) \\ &\Delta E = -1313.5\ kJ\,mol^{-1} \end{aligned} \tag{4}$$

For comparison purposes, we also calculated the thermodynamics of the reaction of Zn^{2+} with two dimethyldithiocarbamate anions $Me_2NCS_2^-$ (dtc), derived from TMTD by two-electron reduction [Eq. (5)]. This anion is also of C_{2v} symmetry with an S–S distance of 302.8 pm and a S-C-S bond angle of only 122.5° compared to 108.1° in the $Me_2NCS_2^{\bullet}$ radical.

$$\begin{aligned} &Zn^{2+} + 2\,Me_2NCS_2^- \rightarrow [Zn(S_2CNMe_2)_2]\ (\mathbf{3}) \\ &\Delta E = -2667.7\ kJ\,mol^{-1} \end{aligned} \tag{5}$$

The enormous reaction energy liberated in the reaction shown in Equation (5) is still smaller than the lattice energy of ZnO (−4033 kJ mol^{-1}[15]). The structure of complex **3** is shown in Figure 2. The coordination at the metal atom is approximately tetrahedral, in agreement with previous DFT calculations (C_2 symmetry).[3a] However, in the solid state, zinc bis-dithiocarbamate is dimeric with two bridging and two terminal chelating $Me_2NCS_2^-$ ligands.[16] For the two terminal ligands the average observed bond lengths are Zn–S 238.1, C–S 172.4, and C–NMe$_2$ 132.5 pm,[16] in good agreement with our calculated data (Figure 2). Despite the stronger interaction of dtc anions with Zn^{2+} compared to thiuram radicals, the Zn–S bonds of **3** are longer than those in **2**.

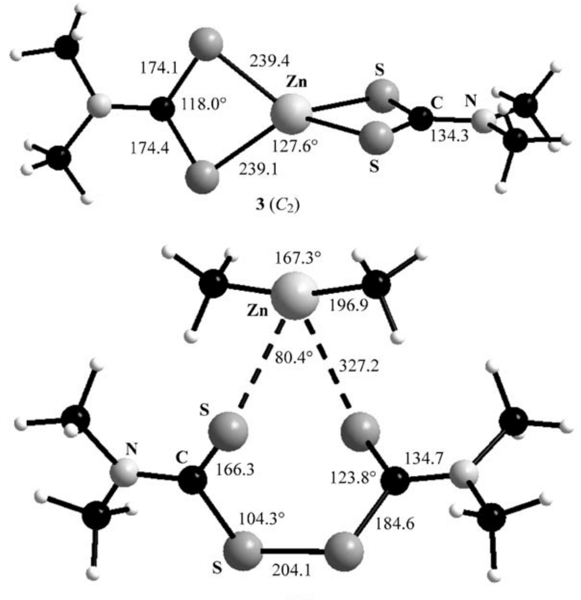


Figure 2. Structures of [Zn(dtc)$_2$] (**3**) and [Me$_2$Zn(TMTD)] (**5**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

Reaction of TMTD with dimethylzinc: TMTD is known to react with Me_2Zn at 0 °C as shown in Equation (6).[17] For the first time, we have obtained thermodynamic data of this reaction.

$$\begin{aligned} &ZnMe_2 + 2\,TMTD \rightarrow [Zn(S_2CNMe_2)_2]\ (\mathbf{3}) \\ &\qquad + 2\,Me_2NC(=S)SMe\ (\mathbf{4}) \\ &\Delta E = -364.4\ kJ\,mol^{-1} \end{aligned} \tag{6}$$

In this process, the S–S bonds of the two TMTD molecules are formally cleaved heterolytically and the resulting thiolate anions add to the formal Zn^{2+} center of $ZnMe_2$, while the sulfonium ions $Me_2NCS_2^+$ combine with the formal methyl anions of $ZnMe_2$ with formation of **4**. The hitherto-unknown structure of **4** does not show any unusual geometrical features. The symmetry is C_s and the SCSC torsion angle is 0° (atomic coordinates are given in the Supporting Information).

The first step in the reaction shown in Equation (6) is probably exothermic coordination of TMTD to $ZnMe_2$ [Eq. (7)].

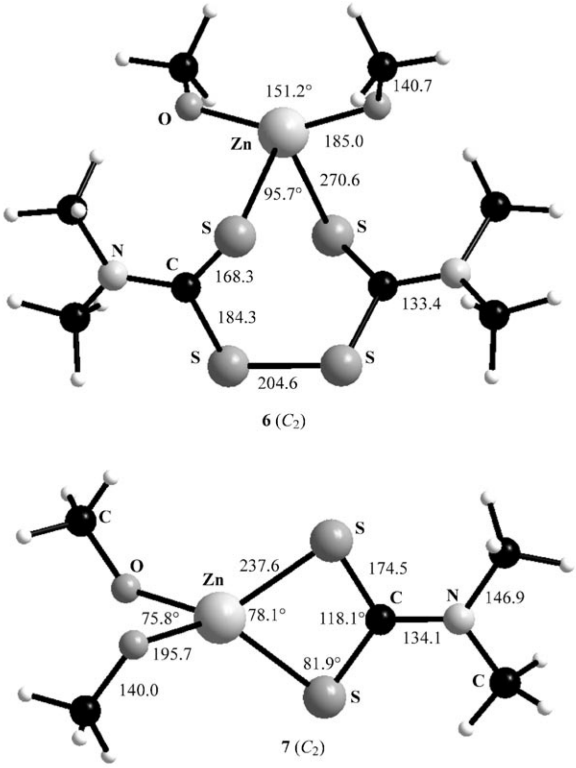
$$\begin{aligned} &ZnMe_2 + TMTD \rightarrow [ZnMe_2(TMTD)]\ (\mathbf{5}) \\ &\Delta E = -58.5\ kJ\,mol^{-1} \end{aligned} \tag{7}$$

Complex **5** is of C_2 symmetry and has two rather long Zn–S bonds of 327 pm (Figure 2). The C-Zn-C bond angle has decreased from 180° in dimethylzinc to 167.3° in **5**. Thus, the interaction can best be described as an ion–dipole attraction (NBO charge on Zn in Me_2Zn: +1.22; on the thione sulfur atoms of TMTD: −0.12). The C-S-Zn bond angles of **5** are 99.1°.

Reaction of TMTD with dimethoxyzinc: In the rubber vulcanization mixture, the added stearic acid is assumed to react on heating with zinc oxide to give zinc stearate, which in turn may interact with the accelerator molecules.[6b] For this reason, we have studied the reactions of TMTD with various Zn–O compounds to find out which type of zinc salt is powerful enough to cleave the TMTD molecule into two radicals $Me_2NCS_2^{\cdot}$. Dimethoxyzinc serves here as a first simple model species. Its donor–acceptor interaction with TMTD is more exothermic than that of $ZnMe_2$ [Eq. (8)].

$$\mathrm{Zn(OMe)_2 + TMTD \rightarrow [Zn(OMe)_2(TMTD)]}\ (\mathbf{6}) \qquad \Delta E = -127.7\ \mathrm{kJ\,mol^{-1}} \tag{8}$$

Complex **6** is of C_2 symmetry with distorted tetrahedral coordination of the zinc atom and Zn−S bonds of length 270.6 pm (Figure 3). The Zn−O bond lengths have increased from 177.0 pm in $Zn(OMe)_2$ to 185.0 pm in **6**, while the OZnO bond angle decreased simultaneously from 172.5° to 151.2° in **6**. The C-S-Zn bond angles are 93.7°. The TMTD ligand slightly changed its conformation, as can be seen from the CSSC torsion angles of ±88.0° in the free TMTD molecule and −78.5° in **6**. The energy released on coordination of TMTD to $Zn(MeO)_2$ is more than twice the reaction energy in the case of $ZnMe_2$, most probably as the result of the higher positive charge on the zinc atom. The NBO atomic charges on Zn are +1.51 in $Zn(OMe)_2$ and +1.54 in **6**.



6 (C_2)

7 (C_2)

Figure 3. Structures of $[Zn(OMe)_2(TMTD)]$ (**6**) and $[Zn(OMe)_2(S_2CNMe_2)]^{\cdot}$ (**7**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

As shown above and in our previous work,[5] the thiuram radicals produced in Equation (2) may also serve as bidentate ligands in metal complexes. To cleave a TMTD molecule homolytically on reaction with a zinc compound requires that two thiuram radicals release a considerably higher binding energy on coordination to the zinc center than TMTD itself. To predict the interaction energy for these radical ligands with a zinc atom linked to two oxygen atoms, we studied the reaction shown in Equation (9), during which zinc acquires the normal coordination number of four (see Figure 3).

$$\mathrm{Zn(OMe)_2 + Me_2NCS_2^{\cdot} \rightarrow [Zn(OMe)_2(S_2CNMe_2)]^{\cdot}}\ (\mathbf{7}) \qquad \Delta E = -57.7\ \mathrm{kJ\,mol^{-1}} \tag{9}$$

From the data in Equations (2) and (9), it follows that the reaction given in Equation (10) is slightly endothermic; in addition, it is disfavored at higher temperatures by a decrease in entropy.

$$\mathrm{2\,Zn(OMe)_2 + TMTD \rightarrow 2\,[Zn(OMe)_2(S_2CNMe_2)]^{\cdot}}\ (\mathbf{7}) \qquad \Delta E = +41.1\ \mathrm{kJ\,mol^{-1}} \tag{10}$$

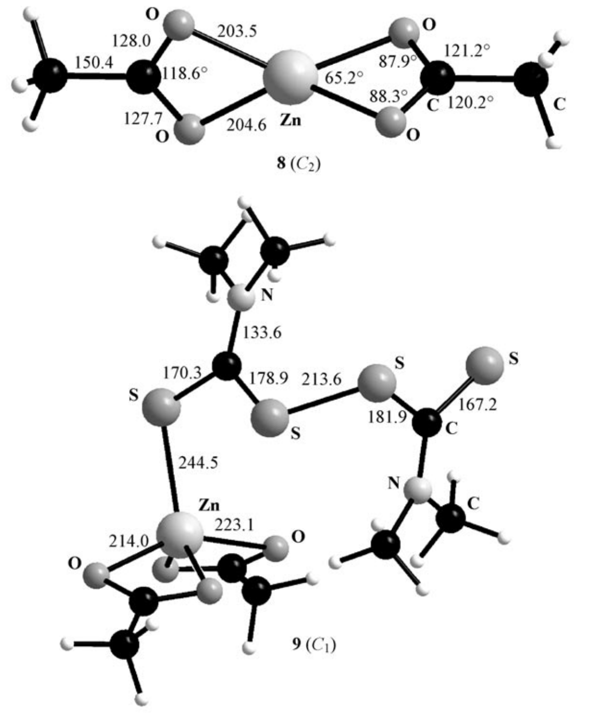
Evidently, a stronger Lewis acid than $Zn(OMe)_2$ is needed to cleave the TMTD molecule on coordination to a zinc center.

Reaction of TMTD with zinc acetate: Zinc acetate is used here as a model compound for zinc stearate, which has often been discussed as a component of rubber vulcanization mixtures.[2] The crystal and molecular structure of zinc diacetate are unknown, but the related oxo acetate $[Zn_4O(OOCMe)_6]$ has been characterized by X-ray crystallography.[18] In this structure the shortest Zn−O(ac) bond length is 197.6 pm, in good agreement with our calculations on the hypothetical mononuclear acetate $[Zn(OOCMe)_2]$ (**8**), in which the coordination number of Zn is four, with a distorted tetrahedral geometry of symmetry C_2 and an atomic charge on the Zn atom of +1.56 (Figure 4). The atoms CCZnCC are collinear. The two independent ZnO distances are 203.5 and 204.6 pm, and the O-Zn-O angle is 65.2°.

Coordination of TMTD to the acetate **8** is exothermic [Eq. (11)]. Two distinct isomers of the resulting complex $[Zn(OOCMe)_2(TMTD)]$ have been found (**9** and **9a**), with a slight preference for isomer **9** (by 2.6 kJ mol^{-1}).

$$\mathrm{[Zn(OOCMe)_2]}\ (\mathbf{8}) + \mathrm{TMTD} \rightarrow \mathrm{[Zn(OOCMe)_2(TMTD)]}\ (\mathbf{9}) \qquad \Delta E = -93.4\ \mathrm{kJ\,mol^{-1}} \tag{11}$$

Both **9** and **9a** have a quite unusual distorted trigonal-bipyramidal coordination sphere at the zinc atom (Figures 4



8 (C_2)

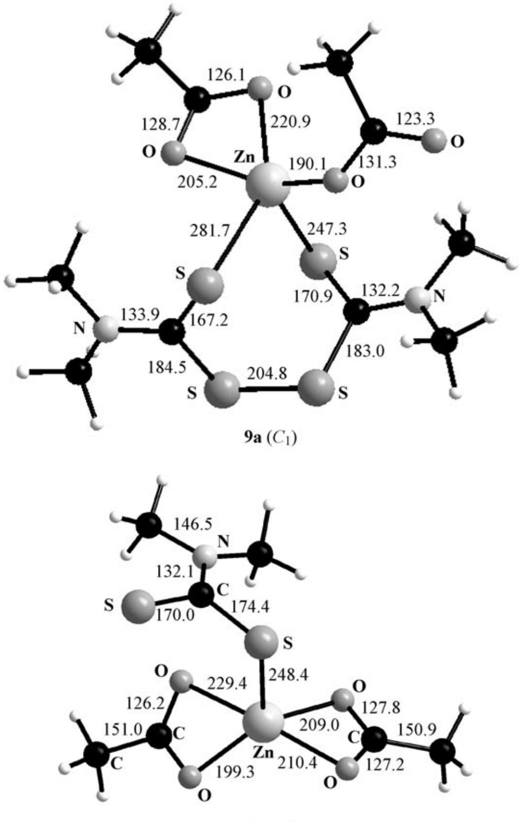
9 (C_1)

Figure 4. Structures of $[Zn(OOCMe)_2]$ (**8**) and $[Zn(OOCMe)_2(TMTD)]$ (**9**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

and 5). TMTD serves as a monodentate ligand in **9** but as a bidentate ligand in **9a**. Accordingly, both acetate anions are bidentate in **9**, while one of the acetate anions is monodentate in **9a**. We were unable to locate a local energy minimum of $[Zn(OOCMe)_2(TMTD)]$ with a six-coordinate zinc center. In the structure of **9** the Zn–O bond lengths range from 204.1 to 223.1 pm. The Zn–S distance (244.5 pm), the ZnSC bond angle (110.1°), and the CSSC torsion angle (−79.7°) all have normal values. On the other hand, the bidentate TMTD ligand in the structure of **9a** occupies two sites at the zinc atom with Zn–S distances of 247.3 pm (eq) and 281.7 pm (ax). One of the acetate anions is linked to the metal atom by just one Zn–O bond (190.1 pm), while the other ligand is bidentate but with two differing Zn–O distances of 205.2 pm (eq) and 220.9 pm (ax). Thus, the TMTD ligand has pushed one oxygen atom out of the coordination sphere of the central atom to keep the coordination number lower than six. This may be the reason for the moderate interaction energy. The TMTD ligand of **9a** has C_1 symmetry with an S–S bond length of 204.8 pm and a CSSC torsion angle of −81.7°.

Addition of a thiuram radical to zinc acetate complex **8** is also moderately exothermic [Eq. (12)].

$$[Zn(OOCMe)_2]\ (\mathbf{8}) + Me_2NCS_2^{\cdot} \rightarrow [Zn(OOCMe)_2(S_2CNMe_2)]^{\cdot}\ (\mathbf{10}) \qquad (12)$$
$$\Delta E = -57.2\ \mathrm{kJ\,mol^{-1}}$$



9a (C_1)

10 (C_1)

Figure 5. Structures of $[Zn(OOCMe)_2(TMTD)]$ (**9a**) and of the radical $[Zn(OOCMe)_2(S_2CNMe_2)]^{\cdot}$ (**10**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

As in the case of **9**, the radical enters as a monodentate ligand and the coordination number of zinc increases from four to five with a distorted square-pyramidal geometry and Zn–O bond lengths in the range of 199.3–229.4 pm in **10** (Figure 5). The torsion angle ZnSCS at the η^1 ligand is 108.6°. Due to the relatively small binding energy [Eq. (12)], the hypothetical cleavage reaction of TMTD by two molecules of the acetate **8** is predicted to be endothermic [Eq. (13)].

$$2\,[Zn(OOCMe)_2]\ (\mathbf{8}) + TMTD \rightarrow 2\,[Zn(OOCMe)_2(S_2CNMe_2)]^{\cdot}\ (\mathbf{10}) \qquad (13)$$
$$\Delta E = +42.3\ \mathrm{kJ\,mol^{-1}}$$

This result is of considerable importance since it demonstrates that zinc carboxylates are not equally active substitutes for zinc oxide as vulcanization activators. The main reason for this finding is the fourfold coordination of the zinc atoms in conjunction with the strong Zn–O bonds. The same situation is expected for di-, tri-, and tetranuclear zinc carboxylate complexes and similar species such as zinc glycerolate. Below we will show that the surface atoms of solid zinc oxide, on the other hand, can cleave TMTD easily due to their lower coordination number of three.

Reaction of TMTD with zinc oxide: To simulate the situation of the atoms on the surface of zinc oxide particles, we used a small cluster of zinc oxide, namely, the heterocubane Zn_4O_4. The coordination chemistry of similar M_4O_4 cubanes ($M = Co, Ni$) has recently been reviewed.[19] In the highly symmetrical Zn_4O_4 cluster, all zinc atoms are equivalent and coordinated to three oxygen atoms, as is expected for the surface atoms of bulk crystalline zinc oxide. This structure is a local energy minimum on the potential-energy hypersurface (PES) of Zn_4O_4.[20] The Zn_4O_4 cluster has already been successfully used to study the interaction of other vulcanization-related molecules with zinc oxide, for example, the accelerator mercaptobenzothiazole (MBT).[12] The NBO atomic charges on the zinc atoms of Zn_4O_4 are $+1.60$; the Zn−O and Zn−Zn internuclear distances are 199 and 263 pm, respectively. In the ideal tetrahedral wurtzite structure of bulk ZnO these distances are 198 and 323 pm.

On coordination of TMTD to the Zn_4O_4 molecule, two zinc atoms increase their coordination number from three to four while the cubelike cluster remains intact (Figure 6). This complexation reaction is fairly strongly exothermic [Eq. (14)].

$$\begin{aligned} &Zn_4O_4 + \mathrm{TMTD} \rightarrow [Zn_4O_4(\mathrm{TMTD})]\ (\mathbf{11}) \\ &\Delta E = -238.8\ \mathrm{kJ\,mol^{-1}} \end{aligned} \qquad (14)$$

The structure of **11** is of C_1 symmetry with Zn−S bond lengths of 242.0 and 244.3 pm and Zn−O bond lengths in the range 194.8–207.4 pm. Two zinc atoms acquire a distorted tetrahedral coordination sphere. The Zn-S-C bond angles are 91.7 and 95.9°. The conformation of the TMTD ligand with a torsion angle τ(CSSC) of $-80.5°$ is almost the same as calculated for the free molecule ($\tau = \pm 88.0°$).[5]

One might argue that the surface of commercial zinc oxide is covered by water molecules and that there are no three-coordinate zinc atoms. In fact, Zn_4O_4 clusters react exothermically with water to give the oxide hydroxide $Zn_4O_3(OH)_2$.[12] However, the interaction of TMTD with Zn_4O_4 according to Equation (14) is much stronger than the chemisorption of H_2O molecules, which liberates only $-176.7\ \mathrm{kJ\,mol^{-1}}$, calculated at the present MP2 level. Therefore, should H_2O be adsorbed on the surface of zinc oxide it is expected to be replaced by TMTD during rubber vulcanization.

As a result of the high thermodynamic stability of the complex $[Zn_4O_4(\mathrm{TMTD})]$, zinc oxide in the form of Zn_4O_4 is predicted to strip off the TMTD ligand from the carboxylate complexes **9** and **9a** discussed above [Eqs. (15) and (15a)].

$$\begin{aligned} &[Zn(OOCMe)_2(\mathrm{TMTD})]\ (\mathbf{9}) + Zn_4O_4 \\ &\quad \rightarrow [Zn_4O_4(\mathrm{TMTD})]\ (\mathbf{11}) + [Zn(OOCMe)_2]\ (\mathbf{8}) \qquad (15) \\ &\Delta E = -150.6\ \mathrm{kJ\,mol^{-1}} \end{aligned}$$

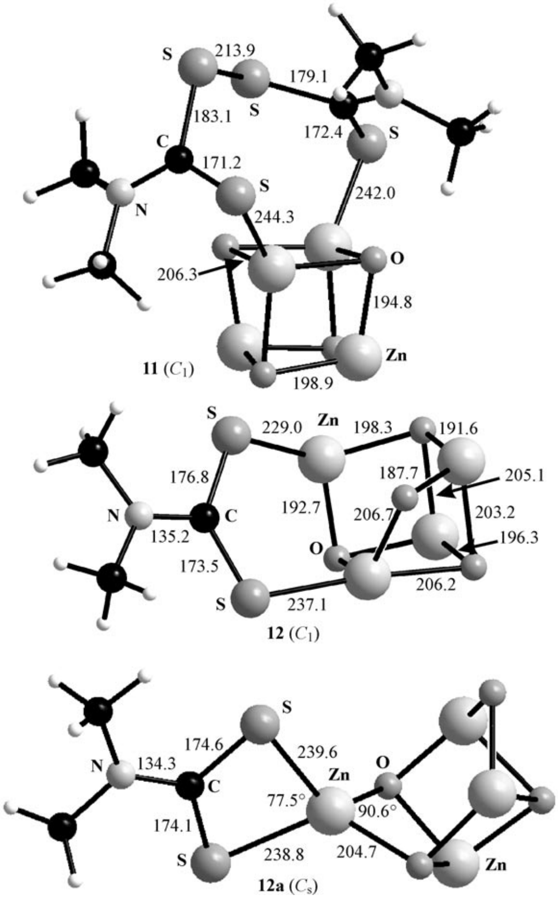


Figure 6. Structures of $[Zn_4O_4(\mathrm{TMTD})]$ (**11**), $[Zn_4O_4(S_2CNMe_2)]^{\bullet}$ (**12**), and its isomer **12a**, calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

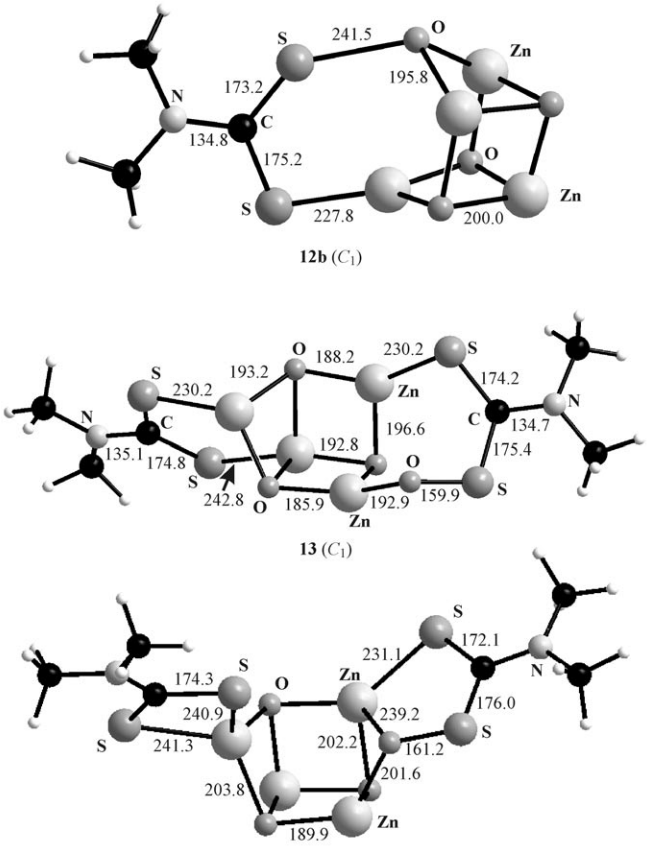
$$\begin{aligned} &[Zn(OOCMe)_2(\mathrm{TMTD})]\ (\mathbf{9a}) + Zn_4O_4 \\ &\quad \rightarrow [Zn_4O_4(\mathrm{TMTD})]\ (\mathbf{11}) + [Zn(OOCMe)_2]\ (\mathbf{8}) \qquad (15a) \\ &\Delta E = -148.0\ \mathrm{kJ\,mol^{-1}} \end{aligned}$$

The interaction between Zn_4O_4 and the radical $Me_2NCS_2^{\bullet}$ is also exothermic [Eq. (16)]. Three isomers of the corresponding adduct have been located on the PES. In the most stable form **12**, the radical binds to two zinc atoms through both sulfur atoms (Figure 6).

$$\begin{aligned} &Zn_4O_4 + Me_2NCS_2^{\bullet} \rightarrow [Zn_4O_4(\mu\text{-}S_2CNMe_2)]^{\bullet}\ (\mathbf{12}) \\ &\Delta E = -102.7\ \mathrm{kJ\,mol^{-1}} \end{aligned} \qquad (16)$$

The isomer with the $Me_2NCS_2^{\bullet}$ ligand attached to one zinc atom (**12a**) is 14.8 kJ mol^{-1} less stable than **12**. In the structures of **12** and **12a**, the Zn_4O_4 cube has opened up to a more basketlike conformation on coordination of $Me_2NCS_2^{\bullet}$ (Figure 6).

In the least stable isomer **12b** the $Me_2NCS_2^{\bullet}$ ligand is also bidentate but is connected to one zinc and one oxygen atom with a rather long S−O bond of length of 241.5 pm (Figure 7). This structure is 35.9 kJ mol^{-1} less stable than isomer **12**. Similar "expanded" ligand geometries have been



12b (C_1)

13 (C_1)

13a (C_1)

Figure 7. Structures of $[Zn_4O_4(S_2CNMe_2)]^{\bullet}$ (**12b**) and of two isomeric singlet species of composition $[Zn_4O_4(S_2CNMe_2)_2]$ (**13** and **13a**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

observed for oxidized dithiocarbamate ligands, for example, in the structure of the hexacoordinate chromium(III) complex $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$, prepared by dichromate oxidation of $[Cr(dtc)_3]$ and containing two four- and one five-membered metallacycles (R = Me, Et). The S–O bond length was determined by X-ray crystallography as 126(2) pm.[21] The S,O-bound ligand $R_2NCS_2O^-$ is also present in the dinuclear zinc complexes $[\{Zn(OS_2CNBu_2)_2\}_2]$[22] and $[\{Zn(OS_2CNEt_2)_2\}_2]$.[23] However, in the last three compounds the ligands are anions, not radicals as in **12a**.

Another difference between the two doublet structures **12a** and **12b** is the coordination number of the zinc and oxygen atoms. In **12b** all atoms of the Zn_4O_4 unit are three-coordinate, while **12a** has a four-coordinate zinc atom and, as a consequence, a two-coordinate oxygen atom. The two binding schemes observed in the structures of **12a** and **12b** are also found in the reaction products **13** and **13a** formed between Zn_4O_4 and two $Me_2NCS_2^{\bullet}$ radicals [Eqs. (17) and (17a)].

$$Zn_4O_4 + 2\,Me_2NCS_2^{\bullet} \rightarrow [Zn_4O_4(S_2CNMe_2)_2]\ (\mathbf{13}) \quad \Delta E = -560.0\ \mathrm{kJ\,mol^{-1}} \tag{17}$$

$$Zn_4O_4 + 2\,Me_2NCS_2^{\bullet} \rightarrow [Zn_4O_4(S_2CNMe_2)_2]\ (\mathbf{13a}) \quad \Delta E = -530.4\ \mathrm{kJ\,mol^{-1}} \tag{17a}$$

Unexpectedly, the ground state of $[Zn_4O_4(S_2CNMe_2)_2]$ is a singlet structure with two bridging ligands (**13**). The corresponding triplet state (**13b**) is much higher in energy (see Table S1 in the Supporting Information).

Complexes **13** and **13a** are remarkably stable and exhibit several extraordinary structural features (Figure 7). The two ligands are bound in differing ways, resembling the coordination patterns of the complexes **12a** and **12b**. The most remarkable feature, which is probably responsible for the rather high binding energies, are the sulfur–oxygen bonds of lengths 159.9 (**13**) and 161.2 pm (**13a**) involving an oxygen atom which is still linked to one (**13**) or two (**13a**) zinc atoms. The formation of this S–O bond may be the first step towards sulfate production, which has been observed on heating of TMTD with bulk ZnO (see Introduction). The formerly cubelike Zn_4O_4 cluster has opened up to a basket-like structure in both **13** and **13a**. Major differences between these two isomers are the coordination numbers at zinc and oxygen. In **13** one Zn atom is four-coordinate and three are three-coordinate, while **13a** has two four-coordinate and two three-coordinate zinc atoms.

As a result of the high stability of **13**, the isomerization reaction $[Zn_4O_4(TMTD)]$ (**11**)→$[Zn_4O_4(S_2CNMe_2)_2]$ (**13**) is exothermic, by $-164.7\ \mathrm{kJ\,mol^{-1}}$. Thus, complexes analogous to **13** and **13a** are predicted to be key intermediates in vulcanization mixtures containing ZnO and TMTD. This statement also holds for other diorganylthiuram disulfides since the homolytic S–S dissociation energy decreases with larger alkyl groups on the nitrogen atom.[5]

In addition to the singlet species **13** and **13a**, we identified four triplet isomers of composition $[Zn_4O_4(S_2CNMe_2)_2]$ (**13b–e**) which are considerably less stable than **13** (see Table S1 and Figure S1 in the Supporting Information). The relative energies of these complexes with respect to the singlet ground state **13** are 201.6 (**13b**), 326.4 (**13c**), and 324.2 $\mathrm{kJ\,mol^{-1}}$ (**13d**), respectively (we did not obtain the MP2 energy for the least stable adduct **13e**). Only in the two least stable of these structures, **13d** and **13e**, is the Zn_4O_4 cube preserved (see Figure S1 in the Supporting Information).

As a consequence of the high stability of species **13**, dissociation of TMTD on reaction with the Zn_4O_4 cluster is predicted to be more exothermic than the simple adduct formation shown in Equation (14); see Equation (18).

$$Zn_4O_4 + TMTD \rightarrow [Zn_4O_4(S_2CNMe_2)_2]\ (\text{singlet})\ (\mathbf{13}) \quad \Delta E = -403.5\ \mathrm{kJ\,mol^{-1}} \tag{18}$$

$$[Zn_4O_4(TMTD)]\ (\mathbf{11}) \rightarrow [Zn_4O_4(S_2CNMe_2)_2]\ (\text{triplet})\ (\mathbf{13b}) \quad \Delta E = 36.9\ \mathrm{kJ\,mol^{-1}} \tag{18a}$$

When TMTD is coordinated to Zn_4O_4, homolytic cleavage of the S–S bond to form two thiuram radicals [Eq. (18a)] requires 36.9 kJ mol^{-1}, considerably less than in the case of free TMTD [Eq. (2)]. We also examined the kinetic requirements of the homolytic process in **11**. For homolytic fission of the S–S single bond in **11**, one would expect a large degree of diradical character in the transition state. Therefore, unrestricted methods (i.e., UB3LYP and UMP2) were employed for the transition-state calculations. The identity of this transition state for S–S bond dissociation (**TS**) was confirmed by intrinsic reaction coordinate (IRC) calculations. We note that the UMP2 wave function of the calculated transition state is severely spin contaminated, with $\langle S^2 \rangle = 0.70$. This suggests that the UMP2 barrier may not be reliable.[24] Hence, a significantly improved barrier height was obtained by using the projected Møller–Plesset (PMP2) theory.[25] The calculated transition state **TS** is characterized by an S···S distance of 301.8 pm (Figure 8). With respect to **11**, the calculated barrier is 138.9 kJ mol^{-1}. For comparison, the energy barrier associated with the S–S bond dissociation of free TMTD is significantly higher (156.0 kJ mol^{-1}) Hence, Zn_4O_4 appears to promote the dissociation of TMTD kinetically as well as thermodynamically.

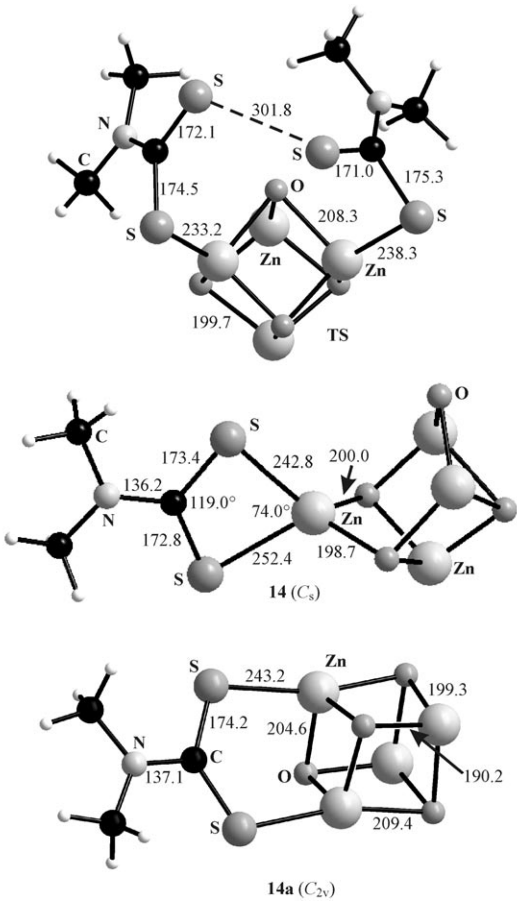


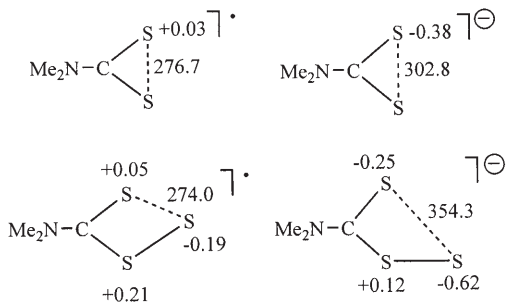
Figure 8. Structures of transition state **TS** for dissociation of TMTD coordinated to Zn_4O_4 and of the two isomeric complexes $[Zn_4O_4(dtc)]$ (**14** and **14a**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

The interaction between a dithiocarbamate anion and the Zn_4O_4 cluster [Eq. (19)] is expectedly more exothermic than the analogous reaction shown in Equation (16).

$$Zn_4O_4 + Me_2NCS_2^- \rightarrow [Zn_4O_4(S_2CNMe_2)]^-\ (\mathbf{14}) \qquad \Delta E = -261.3\ \text{kJ mol}^{-1} \tag{19}$$

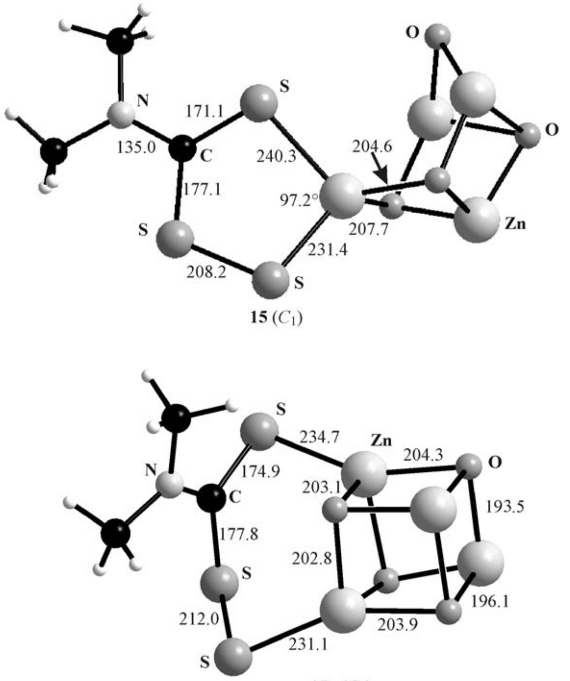
The structure of complex **14** depicted in Figure 8 is very similar to that of the neutral species **12** shown in Figure 6. An isomeric complex **14a** with the dtc anion attached to two zinc atoms is of C_{2v} symmetry with the Zn_4O_4 cluster intact (Figure 8). However, this species is slightly less stable than **14**, by 2.5 kJ mol^{-1}. This small energy difference indicates that dtc anions can thermally "walk" over the surface of ZnO particles by coordinating alternatingly to either one or two neighboring zinc atoms. However, the above-mentioned energy difference probably depends on the internuclear distance of the closest zinc atoms. Since this distance is somewhat larger in the wurtzite structure of ZnO than in our Zn_4O_4 cluster, the isomer analogous to **14** may be slightly more stable than that analogous to **14a**. On the other hand, these Zn–Zn distances are modified by the incoming ligands, as can be seen in the structures of many of the complexes described in this work.

Sulfurization reactions: Rubber vulcanization accelerated by TMTD and activated by ZnO is usually performed in the presence of elemental sulfur. Therefore, we have studied the uptake of a single sulfur atom from S_8 by various complexes resulting in ligands of the type $Me_2NCS_3^{\bullet}$ and $Me_2NCS_3^-$ (ttc). The different ligand properties may be judged by comparing the NBO atomic charges of the terminal sulfur atoms and the nonbonding distances between them (Scheme 2).



Scheme 2. NBO atomic charges on terminal S atoms and nonbonding S···S distances [pm] in neutral and anionic ligands.

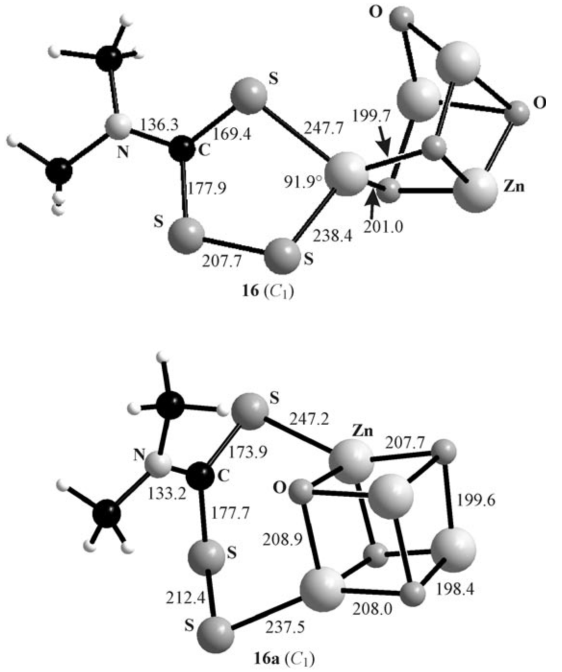
The data in Scheme 2 reveal considerable differences between the neutral and anionic species. In all cases the CS_n groups are practically planar. The higher negative charge on the terminal S atoms favors the anions over the neutral species as ligands, but the two anions differ considerably in their bite angles, that is, the distance between these terminal atoms. These bidentate ligands can form five-membered rings with a single metal atom or can be attached to two neighboring metal atoms of the Zn_4O_4 cluster to give sevenmembered rings (Figures 9 and 10). One would expect that dtc prefers the former case, while ttc would favor formation of a bridge between two metal atoms. However, our calculations show that the trithiocarbamate anion is an excellent ligand even towards a single zinc atom, while the neutral $Me_2NCS_3^{\bullet}$ radical is not, since its reaction with Zn_4O_4 is calculated to be slightly endothermic [Eqs. (20) and (21)].



15 (C_1)

15a (C_1)

Figure 9. Structures of the isomeric doublet complexes $[Zn_4O_4(S_3CNMe_2)]$ (**15** and **15a**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.



16 (C_1)

16a (C_1)

Figure 10. Structures of the isomeric singlet complexes $[Zn_4O_4(ttc)]$ (**16** and **16a**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

$$Zn_4O_4 + Me_2NCS_3^{\bullet} \rightarrow [Zn_4O_4(S_3CNMe_2)]^{\bullet}\ (\mathbf{15}) \quad \Delta E = 19.5\ \text{kJ mol}^{-1} \tag{20}$$

$$Zn_4O_4 + Me_2NCS_3^{-} \rightarrow [Zn_4O_4(S_3CNMe_2)]^{-}\ (\mathbf{16}) \quad \Delta E = -269.5\ \text{kJ mol}^{-1} \qquad (21$$

The seemingly poor ligand properties of the radical $Me_2NCS_3^{\bullet}$ towards a single metal atom may be the result of the strain in the almost planar five-membered ring of **15**, as reflected in the unfavorable torsion angle of −24.3° at the S–S bond (see Figure 9). In addition, the weak bonding interaction between the terminal S atoms in the free ligand[5] must be dissolved on complex formation. Furthermore, the basketlike structure of the Zn_4O_4 unit of **15** with one "missing" ZnO bond lowers the reaction energy. If the ring size is increased by linking the ligand to two metal centers, as in **15a** and similarly in **16a**, the thermodynamics change considerably [Eqs. (20a) and (21a)].

$$Zn_4O_4 + Me_2NCS_3^{\bullet} \rightarrow [Zn_4O_4(\mu\text{-}S_3CNMe_2)]^{\bullet}\ (\mathbf{15a}) \quad \Delta E = -171.1\ \text{kJ mol}^{-1} \tag{20a}$$

$$Zn_4O_4 + Me_2NCS_3^{-} \rightarrow [Zn_4O_4(\mu\text{-}S_3CNMe_2)]^{-}\ (\mathbf{16a}) \quad \Delta E = -399.2\ \text{kJ mol}^{-1} \tag{21a}$$

Isomer **15a** has an intact Zn_4O_4 cube and the $Me_2NCS_3^{\bullet}$ ligand bridges two metal atoms to form a chair-shaped Zn_2OCS_3 ring with an S–S torsion angle of −68.2° (Figure 9). As a free radical, species **15a** is expected to be highly reactive.

Formation of the $Me_2NCS_3^{\bullet}$ radical from $Me_2NCS_2^{\bullet}$ and $^1/_8\,S_8$ is known to be endothermic,[5] by 45.6 kJ mol^{-1} at the MP2 level used in this work. Similarly, formation of the trithiocarbamate anion (ttc) from dtc and $^1/_8\,S_8$ is calculated to be endothermic by 14.9 kJ mol^{-1} in the gas phase. At the B3LYP level, these two sulfurization reactions are even more endothermic.

The reaction of the singlet complex $[Zn(S_2CNMe_2)_2]^{2+}$ with sulfur does not produce the expected cation $[Zn(S_2CNMe_2)(S_3CNMe_2)]^{2+}$; instead the isomeric tetramethylthiuram trisulfide (TMTT) complex **17** is formed. In other words, the two ligands have combined to give TMTT [Eq. (22)].

$$[Zn(S_2CNMe_2)_2]^{2+}\ (\mathbf{2a}) + {}^1/_8\,S_8 \rightarrow [Zn(TMTT)]^{2+}\ (\mathbf{17}) \quad \Delta E = -121.7\ \text{kJ mol}^{-1} \tag{22}$$

In the triplet state the cation $[Zn(S_2CNMe_2)(S_3CNMe_2)]^{2+}$ with two separate ligands (**17a**) is a local minimum on the PES. However, **17a** is 78.4 kJ mol^{-1} less stable than **17**. The structures of **17** and **17a** are shown in Figure 11. The zinc ion is three-coordinate in **17** but four-coordinate in **17a**.

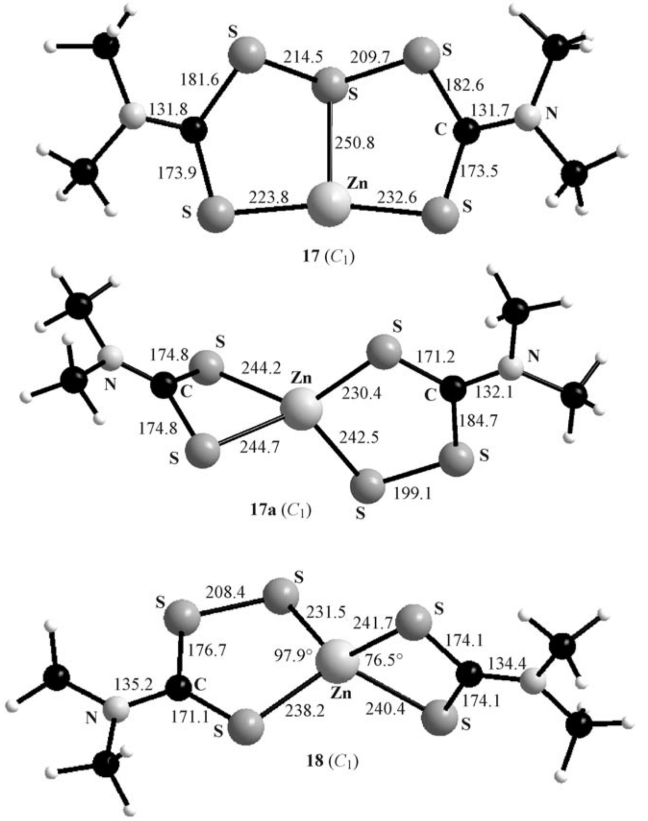


Figure 11. Structures of the two isomeric cationic complexes [Zn(S_2CNMe_2)(S_3CNMe_2)]$^{2+}$ (**17** and **17a**) and of the neutral species [Zn(S_2CNMe_2)(S_3CNMe_2)] (**18**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

The following isodesmic sulfurization reactions leading to the most stable isomers of the corresponding compositions are predicted to be partly endothermic and partly exothermic [Eqs. (23)–(26)].

$$[\mathrm{Zn(dtc)_2}]\ (\mathbf{3}) + {}^1\!/_8\,\mathrm{S_8} \rightarrow [\mathrm{Zn(dtc)(ttc)}]\ (\mathbf{18}) \qquad \Delta E = +8.8\ \mathrm{kJ\,mol^{-1}} \tag{23}$$

$$[\mathrm{Zn_4O_4(S_2CNMe_2)}]^{\cdot}\ (\mathbf{12}) + {}^1\!/_8\,\mathrm{S_8} \rightarrow [\mathrm{Zn_4O_4(S_3CNMe_2)}]^{\cdot}\ (\mathbf{15a}) \qquad \Delta E = -22.8\ \mathrm{kJ\,mol^{-1}} \tag{24}$$

$$[\mathrm{Zn_4O_4(dtc)}]^{-}\ (\mathbf{14}) + {}^1\!/_8\,\mathrm{S_8} \rightarrow [\mathrm{Zn_4O_4(ttc)}]^{-}\ (\mathbf{16a}) \qquad \Delta E = -62.9\ \mathrm{kJ\,mol^{-1}} \tag{25}$$

$$[\mathrm{Zn_4O_4(S_2CNMe_2)_2}]\ (\mathbf{13}) + {}^1\!/_8\,\mathrm{S_8} \rightarrow [\mathrm{Zn_4O_4(S_2CNMe_2)(S_3CNMe_2)}]\ (\mathbf{19}) \qquad \Delta E = +0.3\ \mathrm{kJ\,mol^{-1}} \tag{26}$$

A complex of composition [$Zn_4O_4(S_2CNMe_2)(S_3CNMe_2)$] as shown in Equation (26) may exist as several isomers. We have located four additional connectivities in singlet state (**19a–d**) and one in triplet state (**19e**). At the B3LYP/6-31+G* level, structure **19** shown in Figure 12 is the most stable form, while the other five isomers **19a–e** (see Figures S2 and S2a in the Supporting Information) are at least 32.0 kJ mol^{-1} less stable. All six isomers are characterized by a basket-shaped Zn_4O_4 cluster and two separate ligands. In the less stable isomers one ligand is always connected to one zinc atom, while the other is attached to one zinc and one oxygen atom, that is, there is always one sulfur–oxygen bond, similar to complexes **12a** and **13a** discussed above. In the most stable form **19** both ligands are bridging but in differing manners, as indicated by the formula [Zn_4O_3(μ-OS_2CNMe_2)(μ-S_3CNMe_2)]. The corresponding triplet state **19e** is 152 kJ mol^{-1} less stable than the related singlet isomer **19a** (B3LYP/6-31+G* level). Atomic coordinates of all six isomers are given in the Supporting Information.

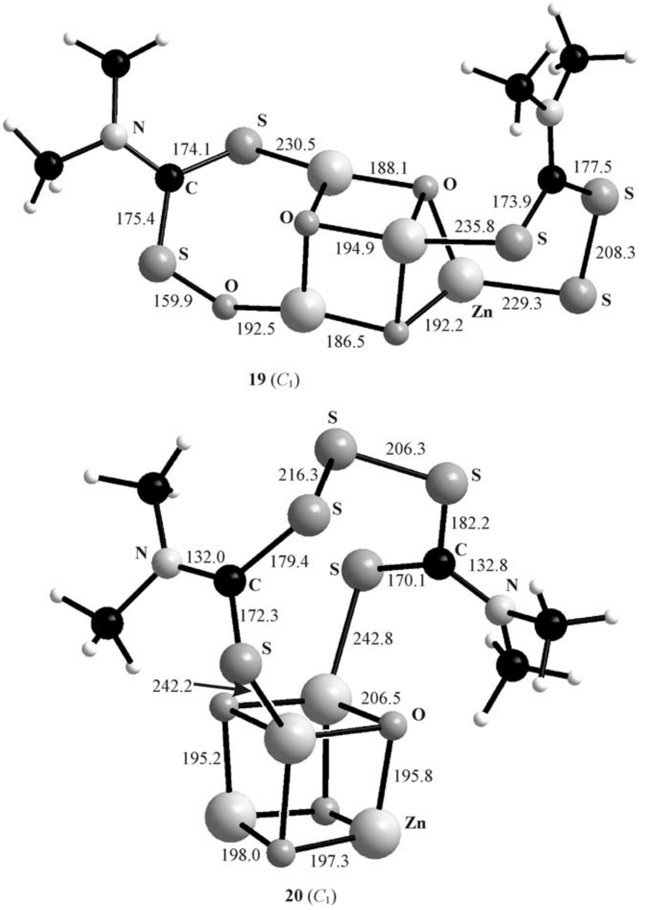


Figure 12. Structures of the isomeric complexes [$Zn_4O_4(S_2CNMe_2)(S_3CNMe_2)$] (**19**) and [$Zn_4O_4$(TMTT)] (**20**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

The hypothetical isomerization of **19** to the trisulfido complex [Zn_4O_4(TMTT)] (**20**) is strongly endothermic. Therefore, we predict that TMTT dissociates at one of the S–S bonds on contact with zinc oxide according to Equations (27) and (28).

$$\begin{array}{l} Zn_4O_4 + \text{TMTT} \rightarrow [Zn_4O_4(\text{TMTT})]\ (\mathbf{20}) \\ \Delta E = -251.3\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{27}$$

$$\begin{array}{l} [Zn_4O_4(\text{TMTT})]\ (\mathbf{20}) \rightarrow [Zn_4O_4(S_2CNMe_2)(S_3CNMe_2)]\ (\mathbf{19}) \\ \Delta E = -156.1\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{28}$$

The structure of **20** is analogous to that of $[Zn_4O_4(\text{TMTD})]$ (**11**) with CSSS torsion angles of +92.7° and −116.2° (Figure 12).

Sulfurization of dithiocarbamato complexes and their radical derivatives may not only occur by reaction with elemental sulfur but TMTD itself may function as a sulfurizing agent which then is turned into the monosulfide TMTM. The corresponding reactions are either slightly endothermic or exothermic, as the examples in Equations (29)–(31) show.

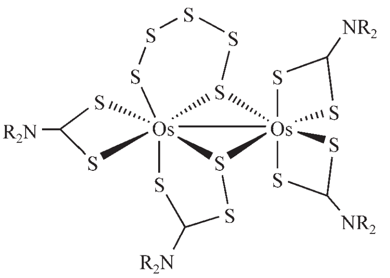
$$\begin{array}{l} [Zn(\text{dtc})_2]\ (\mathbf{3}) + \text{TMTD} \rightarrow [Zn(\text{dtc})(\text{ttc})]\ (\mathbf{18}) + \text{TMTM} \\ \Delta E = +17.1\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{29}$$

$$\begin{array}{l} [Zn_4O_4(\text{dtc})]^-\ (\mathbf{14}) + \text{TMTD} \\ \qquad \rightarrow [Zn_4O_4(\text{ttc})]^-\ (\mathbf{16a}) + \text{TMTM} \\ \Delta E = -54.6\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{30}$$

$$\begin{array}{l} [Zn_4O_4(S_2CNMe_2)_2]\ (\mathbf{13}) + \text{TMTD} \\ \rightarrow [Zn_4O_4(S_2CNMe_2)(S_3CNMe_2)]\ (\mathbf{19}) + \text{TMTM} \\ \Delta E = +8.6\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{31}$$

On the basis of the results presented in Equations (23)–(31), we predict that polynuclear trisulfido zinc complexes will be formed under the equilibrium conditions to be expected during rubber vulcanization at temperatures near 150 °C, even though the decrease in entropy makes the Gibbs energies of some of these reactions slightly more positive than the reported reaction energies. On the other hand, the formation of mononuclear trisulfido complexes such as **18** is predicted to be endothermic, and therefore such species are not expected to form in noticeable concentrations during rubber vulcanization. Zinc complexes with the sulfur-rich ligands $Me_2NCS_3^{\bullet}$ and $Me_2NCS_3^-$ have never been prepared as pure materials. The only experimental evidence for their existence comes from MALDI-MS studies. In a laser-desorption mass spectrometry experiment, mixtures of $[Zn_2(\text{dtc})_4]$ with S_8 produced positive ions which in some cases contained more than four sulfur atoms per zinc atom.[3a] However, The connectivity of these cations is unknown, and the energy of the laser may trigger even highly endothermic reactions. On the other hand, bridging trithiocarbamate (ttc) ligands have been found in the structure of a dinuclear osmium complex (Scheme 3). This species was prepared by refluxing $[Os(\text{dtc})_3]$ with S_8 in dimethylformamide.[26]

Bridging and terminal dithiocarbamato ligands are present in commercial $[Zn_2(\text{dtc})_4]$ and they may behave differently on sulfurization. Therefore, we optimized the structures of $[Zn_2(\text{dtc})_4]$ (**21**) and $[Zn_2(\text{dtc})_3(\text{ttc})]$. In the latter the ttc ligand may be bridging (**22**) or terminal (**22a**). According to the results presented above, terminal ttc ligands are less favorable thermodynamically than dtc ligands. Hence, we investigated only the complexes **21** and **22** (see Figure 13). The C_2-symmetric structure of **21** is in good agreement with the X-ray diffraction analysis of zinc bis-dithiocarbamate.[16] The dimerization reaction $2\,[Zn(\text{dtc})_2]$ (**3**)→$[Zn_2(\text{dtc})_4]$ (**21**) is predicted to be exothermic, by $-81.7\ \text{kJ}\,\text{mol}^{-1}$, but the isodesmic sulfurization of **21** by either S_8 or TMTD to give **22** is clearly endothermic [Eqs. (32) and (33)].



Scheme 3. Structure of osmium complex.

$$\begin{array}{l} [Zn_2(\text{dtc})_4]\ (\mathbf{21}) + {}^1\!/_8\, S_8 \rightarrow [Zn_2(\text{dtc})_3(\text{ttc})]\ (\mathbf{22}) \\ \Delta E = +50.9\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{32}$$

$$\begin{array}{l} [Zn_2(\text{dtc})_4]\ (\mathbf{21}) + \text{TMTD} \\ \qquad \rightarrow [Zn_2(\text{dtc})_3(\text{ttc})]\ (\mathbf{22}) + \text{TMTM} \\ \Delta E = +59.2\ \text{kJ}\,\text{mol}^{-1} \end{array} \tag{33}$$

Complex **22** is rather unsymmetrical and contains a puckered nine-membered ring with five sulfur atoms. The two terminal ZnS_2CNMe_2 units are of C_s symmetry with staggered methyl groups. In contrast to the structure of **21**, the bridging S_2CNMe_2 groups of **22** are no longer of C_s symmetry. The S–S torsion angle of **22** is 114.2°. The Zn–S bonds to the terminal ligands are considerably longer than those to the bridging ligands (av 242.7 vs. 237.1 pm). Thus, there seems to be a certain amount of strain in the four-membered ZnS_2C rings, also in the structure of **21**, as can also be seen in the S-Zn-S bond angles of 75.5° in the four-membered ring and 114.3° in the eight-membered ring. This strain probably produces the driving force for the spontaneous dimerization 2 **3**→**21**.

Conclusion

We have shown for the first time that tetramethylthiuram disulfide (TMTD) reacts with a variety of zinc species to give chelate complexes with strong Zn–S bonds. In the case of Zn^{2+} and Zn_4O_4 as a model for solid zinc oxide, the initially formed adducts are predicted to isomerize exothermically to the more stable complexes with dimethylthiuram radical ligands resulting from dissociation of TMTD at the sulfur–

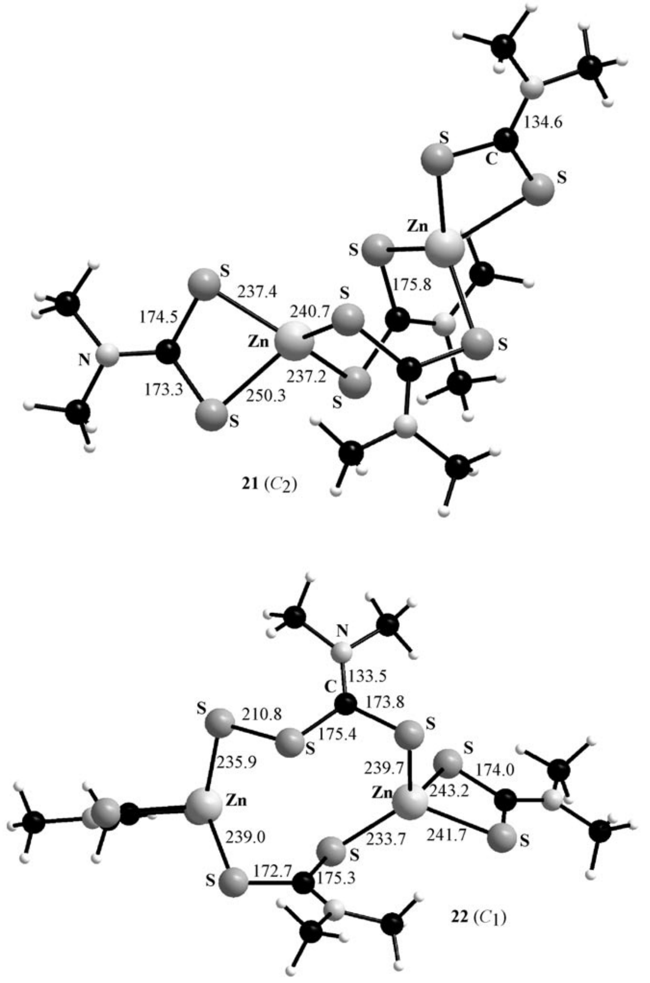


Figure 13. Structures of the dithio- and trithiocarbamato complexes $[Zn_2(dtc)_4]$ (**21**) and $[Zn_2(dtc)_3(ttc)]$ (**22**), calculated at the B3LYP/6-31+G* level. Bond lengths in picometers.

sulfur bond. Thus, for the first time it has been shown that ZnO functions not only as a reinforcing filler and a trap for acids formed during rubber vulcanization, but it also activates the TMTD accelerator by a true chemical reaction. The same holds for the corresponding trisulfide TMTT. During complex formation, the ZnO structure is partly dissolved and disintegrated by the incoming ligands, that is, Zn−O bonds are broken. In this way, more Zn centers become available for reactions with TMTD or its derivatives. Surprisingly, in some cases the ligands form additional S−O bonds with the Zn_4O_4 cluster. In the presence of elemental sulfur or an excess of TMTD as sulfur donor trithiocarbamato complexes are predicted to form, but only the corresponding polynuclear complexes derived from ZnO are formed exothermically, while the sulfurization of mono- and dinuclear zinc dithiocarbamato complexes such as $[Zn(dtc)_2]$ and $[Zn_2(dtc)_4]$ to produce $[Zn(dtc)(ttc)]$ and $[Zn_2(dtc)_3(ttc)]$, respectively, is definitely endothermic.

Computational Details

Ab initio and density functional theory (DFT) calculations were performed with the Gaussian 03 series of programs.[27] The geometries of the various complexes and their components were examined by using the hybrid functional B3LYP[28] together with the 6-31+G* basis set. The B3LYP/6-31+G* level of theory has previously been shown to reproduce the structures of similar zinc compounds very well.[29] Full geometry optimizations were carried out without any geometrical constraint. The Cartesian coordinates of the investigated complexes are given in the Supporting Information. To obtain improved energies, single-point calculations at the MP2/6-31+G(2df,p) level were performed for all species. Thus, all thermodynamic data are related to the MP2/6-31+G(2df,p)//B3LYP/6-31+G* level of theory unless noted otherwise. The reaction and binding energies are given as ΔE at the potential-energy minimum. The absolute energies and dipole moments of all investigated species are presented in Table S1 in the Supporting Information, which also contains the Cartesian coordinates of all complexes. Harmonic fundamental frequencies were calculated at the same level as the corresponding geometry to characterize stationary points as equilibrium structures, with all frequencies real. Since the rubber matrix is rather unpolar, the gas-phase reaction energies obtained in this work should provide a realistic approximation to the "real world". For all investigated molecules a charge density analysis at the B3LYP/6-31+G* level was carried out by using the natural bond orbital (NBO) approach.[30] NBO atomic charges of small molecules have been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[31] The benchmark calculations on $[(CS_2)ZnO]$ and HC(=S)S−SCH(=S) were performed with Møller–Plesset perturbation theory (MP2, MP3, and MP4) and coupled-cluster theory (CCSD and CCSD(T)).[32]

Acknowledgements

We appreciate the help of Jeffri Tan with some calculations and support by the Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen (HLRN) and the National University of Singapore.

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Received: July 16, 2007