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Interaction of Zinc Oxide Clusters with Molecules Related to the Sulfur Vulcanization of Polyolefins ("Rubber")

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Abstract: The vulcanization of rubber by sulfur is a large-scale industrial process that is only poorly understood, especially the role of zinc oxide, which is added as an activator. We used the highly symmetrical cluster Zn_4O_4 (T_d) as a model species to study the thermodynamics of the initial interaction of various vulcanization-related molecules with ZnO by DFT methods, mostly at the B3LYP/6-31+G* level. The interaction energy of Lewis bases with Zn_4O_4 increases in the following order: $CO < S_6 < C_2H_4 < C_3H_6 < Me_2S_2 <$ 1,4-$C_5H_8 <$ MeSH $< Me_2O < Me_2S < Me_3N \ll CH_3COO^-$. The corresponding binding energies range from −57 to −262 kJ mol^{-1}. However, Brønsted acids react with the Zn_4O_4 cluster with proton transfer from the ligand molecule to one of the oxygen atoms of Zn_4O_4, and these reactions are all strongly exothermic [binding energies [kJ mol^{-1}] in parentheses: H_2O (−183), MeOH (−171), H_2S (−245), MeSH (−230), C_3H_6 (−121), and CH_3COOH (−255)]. The important vulcanization accelerator mercaptobenzothiazole ($C_7H_5NS_2$, MBT) containing several donor sites reacts with the Zn_4O_4 cluster with proton transfer from the NH group to one of the oxygen atoms of ZnO, and in addition the exocyclic thiono sulfur atom and the nitrogen atom coordinate to one and the same zinc atom, resulting in a binding energy of −247 kJ mol^{-1}. A second isomer of [(MBT)Zn_4O_4] with a strong O−H···N hydrogen bond rather than a Zn−N bond is only slightly less stable (binding energy −243 kJ mol^{-1}). The NH form of free MBT is 36 kJ mol^{-1} more stable than the tautomeric SH form, while the sulfurized MBT derivative benzothiazolyl hydrodisulfide $C_7H_5NS_3$ (BtSSH) is most stable with the connectivity >CSSH.

Keywords: density functional calculations • rubber • sulfur • vulcanization • zinc

Introduction

Vulcanization of polyolefins including natural rubber by sulfur or sulfur donors is one of the most important industrial chemical processes. In 1997 global rubber production was approximately 17 million tons, and more than half of this was used for the manufacture of tires.[1] Despite its importance, the chemistry of the vulcanization process is only poorly understood, mainly due to the polymeric and insoluble nature of the product. Therefore, only a few analytical tools can be applied to elucidate the structure and composition of vulcanized rubber and to monitor the reactions taking place during the vulcanization procedure. In addition, the very complex composition of the vulcanization mixture makes it almost impossible to establish a "reaction mechanism". A complicated sequence of reactions occurs, many of which are competitive and most of which involve equilibria.[2] Typically, the vulcanization mixture consists of a natural or synthetic polyolefin (100 parts by weight), 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).[3] The function of most of these constituents is reasonably well understood,[4] but the possible reactions of zinc oxide with the other components have not been studied to such an extent that the role of this material is clear. It is known that zinc thiolate complexes also accelerate the vulcanization process,[1] and most likely such compounds are formed from zinc oxide on heating with some of the chemicals mentioned above. However, the role of solid ZnO particles must be more complex, since the vulcanization reaction markedly depends on whether bulk ZnO or mononuclear zinc complexes are used

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as activators. In fact, ZnO is generally known as the best activator for sulfur vulcanization.[4] In a recent review it has been stated that "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".[4]

Recently, there has been pressure on the rubber industry to reduce the zinc content of rubber products because of concerns that zinc chemicals may have adverse effects on the aquatic environment. About 90000 t of zinc oxide, together with smaller amounts of other zinc chemicals, are consumed annually by the rubber industry in the EU.[3] The wear of tire treads is the primary route by which zinc is released from rubber products to the environment. Therefore, there are ongoing efforts to reduce the zinc content of vulcanization mixtures without reducing the overall quality of the product. To make these efforts successful and to develop alternative activators, one first must better understand the role and the fate of ZnO during the vulcanization process.

We have investigated the initial interaction of zinc oxide with typical components of the rubber mixture using theoretical methods. To simulate the situation of the atoms on the surface of zinc oxide particles we used small zinc oxide clusters, namely, Zn_4O_4 and Zn_6O_6. These clusters are characterized by the fact that all zinc atoms are equivalent and coordinated to three oxygen atoms, as expected for the surface atoms of bulk crystalline zinc oxide. Similar $(ZnO)_n$ clusters were previously studied by DFT calculations.[5] It was shown that for $n=4$ and 6 planar rings with alternating zinc and oxygen atoms are the most stable structures. However, in these molecules the coordination number (CN) of Zn is just 2, quite different from the structure of bulk zinc oxide with CN = 4. Therefore, we feel that these global minimum structures cannot serve as models for the surface of zinc oxide particles as used in rubber vulcanization. Instead, we used the highly symmetrical clusters Zn_4O_4 (**1**) and, in some cases, Zn_6O_6 (**2**) with CN = 3 for all atoms as suitable model compounds; see Figure 1. These structures are local energy minima on the particular potential energy hypersurfaces (PES).[5] Related species are the sulfur-containing clusters Zn_4O_3S (**3**) and Zn_4S_4 (**4**) which are also shown in Figure 1. The global minimum structure of Zn_4S_4 at the B3LYP/6-311+G* level of theory is also a planar ring.[6]

A zinc oxide cluster of composition Zn_4O_4 but of C_{3v} symmetry (**1a**) was used before to study the adsorption of CO by DFT calculations.[7] However, in this cluster neither the zinc nor the oxygen atoms are all equivalent, and this results in a strongly dipolar character. Zinc sulfide clusters[6,8] and polythiocarbamatozinc(II) complexes[9] have also been studied previously by DFT calculations, and in the case of ZnS the drum-shaped cluster Zn_6S_6 is the global minimum structure for this molecular size.[8]

The adsorption of small molecules on ZnO powder and, in some cases, on ZnO single crystals has been extensively studied before, for example, in the case of alkenes, alkynes, aromatic systems, alcohols, ketones, H_2O, NH_3, H_2S, MeSH, and various intermediates of methanol synthesis from CO/CO_2 mixtures and H_2. Sometimes DFT calculations were carried out in addition. This work will be discussed below.

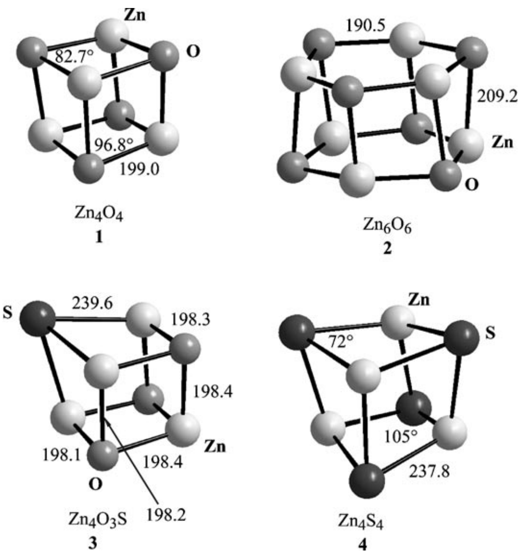


Figure 1. Structures of the clusters Zn_4O_4 (**1**), Zn_6O_6 (**2**), Zn_4O_3S (**3**), and Zn_4S_4 (**4**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian03 program package.[10] The energies of various equilibrium structures were examined at the B3LYP/6-31+G* level of theory, which has previously been shown to reproduce the structures and thermodynamics of similar zinc compounds very well.[11] Exploratory calculations were also done with the B3LYP/6-31+G(3df,p) and BP86/6-311++G* methods and at the G3X(MP2) level of theory (see below). The main purpose of the present work was to determine the order of binding energies of various substrates to small ZnO clusters. No restrictions were used in the geometry calculations. The Cartesian coordinates of the investigated complexes are given in the Supporting Information. The study of ZnO clusters larger than **2** was beyond our computational resources. For all investigated molecules a charge density analysis at the B3LYP/6-31+G* level was performed using the natural bond orbital (NBO) approach.[12] NBO atomic charges of small molecules have been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[13]

All relative energies reported in this publication are given as ΔE at the potential energy minimum. The absolute energies and dipole moments of all species calculated are given in the Supporting Information. Harmonic fundamental vibrations (unscaled) of all species were calculated at the same level as the corresponding geometry to characterize stationary points as equilibrium structures, with all frequencies real. Gibbs reaction energies were obtained from the second law of thermodynamics $\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T$, where ΔS°_T is the entropy change and $\Delta H_T = \Delta H_o + (H_T - H_o)$.

Results and Discussion

Zinc chalcogenide clusters Zn_4O_4 (1), Zn_6O_6 (2), Zn_4O_3S (3), and Zn_4S_4 (4): The four zinc chalcogenide clusters studied in this work are shown in Figure 1 with calculated bond lengths. All four clusters are of high symmetry and simulate the situation of the zinc atoms on the 0001 surface of the bulk crystalline material (local symmetry C_{3v}). In the three binary compounds all like atoms are equivalent. Thus, all the positively charged adsorption sites are identical. The NBO atomic charges on the zinc atoms are +1.60 for Zn_4O_4, +1.63 for Zn_6O_6, and +1.21 for Zn_4S_4, that is, the surface zinc atoms of ZnO and ZnS are the most electrophilic centers in the whole vulcanization mixture, more so than the hydrogen atoms of any possible OH groups on the surface of ZnO.

The transformation of Zn_4O_4 into Zn_4O_3S and eventually into Zn_4S_4 by reaction with hydrogen sulfide is predicted to be exothermic [Eq. (1) and (2)].

$$\begin{aligned}&Zn_4O_4\ (\mathbf{1}) + H_2S \rightarrow Zn_4O_3S\ (\mathbf{3}) + H_2O\\&\Delta E_o = -164.3\ \text{kJ}\,\text{mol}^{-1}\end{aligned} \tag{1}$$

$$\begin{aligned}&{}^1\!/_4\,Zn_4O_4\ (\mathbf{1}) + H_2S \rightarrow {}^1\!/_4\,Zn_4S_4(\mathbf{4}) + H_2O\\&\Delta E_o = -148.5\ \text{kJ}\,\text{mol}^{-1}\end{aligned} \tag{2}$$

For comparison, the experimental reaction enthalpy for the conversion of crystalline ZnO to bulk ZnS is given by Equation (3).[14]

$$\begin{aligned}&ZnO(s) + H_2S(g) \rightarrow ZnS(s) + H_2O(g)\\&\Delta H^\circ_{298} = -78.1\ \text{kJ}\,\text{mol}^{-1}\end{aligned} \tag{3}$$

Expectedly, the latter enthalpy is absolutely smaller than the energy calculated for reaction (2), since the enthalpy of sublimation of ZnO is larger than that of ZnS.

In conventional vulcanization of natural rubber (*cis*-polyisoprene) approximately 1 mol of ZnS is produced per mol of cross-links formed,[3] which indicates that the ZnS originates from the H_2S produced by substituting hydrogen atoms of the polyolefin by sulfur (see below).

Reference calculations: The adsorption of carbon monoxide on macroscopic zinc oxide crystals has been studied many times because of its importance for the industrial synthesis of methanol by reduction of CO/CO_2 mixtures with H_2 on a ZnO/Cu catalyst.[15] The adsorption enthalpy of CO depends slightly on the crystal surface and on coverage. On the 1010 surface a value of −50.2 kJ mol^{-1} was obtained experimentally,[16] while periodic correlated Hartree–Fock calculations gave −39.7 kJ mol^{-1} for low coverage (near zero) and −35.6 kJ mol^{-1} for a monolayer of CO.[17] Density functional calculations using the above-mentioned highly polar Zn_4O_4 cluster of C_{3v} symmetry (**1a**) yielded a CO binding energy of −50 kJ mol^{-1} at the two-coordinate zinc atoms and −32 kJ mol^{-1} at the three-coordinate zinc atom[7] (note that the geometries of both the cluster and of the CO ligand were restricted in these calculations). These data clearly indicate that the local environment (and therefore the local dipole moment) at the metal atoms is of decisive influence. We used these results to check our own calculation method.

A carbon monoxide molecule can bind to the tetrahedral cluster **1** in two ways, with either the carbon or the oxygen atom as anchor (Figure 2). Both adducts are of C_{3v} symmetry. At the B3LYP/6-31+G* level, complex **5** is more stable than **5a** by 39.5 kJ mol^{-1} [Eqs. (4) and (5)].

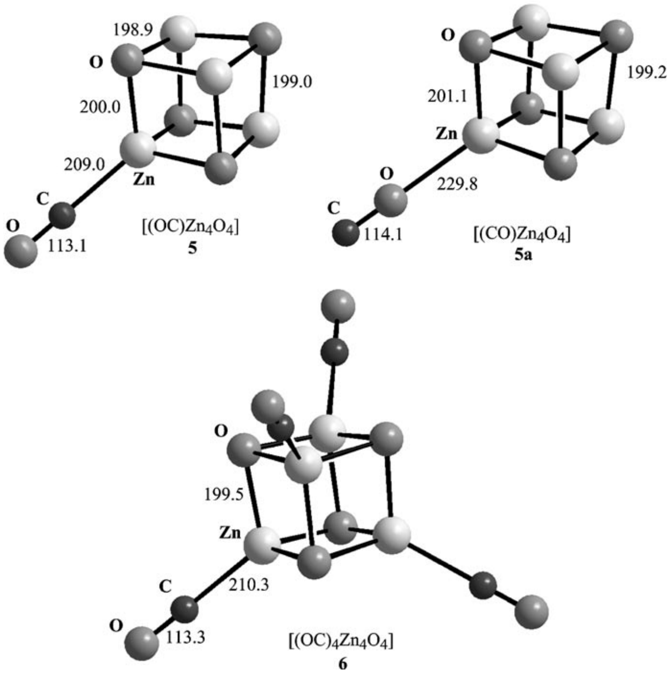


Figure 2. Structures of the carbon monoxide complexes $[(OC)Zn_4O_4]$ (**5**), $[(CO)Zn_4O_4]$ (**5a**), and $[(OC)_4Zn_4O_4]$ (**6**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

$$\begin{aligned}&Zn_4O_4\ (\mathbf{1}) + CO \rightarrow [(OC)Zn_4O_4]\ (\mathbf{5})\\&\Delta E_o = -56.8\ \text{kJ}\,\text{mol}^{-1}\end{aligned} \tag{4}$$

$$\begin{aligned}&Zn_4O_4\ (\mathbf{1}) + CO \rightarrow [(CO)Zn_4O_4]\ (\mathbf{5a})\\&\Delta E_o = -17.2\ \text{kJ}\,\text{mol}^{-1}\end{aligned} \tag{5}$$

The reaction enthalpy and Gibbs energy of reaction (4) are $\Delta H^\circ_{298} = -55.0\ \text{kJ}\,\text{mol}^{-1}$ and $\Delta G^\circ_{298} = -19.5\ \text{kJ}\,\text{mol}^{-1}$. These results are in excellent agreement with the reported experimental data for low coverage of CO on ZnO crystals. At the BP86/6-311++G* level of theory the following data were obtained which agree less well with the cited experiments: $\Delta H^\circ_{298} = -66.0\ \text{kJ}\,\text{mol}^{-1}$, $\Delta G^\circ_{298} = -31.3\ \text{kJ}\,\text{mol}^{-1}$. More examples for good agreement between calculated and experimental binding energies are presented below. Consequently, we carried out most of our calculations at the B3LYP/6-31+G* level.

On complex formation the CO bond length changes from 113.7 pm in the free molecule to 113.1 pm in **5** and to 114.1 pm in **5a**. The decrease predicted for **5** can be explained by the withdrawal of electron density from the HOMO of the CO molecule. This molecular orbital is of σ symmetry and mainly located at the carbon atom. In this context it is interesting to note that the bond of the cation CO^+ is 1.3 pm shorter than that of the neutral molecule.[18] Evidently, there is no significant π backbonding in **5**, as was found before by UV photoelectron spectroscopy of bulk ZnO covered by CO.[16] The total charge transfer from the ligand to the Zn_4O_4 unit of **5** is calculated as only 0.05 electrostatic units. Therefore, the size of the ZnO cluster should have little influence on our results. Previous DFT calculations on a $Zn_{22}O_{22}$ cluster led to a CO binding energy of $-38\,kJ\,mol^{-1}$ for the atoms simulating the 0001 surface of bulk ZnO.[19] Our data are in better agreement with the experimental enthalpy of $-50\,kJ\,mol^{-1}$.[16] The Zn–O bonds of **5** are little affected by the coordination of CO to the Zn_4O_4 cluster. Only the three bonds originating from the four-coordinate zinc atom are 2 pm or 1 % longer in **5** than in **1**.

To study the effect of increasing coverage of the ZnO surface by CO, we optimized the structure of tetrahedral cluster **6** [Figure 2, Eq. (6)].

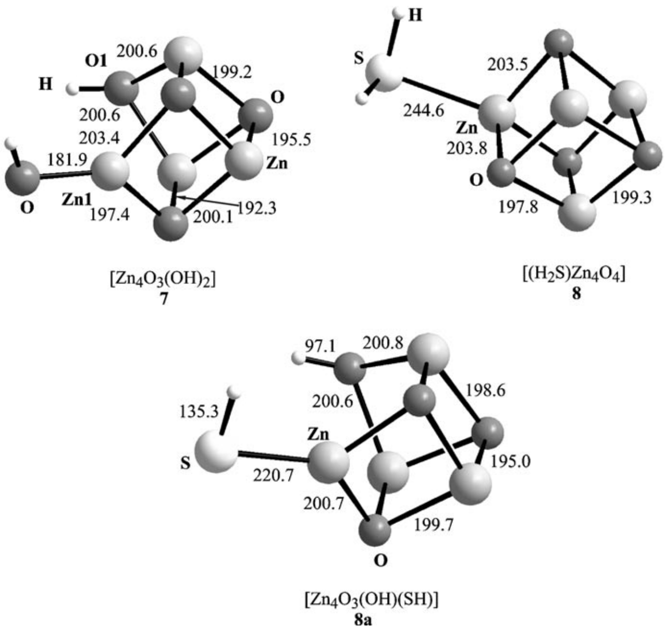
$$Zn_4O_4\ (\mathbf{1}) + 4\,CO \rightarrow [(OC)_4Zn_4O_4]\ (\mathbf{6}) \qquad \Delta E_o = -199.1\ kJ\,mol^{-1} \tag{6}$$

Expectedly, the binding energy per CO ligand decreases to from $-56.8\,kJ\,mol^{-1}$ in **5** to $-49.8\,kJ\,mol^{-1}$ in **6**, in perfect accord with the experimental findings for a monolayer of CO on zinc oxide crystals.[17] The Zn–O bonds of **6** are 1.6 pm shorter than in **5**, while the Zn–C bonds are 1.3 pm longer, in agreement with the smaller binding energy. As far as the bonding mechanism is concerned, the CO ligands most probably function as σ donors rather than π acceptors, but the main contribution is the dipole–ion attraction. The originally small dipole moment of free CO (0.12 D) is expected to be significantly enhanced by an induced component. This situation more or less also applies to the other adducts discussed below.

Adsorption of small molecules on Zn_4O_4: During the course of the vulcanization process water and hydrogen sulfide are expected to be formed, for example, from the reaction of carboxylic acids or thiols with zinc oxide (to give H_2O) and by substitution of C–H bonds by sulfur ligands (producing H_2S). Therefore, we investigated reactions of H_2O and H_2S with the tetrahedral Zn_4O_4 cluster. In the first case, no stable adduct $[H_2O{\cdot}Zn_4O_4]$ was obtained. Instead, this suspected initial product is transformed spontaneously into the corresponding dihydroxo complex **7** (Figure 3). Expectedly, this proton-transfer reaction yielding one planar coordinate zinc atom is strongly exothermic [Eq. (7)].

$$Zn_4O_4 + H_2O \rightarrow [Zn_4O_3(OH)_2]\ (\mathbf{7}) \qquad \Delta E_o = -183.2\ kJ\,mol^{-1} \tag{7}$$

In the case of H_2S the initial adduct $[(H_2S)Zn_4O_4]$ (**8**) and isomeric hydroxo mercapto complex **8a** could be identified on the PES [Eqs. (8) and (9)].



$[Zn_4O_3(OH)_2]$ **7**

$[(H_2S)Zn_4O_4]$ **8**

$[Zn_4O_3(OH)(SH)]$ **8a**

Figure 3. Structures of the complexes $[Zn_4O_3(OH)_2]$ (**7**), $[(H_2S)Zn_4O_4]$ (**8**), and $[Zn_4O_3(OH)(SH)]$ (**8a**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

$$Zn_4O_4 + H_2S \rightarrow [(H_2S)Zn_4O_4]\ (\mathbf{8}) \qquad \Delta E_o = -75.8\ kJ\,mol^{-1} \tag{8}$$

$$Zn_4O_4 + H_2S \rightarrow [Zn_4O_3(OH)(SH)]\ (\mathbf{8a}) \qquad \Delta E_o = -245.2\ kJ\ mol^{-1} \tag{9}$$

Reactions (7)–(9) remove water and hydrogen sulfide but also other SH compounds such as carbaminic acids from the rubber mixture if ZnO is present. Remarkably, the reaction energy for the hydrolysis of ZnO is smaller than for the thiolysis shown in Equation (9). This result may be rationalized by the relatively weak S–H bonds in H_2S, one of which is turned into a strong O–H bond, while in the case of H_2O no such change in bond energy occurs. From the above it follows that the thiolysis of **7** is also predicted to be exothermic [Eq. (10)].

$$[Zn_4O_3(OH)_2](\mathbf{7}) + H_2S \rightarrow [Zn_4O_3(OH)(SH)](\mathbf{8a}) + H_2O \qquad \Delta E_o = -62.0\ kJ\,mol^{-1} \tag{10}$$

The structures of the analogous products **7** and **8a** are very similar (see Figure 3). The former Zn_4O_4 cube has opened up to a basketlike structure of approximate C_s symmetry if the hydrogen atom of the exocyclic OH/SH group is ignored. The "missing edge" of the former cube has now a nonbonding Zn1···O1 distance of about 346 pm in both molecules. While the coordination geometry at Zn1 is practically planar, the geometry at O1 is pyramidal with the hydrogen atom in an axial position. The other hydrogen atom is approximately located in the plane of the neighboring

ZnO_3/ZnO_2S unit. Because of the importance of model reaction (9) for the interaction of certain vulcanization accelerators with zinc oxide, we calculated the reaction energy also at the B3LYP/6-31+G(3df,p) level. Practically the same binding energy as in Equation (9) was obtained ($-245.8\,kJ\,mol^{-1}$). We conclude that the 6-31+G* basis set is sufficient for the purpose of this work, especially if the size of the larger complexes is taken into account.

The reaction of **1** with methanol (as model alcohol) also leads directly to a hydroxo methoxo complex (**9**), the structure of which is analogous to that of species **7** [Eq. (11)].

$$\begin{aligned} &Zn_4O_4 + MeOH \rightarrow [Zn_4O_3(OH)(OMe)]\ (\mathbf{9}) \\ &\Delta E_o = -171.0\,kJ\,mol^{-1} \end{aligned} \tag{11}$$

This result is in agreement with spectroscopic studies on the chemisorption of MeOH on ZnO single-crystal surfaces (0001 and 1010), which at low coverage also show exclusively dissociative adsorption with deprotonation, even at 140 K.[20] No experimental binding energy was reported.

In contrast to MeOH, the addition of methanethiol to the ZnO cluster gave two products: molecular adduct **10** and mixed hydroxo mercapto complex **10a** resulting from dissociative adsorption [Eqs. (12) and (13)].

$$\begin{aligned} &Zn_4O_4 + MeSH \rightarrow [(MeHS)Zn_4O_4]\ (\mathbf{10}) \\ &\Delta E_o = -95.2\,kJ\,mol^{-1} \end{aligned} \tag{12}$$

$$\begin{aligned} &Zn_4O_4 + MeSH \rightarrow [Zn_4O_3(OH)(SMe)]\ (\mathbf{10a}) \\ &\Delta E_o = -229.9\,kJ\,mol^{-1} \end{aligned} \tag{13}$$

The adsorption of MeSH on the 0001 surface of ZnO crystals was previously studied by Casarin et al. using X-ray photoelectron and infrared spectroscopy as well as DFT calculations.[21] Both molecular and dissociative adsorption were observed. The experimental enthalpy of molecular adsorption decreases with increasing coverage and reaches $-85 \pm 4\,kJ\,mol^{-1}$ at 0% sulfur on the surface. This value is in good agreement with our data [see Eq. (12)], while the following absolute enthalpies calculated by Casarin et al. by local density functional theory for the molecular (nondissociative) adsorption of H_2O (162), NH_3 (212), MeOH (196), and MeSH ($187\,kJ\,mol^{-1}$) on ZnO are all much too large.

Our results indicate that a very stable zinc complex would form if polymeric thiols RSH were produced from the polyolefins during the vulcanization process. Two or more such molecules could then be linked to one and the same macroscopic ZnO particle, which in this way would form a "bridge" or "cross-link" between the two polymer chains by some kind of "salt" formation of the type RS-$[Zn_xO_{x-2}(OH)_2]$-SR. This may be one of the reasons why solid ZnO is a much better activator than mononuclear zinc thiolate complexes. Other arguments in favor of solid ZnO are presented below.

The molecular adsorption of Me_2S on Zn_4O_4 is slightly stronger than that of MeSH [Eq. (14)].

$$\begin{aligned} &Zn_4O_4 + Me_2S \rightarrow [(Me_2S)Zn_4O_4]\ (\mathbf{11}) \\ &\Delta E_o = -106.7\,kJ\,mol^{-1} \end{aligned} \tag{14}$$

Adducts **8**, **10**, and **11** show the expected geometries (Figure 4) evidently the 3p electron lone pair on sulfur (the HOMO of the ligand molecule) is attracted by the positively charged zinc atom. In addition, two weak hydrogen bonds to one and the same oxygen atom can be identified in the structure of **11**, which is of C_s symmetry with a dipole moment of 5.04 D.

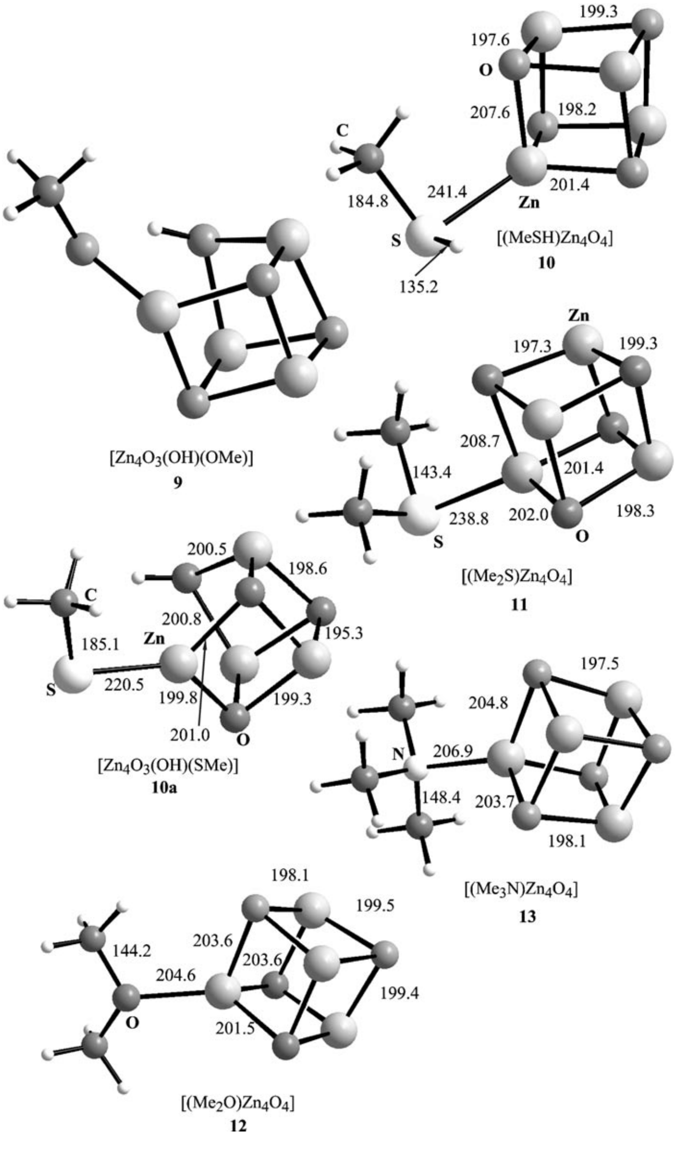


Figure 4. Structures of $[Zn_4O_3(OH)(OMe)]$ (**9**), $[(MeHS)Zn_4O_4]$ (**10**), $[Zn_4O_3(OH)(SMe)]$ (**10a**), $[(Me_2S)Zn_4O_4]$ (**11**), $[(Me_2O)Zn_4O_4]$ (**12**), and $[(Me_3N)Zn_4O_4]$ (**13**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

In the case of dimethyl ether the interaction is weaker due to the lower dipole moment of the ligand ($\mu = 1.46$ D) and the lower polarizability of the oxygen atom compared to the sulfur atom in Me_2S ($\mu = 1.75$ D) [Eq. (15)].

$$\begin{aligned} &Zn_4O_4 + Me_2O \rightarrow [(Me_2O)Zn_4O_4]\ (\mathbf{12}) \\ &\Delta E_o = -93.6\ \mathrm{kJ\,mol^{-1}} \end{aligned} \tag{15}$$

Aromatic and aliphatic amines accelerate the vulcanization process[22] and are often constituents of complex accelerator molecules such as mercaptobenzothiazole (MBT), the corresponding disulfide (BtSSBt), and tetramethylthiuram disulfide (TMTD). However, the basicity of the nitrogen atoms in these accelerator compounds is rather low due to the planar coordination environment at the nitrogen atoms (see complex **21b** below).

To study the interaction energy between a tertiary amine and zinc oxide particles, trimethylamine was used as model compound and the cluster **13** (Figure 4) was obtained [Eq. (16)].

$$\begin{aligned} &Zn_4O_4 + Me_3N \rightarrow [(Me_3N)Zn_4O_4]\ (\mathbf{13}) \\ &\Delta E_o = -135.1\ \mathrm{kJ\,mol^{-1}} \end{aligned} \tag{16}$$

The calculated dipole moment of Me_3N (0.59 D) is much smaller than those of Me_2S and Me_2O. Nevertheless, the interaction with Zn_4O_4 is considerably stronger, since tertiary amines are stronger Lewis bases than ethers and thioethers, partly as a consequence of the lower electronegativity of nitrogen compared to oxygen. The polarization of the amine by the zinc oxide cluster can be seen in the increase of the NBO atomic charge on the nitrogen atom from −0.59 in Me_3N to −0.64 in **13**. Remarkably, the Zn−O bond lengths at the four-coordinate zinc atom are 5 pm longer in **13** than in **1**. Complex **13** is a model for the initial interaction of sulfenamide and morpholine accelerators with zinc oxide. Primary and secondary amines are expected to coordinate to Zn_4O_4 in a similar fashion to Me_3N but with subsequent transfer of one proton to an oxygen atom. The binding energy of undissociated ammonia to bulk ZnO (0001 surface) has been determined by photoelectron spectroscopy as $-117 \pm 13\ \mathrm{kJ\,mol^{-1}}$.[23] This value is in good agreement with our results for Me_3N.

The strong interaction of amines with ZnO prevents any attack of nitrogen bases on elemental sulfur and organic polysulfides (R_2S_n) as long as the surface of the ZnO particles has not been fully covered by stronger donors. The ZnO will simply function as a trap for amines. Thus, the seemingly reasonable and still-cited proposal by Krebs[24] that the simultaneous interaction of *cyclo*-S_8 with R_3N and ZnO or a mononuclear zinc complex in the rubber mixture may result in an activated zwitterionic complex of the type $R_3N \rightarrow S_8 \rightarrow Zn^{2+}$ must be regarded as obsolete, since the amine will go directly to the zinc site leaving the S_8 molecule unaffected. As will be shown below, the absolute binding energies of sulfur homocycles to ZnO clusters are much smaller than those of tertiary amines.

Adsorption of olefins on Zn_4O_4: The interaction of ethene, propene, and pentadiene with the tetrahedral Zn_4O_4 cluster was studied to simulate the adsorption of polyolefinic natural and synthetic rubber molecules on the zinc oxide particles during compounding of the vulcanization mixture. In addition, we wanted to find out whether any C−H bond activation occurs, since sulfuration of natural rubber during vulcanization in the presence of zinc compounds takes place almost entirely by substitution of allylic hydrogen atoms rather than by the combination of substitution and addition to the C=C bonds that occurs when zinc is absent.[2] However, our study is also of interest in the context of the well-known use of zinc reagents in organic synthesis, for example, with olefins and other unsaturated compounds.[25]

The adsorption of ethene on bulk zinc oxide at room temperature is fast and reversible,[26] but neither the adsorption enthalpy nor the structure of the product is known. Ethene coordinates side-on to one zinc atom of Zn_4O_4 (**1**) [Figure 5, Eq. (17)].

$$\begin{aligned} &Zn_4O_4 + C_2H_4 \rightarrow [(\eta^2\text{-}C_2H_4)Zn_4O_4]\ (\mathbf{14}) \\ &\Delta E_o = -68.9\ \mathrm{kJ\,mol^{-1}} \end{aligned} \tag{17}$$

At the B3LYP/6-31+G(2dp) level the binding energy of **14** was obtained as $-69.3\ \mathrm{kJ\,mol^{-1}}$. This relatively weak interaction is in agreement with the infrared spectroscopic observation that ZnO adsorbs ethene at room temperature and that the olefin can be removed easily under high vacuum.[27] The calculated C=C stretching frequency decreases from 1702 $\mathrm{cm^{-1}}$ in free ethene to 1652 $\mathrm{cm^{-1}}$ in **14**.

The structure of the ethene complex is of C_1 symmetry with a large dipole moment of 3.86 D, despite the fact that the free components are nonpolar. On the basis of the NBO atomic charges, the charge transfer amounts to only 0.06 electrostatic units and takes place from ethene to the five-coordinate zinc atom via the HOMO of C_2H_4, which is the bonding π orbital of the C=C bond. The length of this bond increases by 1.8 pm or 1.3 % as a consequence of the removal of bonding electrons. The C_3 axis of the Zn_4O_4 cluster in **14** passes through the midpoint of the ethene unit, the molecular plane of which is perpendicular to this axis. There seem to be no O···H interactions (shortest distance 338 pm), and the C−H bonds do not change in length, although the C_2H_4 unit is no longer completely planar (*trans* torsion angle: 176.6°). The absolute values of the NBO atomic charges on the ligand atoms (H: +0.26, C: −0.50) are larger than in the free ethene molecule (H: +0.22, C: −0.44). In other words, the charge separation between C and H increases by 15 %, and this may lead to a certain activation of the C−H bonds. In general, the structure of **14** is similar to those of other transition metal olefin complexes, which have been prepared in large numbers, starting in 1827 with Zeise's salt $K[Pt(C_2H_4)Cl_3]$.[28] To further study possible acti-

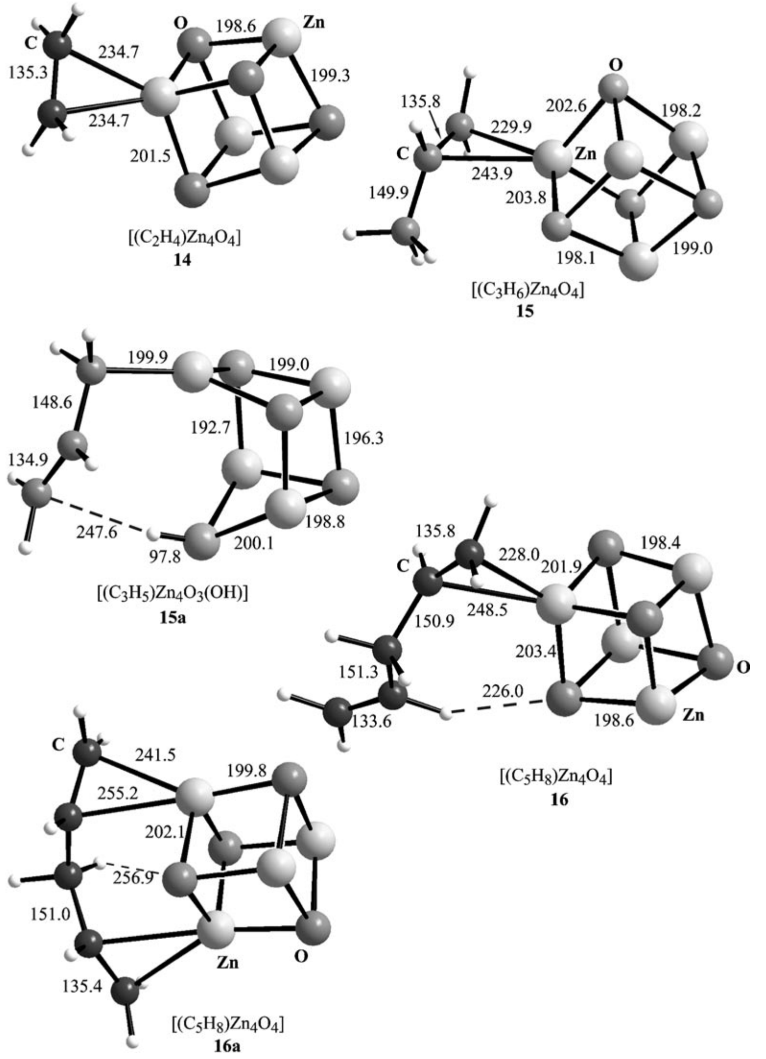


Figure 5. Structures of the olefin complexes $[(\eta^2\text{-}C_2H_4)Zn_4O_4]$ (**14**), $[(\eta^2\text{-}C_3H_6)Zn_4O_4]$ (**15**), $[(\eta^1\text{-}C_3H_5)Zn_4O_3(OH)]$ (**15a**), $[(\eta^2\text{-}C_5H_8)Zn_4O_4]$ (**16**), and $[(\eta^4\text{-}C_5H_8)Zn_4O_4]$ (**16a**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

vation of C–H bonds, we calculated the structure of propene adduct **15**, which contains allylic hydrogen atoms [Figure 5, Eq. (18)].

$$Zn_4O_4 + C_3H_6 \rightarrow [(\eta^2\text{-}C_3H_6)Zn_4O_4]\ (\mathbf{15}) \qquad \Delta E_o = -77.0\,\text{kJ mol}^{-1} \tag{18}$$

The C_3H_5 ligand of **15** is coordinated side-on to a zinc atom with Zn–C distances of 229.9 and 243.9 pm. These distances are in agreement with the corresponding data of the only structurally characterized zinc(II) π complex $[Zn(CMe{=}CH_2)_2]$, for which intermolecular Zn···(C=C) distances of 226–233 pm were determined by X-ray crystallography for the five molecules in the asymmetric unit cell (the π interaction occurs between neighboring molecules).[29] The absolute binding energy of **15** is 11 % larger than with the ethene ligand. An analogous adduct was obtained with 2-methylpent-2-ene (calculated binding energy: $-82.9\,\text{kJ mol}^{-1}$), which is often used as a model olefin in vulcanization studies.[2]

One hydrogen atom of the methyl group of **15** evidently is involved in a weak hydrogen bond to one of the oxygen atoms, although the corresponding O···H distance of 267.1 pm is only slightly shorter than the sum of the van der Waals radii[30] and much larger than for O–H···O hydrogen bonds as in ice I, for which 171 pm has been determined.[31] All other O···H distances of **15** are larger than 340 pm. The two C–C bonds of the propene ligand differ from those of the free molecule insofar as the double bond length has increased by 2.1 pm, while the single bond has contracted by 0.3 pm. The C–H bond lengths are all identical in both compounds to within 0.1 pm. Therefore, activation of the allylic C–H bonds cannot be deduced from these structures. Furthermore, the atomic charges on the methyl hydrogen atoms do not change significantly on complexation with Zn_4O_4.

Dent and Kokes[32] studied the adsorption of propene on bulk ZnO by infrared spectroscopy and demonstrated that two types of products are formed, even at room temperature. The first, more weakly bound, complex has been interpreted as a π-complex in analogy to the ethene adduct **14** reported above. This adduct dissociates in vacuum already at 20 °C and obviously is of the type **15**. The reported C=C stretching vibration of this complex of $1620\,\text{cm}^{-1}$ is in good agreement with the unscaled C=C stretching frequency of $1655\,\text{cm}^{-1}$ calculated for our adduct **15**. However, a second adduct was observed which is much more stable and can be reversibly dissociated to the starting materials only on heating to above 100 °C under vacuum.[32] Since an IR absorption band at $3593\,\text{cm}^{-1}$ assigned to an O–H stretching vibration was observed, this adduct was interpreted as an zinc hydroxo complex with a C_{2v}-symmetrical allyl anion. To establish the structure of this species, we studied the analogous reaction yielding a complex in which an allyl anion is linked to a zinc center [Eq. (19)].

$$\begin{aligned}&Zn_4O_4 + C_3H_6 \rightarrow [(\eta^1\text{-}C_3H_5)Zn_4O_3(OH)]\ (\mathbf{15a})\\&\Delta E_o = -121.0\ \text{kJ mol}^{-1}\end{aligned} \tag{19}$$

In this reaction, the methyl proton of **15** involved in a weak O···H hydrogen bond has migrated to the strongly negatively charged oxygen atom in a similar fashion as was described above for various Brønsted acids. The structure of **15a** shown in Figure 5 resembles those of other η^1-allyl complexes, which are known in large numbers. The formation of allyl complexes by deprotonation of propene by transition metal complexes is also well known.[33] Expectedly, the organometallic adduct **15a** is more stable than the isomeric complex **15**, by 44.0 kJ mol^{-1}. The C–C bond lengths in the allyl ligand (134.9/148.6 pm) are comparable to those of free propene (133.7/150.3 pm); the torsion angles C-C-C-Zn (−96.7°) and (O)H-C-C-C (90.6°) demonstrate that the plane of the ligand is facing the Zn_4O_4 skeleton. The calculated Zn–C bond length of 199.9 pm is in line with the Zn–C σ-bond lengths of 198.7–200.6 pm in $[Zn(CMe{=}CH_2)_2]$.[29]

Allyl complexes are known to be fluxional, since the hapticity of the ligand can switch back and forth between η^1 and η^3.[33] Zinc allyl complexes with both bonding types are known[34] but no crystal structures have been reported. Dent and Kokes[32] interpreted their spectroscopic data and the results from isotopic labeling experiments in terms of a η^3-C_3H_5 complex. However, all our attempts to optimize such a structure with the Zn_4O_4 cluster failed and always led to the η^1 species **15a**. Maybe the hydrogen bond between the OH group and the C=C bond stabilizes this particular structure (shortest OH···C distance: 247.5 pm). In addition, Zn^{2+} ions have a d^{10} configuration and consequently little tendency to accept the π electrons of the allyl ligand. The calculated vibrational spectrum of **15a** (unscaled) shows the two C–C stretching vibrations at 1663 (C=C) and 944 cm^{-1} (C–C), compared to 1719 and 929 cm^{-1} calculated for free propene. The OH stretching and bending modes, all of high infrared intensity, are calculated at 3631, 899, and 674 cm^{-1}. Dent and Kokes[32] assigned bands at 1545 and 1203 cm^{-1} to the two C–C stretching modes of the proposed η^3-allyl ligand and a peak at 3593 cm^{-1} to the OH stretching vibration (these authors did not report data for the region below 1000 cm^{-1}). Our B3LYP/6-31+G* calculations on the free allyl anion resulted in C–C stretching frequencies of 1569 and 1018 cm^{-1}, the latter being of very low infrared intensity.

The possible implications of the deprotonation reaction between olefins and ZnO for the vulcanization of rubber is immediately evident. The allyl anion most probably reacts with sulfur and sulfur donors to form intermediates of the cross-linking process. This aspect will be addressed in detail in an upcoming publication.

Adsorption of dienes on Zn_4O_4: Since polyolefins are used in rubber production, we studied the interaction of 1,4-pentadiene as a model compound with ZnO. Two binding modes were obtained for the adduct with Zn_4O_4: dihapto (**16**) and tetrahapto coordination (**16a**). Expectedly, the tetrahapto form is more stable but only slightly so [Eqs. (20) and (21)], since the bonding geometry at the two five-coordinate zinc atoms of **16a** is far from optimum (Figure 5).

$$\begin{aligned}&Zn_4O_4 + C_5H_8 \rightarrow [(\eta^2\text{-}C_5H_8)Zn_4O_4]\ (\mathbf{16})\\&\Delta E_o = -80.2\ \text{kJ mol}^{-1}\end{aligned} \tag{20}$$

$$\begin{aligned}&Zn_4O_4 + C_5H_8 \rightarrow [(\eta^4\text{-}C_5H_8)Zn_4O_4]\ (\mathbf{16a})\\&\Delta E_o = -86.0\ \text{kJ mol}^{-1}\end{aligned} \tag{21}$$

Whereas the geometry of **16** is analogous to those of **14** and **15**, the structure of C_s-symmetric **16a** indicates that polyolefin molecules can wrap themselves around a zinc oxide particle and occupy several zinc sites with their C=C structural units. In this case, the allylic hydrogen atoms may come close to the oxygen atoms, as can be seen in the structure of **16a** with a relatively short O···H distance of 256.9 pm. However, an even shorter O···H distance of 226.0 pm to one of the olefinic hydrogen atoms was calculated for complex **16**. In this way the various C–H bonds are strongly polarized and activated for ionic-type reactions such as nucleophilic attack on the hydrogen atoms or migration of a proton to one of the oxygen atoms of ZnO.

The two C-C-C-C torsion angles of free 1,4-C_5H_8 are calculated as −11.6° and +119.8°. These values change to −117.3° and −135.4° in **16** and to ±144.1° in **16a**. The NBO atomic charges on the carbon atoms (counting from the zinc-coordinated end of the chain) are −0.58, −0.18, −0.54, −0.23, and −0.43 in **16** and −0.58, −0.15, and −0.56 in **16a** (C_s symmetry). The charges on the eight hydrogen atoms of both compounds all lie in the range +0.22 to +0.27 electrostatic units. These data demonstrate that nucleophilic attack is unlikely to occur at one of the four-coordinate carbon atoms. Instead, the hydrogen atoms are expected to attract nucleophiles. Deprotonation of the diene ligand at the central carbon atom of **16a** with formation of the double π complex $[Zn_4O_3(OH)C_5H_7]$ is exothermic.

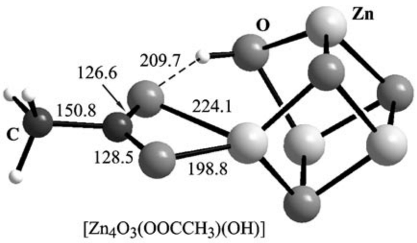
From the geometries of the adducts **15**–**16a** it is obvious that substitution of one of the allylic hydrogen atoms by a methyl group (as in polyisoprene) does not create steric problems in corresponding complexes.

Adsorption of carboxylic acids on Zn_4O_4: Carboxylic acids such as stearic acid or their salts are usually minor but important constituents of the vulcanization mixture, and in conventional vulcanization of natural rubber a small percentage of the added ZnO is transformed into zinc stearate, which is an essential cure activator.[4a,b] If a mixture of ZnO and stearic acid is heated the reaction begins at 154 °C according to DSC measurements.[35] Water would be expected as a byproduct of this reaction, but as we have shown above zinc oxide clusters easily react with H_2O to give a zinc oxide hydroxide [see Eq. (7)]. Thus, the initial reaction of RCOOH with Zn_4O_4 is expected to proceed with formation of a basic carboxylate [Eq. (22)].

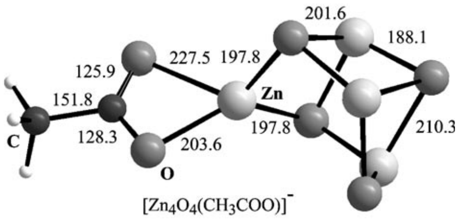
$$Zn_4O_4 + RCOOH \rightarrow [Zn_4O_3(OOCR)(OH)]\ (\mathbf{17}) \qquad (22)$$
$$\Delta E_o = -255.4\ \mathrm{kJ\,mol^{-1}}$$

The liberation of water is expected only after all Zn-O-Zn bridges have been hydrolyzed, that is, if approximately equimolar amounts of carboxylic acid and ZnO are used. However, vulcanization formulations usually contain much more ZnO than carboxylic acid on a molar basis. Strong heating will of course liberate H_2O from zinc hydroxide.

The reaction energy given in Equation (22) applies to $R=CH_3$, that is, to acetic acid as a model compound. The structure of the product **17** is shown in Figure 6. The adsorption and thermal desorption of acetic acid on the various crystal surfaces of bulk ZnO has previously been studied by temperature-programmed desorption with X-ray diffraction and UV photoelectron spectroscopy as analytical tools. Surface acetate was found to be the primary product on the (0001) surface. On heating, H_2O and CH_3COOH were desorbed at 300–400 K, whereas at higher temperatures (>500 K) CH_2CO (ketene), CO, CO_2, and zinc metal were liberated.[36]



$[Zn_4O_3(OOCCH_3)(OH)]$
17



$[Zn_4O_4(CH_3COO)]^-$
18

Figure 6. Structures of the complexes derived from acetic acid and its anion, $[Zn_4O_3(OOCCH_3)(OH)]$ (**17**) and $[Zn_4O_4(OOCCH_3)]^-$ (**18**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

Expectedly, the addition of an acetate anion to the Zn_4O_4 cluster is also strongly exothermic [Eq. (23)].

$$Zn_4O_4 + CH_3COO^- \rightarrow [Zn_4O_4(OOCCH_3)]^-\ (\mathbf{18}) \qquad (23)$$
$$\Delta E_o = -262.6\ \mathrm{kJ\,mol^{-1}}$$

Adducts **17** and **18** have very similar and highly interesting structures of C_s symmetry with one four-coordinate zinc atom connecting the two components. On addition of the acid or the acetate anion one edge of the Zn_4O_4 cluster opens up (Figure 6). The main difference between the two structures is the acidic hydrogen atom, which forms an OH···O hydrogen bond of length 209.7 pm to the acetate ion as if it remembered its former position in the acid molecule. If the methyl groups of **17** or **18** were substituted by a longer alkyl chain, as in stearic acid, the corresponding stearate/ZnO particle would be amphiphilic and hence more easily dispersed in the hydrophobic rubber matrix.

The reaction of acetic acid with hydroxo complex **7** to give H_2O and **17** is predicted to be exothermic by $-72.2\ \mathrm{kJ\,mol^{-1}}$, while only $-10.2\ \mathrm{kJ\,mol^{-1}}$ is liberated if the acid reacts with complex **8a** to give H_2S and **17**.

Reaction of the vulcanization accelerator MBT with ZnO clusters: The exact role of ZnO as an activator is highly dependent on the type of accelerator used in the vulcanization system.[4] Therefore, the initial interaction of ZnO with such chemicals is of crucial importance. It is generally believed that the decisive step in the vulcanization process is the reaction of ZnO with the accelerator to form an "active accelerator complex".[2,4] Mercaptobenzothiazole (MBT) is one of the best known vulcanization accelerators. Theoretically, this substance can exist as two tautomers: 1,3-benzothiazole-2(3*H*)-thione (**19**) and 1,3-benzothiazole-2-thiol (**19a**); see Figure 7. According to our calculations the NH form **19** is more stable than the isomeric SH form **19a**, by $36.4\ \mathrm{kJ\,mol^{-1}}$. This order of stabilities persisted at the much higher G3X(MP2) level of theory[37] and is in agreement with the crystal structure determined by X-ray crystallography,[38] which shows that **19** rather than **19a** is the constituent of commercial MBT. Our calculated bond lengths of **19** deviate from the solid-state values by only 0.3–3.7 pm. Although **19** is a thione rather than a thiol, in the literature commercial **19** is still termed "mercaptobenzothiazole"; for reasons of consistency we will follow this custom.

If the thione **19** is allowed to react with sulfur or a sulfur donor it will take up one (or more) sulfur atom(s). In this "sulfurized form" the relative stability of the two tautomers changes. For instance, species **20** with a CSSH group (1,3-benzothiazol-2-yl hydrodisulfide, BtSSH) is $34.0\ \mathrm{kJ\,mol^{-1}}$ more stable than isomer **20a** with an NSH group, despite the additional stabilization of **20a** by an intramolecular S···H hydrogen bond of length 230.5 pm (see Figure 7). The formation of **20** from **19** and $\frac{1}{8}S_8$ is calculated to be endothermic by $54.1\ \mathrm{kJ\,mol^{-1}}$. While **19**, **19a**, and **20a** are strictly planar, **20** has C_1 symmetry with a C-S-S-H torsion angle of 79.8°. The vulcanization accelerator "MBTS", that is, the disulfide derivative of MBT (BtSSBt), is known to have a molecular structure analogous to that of **20**.[39]

In principle, the coordination of MBT (**19**) to a positively charged zinc atom can be achieved through either the lone pairs at the nitrogen and sulfur atoms or through the π electrons in the C–C bonds of the aromatic ring. In addition, a hydrogen bond can be formed from the NH group to one of the oxygen atoms of zinc oxide. The NBO atomic charges of **19** are as follows: C_{ring} (connected to H): −0.24; N: −0.59; =S: −0.10; −S−: +0.45; the dipole moment of **19** was calculated as 5.14 D. Therefore, coordination of zinc ions to

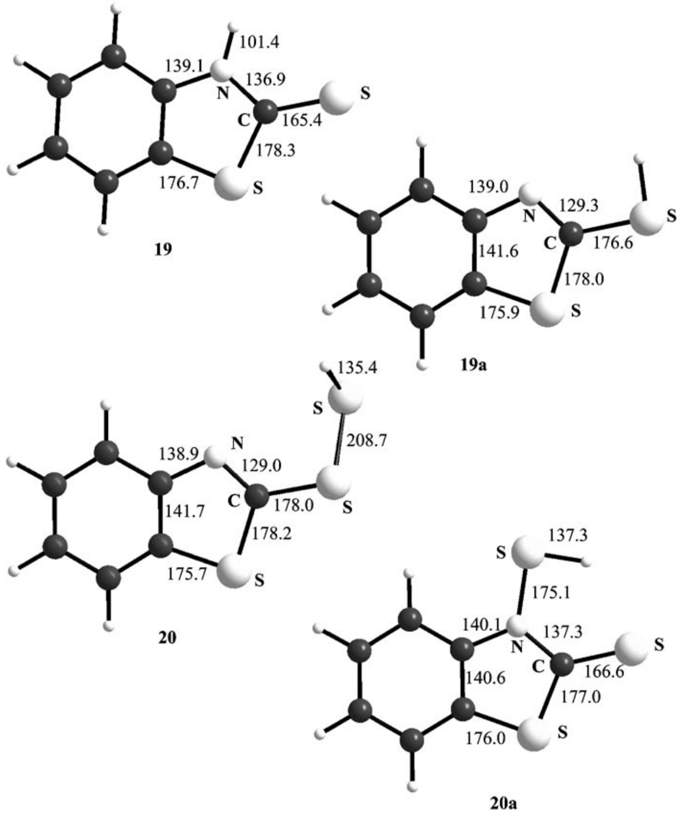


Figure 7. Structures of the vulcanization accelerator MBT (**19**), its tautomer iso-MBT (**19a**), as well as sulfurized derivative BtSSH (**20**) and its isomer (**20a**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

either the aromatic ring, the nitrogen atom, or the exocyclic thiono sulfur atom can be expected. Accordingly, several isomers of composition [(MBT)Zn_4O_4] were obtained (Figure 8).

The most stable form of [(MBT)Zn_4O_4] (**21**) contains the MBT molecule formally dissociated into a thiolate anion (BtS^-) and a proton which is linked to one of the oxygen atoms of the Zn_4O_4 cluster. The linkage of the nitrogen atom and the thiono sulfur atom of the MBT anion to one zinc center results in a very substantial binding energy [Eq. (24)].

$$\begin{aligned}&Zn_4O_4 + \text{MBT } (\mathbf{19}) \rightarrow [Zn_4O_3(OH)(SBt)]\ (\mathbf{21})\\&\Delta E_o = -247.2\ \text{kJ mol}^{-1}\end{aligned} \tag{24}$$

Chelate complex **21** has C_s symmetry with one zinc atom approximately tetrahedrally coordinated. The C=S bond length of the former thione group has increased from 165.4 pm in **19** to 172.0 pm in **21**. There is no hydrogen bond between the OH group and the BtS^- ligand.

Isomer **21a** with a binding energy of −243.0 kJ mol^{-1} is only slightly less stable than **21**. This structure has a very short and almost linear hydrogen bond to the nitrogen atom of the BtS^- anion (O−H⋯⋯N angle: 172.1°, see Figure 8). In addition, this anion is connected to the Zn_4O_4 cluster by a Zn−S bond of length 225.9 pm. This value is in good agreement with experimentally determined Zn−S bond lengths in mononuclear tetracoordinate zinc thiolate complexes (223–225 pm).[40]

During the approach of the MBT molecule **19** to the ZnO cluster the initial interaction is by both an N−H⋯O hydrogen bond and a C=S→Zn donor bond. On further geometry optimization the proton shifts from the nitrogen to the oxygen atom with release of substantial energy. The charges of most atoms change only slightly (<0.08 units) during this complex formation with the exception of the sulfur atom of the C-S-Zn bridge, which becomes much more negative, from −0.10 in **19** to −0.32 in **21a**. The symmetry of **21a** is C_1 but the two components of this complex are each of C_s symmetry, with a small angle between the two mirror planes. Formally, isomer **21a** can be obtained from **21** by rotation of the BtS^- ligand around the Zn1−C1 axis by 180°. During this rotation the nitrogen and sulfur atoms of the N−C=S unit may still be coordinated to the zinc atom. In this context it is notable that most vulcanization accelerators contain the N−C=S structural unit. The simultaneous coordination of BtS^- to a zinc cation via the nitrogen and sulfur atoms allows the thiono sulfur atom to add more sulfur atoms by reaction with elemental sulfur (forming polysulfides), while the nitrogen atom keeps the ligand linked to the zinc ion. The structures of these polysulfido complexes will be reported in Part 2 of this work.

In the other two [(MBT)Zn_4O_4] isomers the undissociated MBT molecule is more or less physically adsorbed to the ZnO cluster. In the more stable of these (**21b**) one of the C−C multiple bonds of the aromatic ring is attached to a zinc atom with a binding energy of −52.6 kJ mol^{-1}. In the least stable [(MBT)Zn_4O_4] isomer **21c** the nitrogen atom functions as an anchor at the zinc oxide cluster with a Zn−N distance of 222.7 pm and a binding energy of only −36.6 kJ mol^{-1}. The evidently low basicity of the MBT nitrogen atom can be ascribed to its planar coordination sphere reducing the local dipole moment in comparison to pyramidal coordination, as in Me_3N. However, on coordination to Zn_4O_4 this planar geometry changes to a slightly pyramidal one (sum of angles at nitrogen of **21c** between the covalent bonds: 343.6°). Complexes analogous to species **21**–**21c** were also obtained with the Zn_6O_6 cluster.

On heating of bulk ZnO with commercial MBT the corresponding zinc salt "$Zn(SBt)_2$" was obtained, probably containing the thiolate anion benzothiazolyl sulfide, BtS^-.[41,42] The likely intermediate of this reaction is adduct **21**. The crystal structure of "$Zn(SBt)_2$" is unknown since the material is insoluble and probably polymeric. On the other hand, the anionic complexes $[Zn(SBt)_3(OH_2)]^-$, $[Zn(SBt)(S_2CNMe_2)_2]^-$ and $[Zn(SBt)_2(S_2CNMe_2)]^-$ with Bu_4N^+ counterions have been characterized by X-ray diffraction.[43] The BtS^- ligands in these species are linked to the zinc atoms either via the nitrogen atom (as in **21c**) or by the thiolate sulfur atoms, as in **21a** (Figure 9). Most interesting is the structure of $[Zn(SBt)_3(OH_2)]^-$, since its aqua ligand is hy-

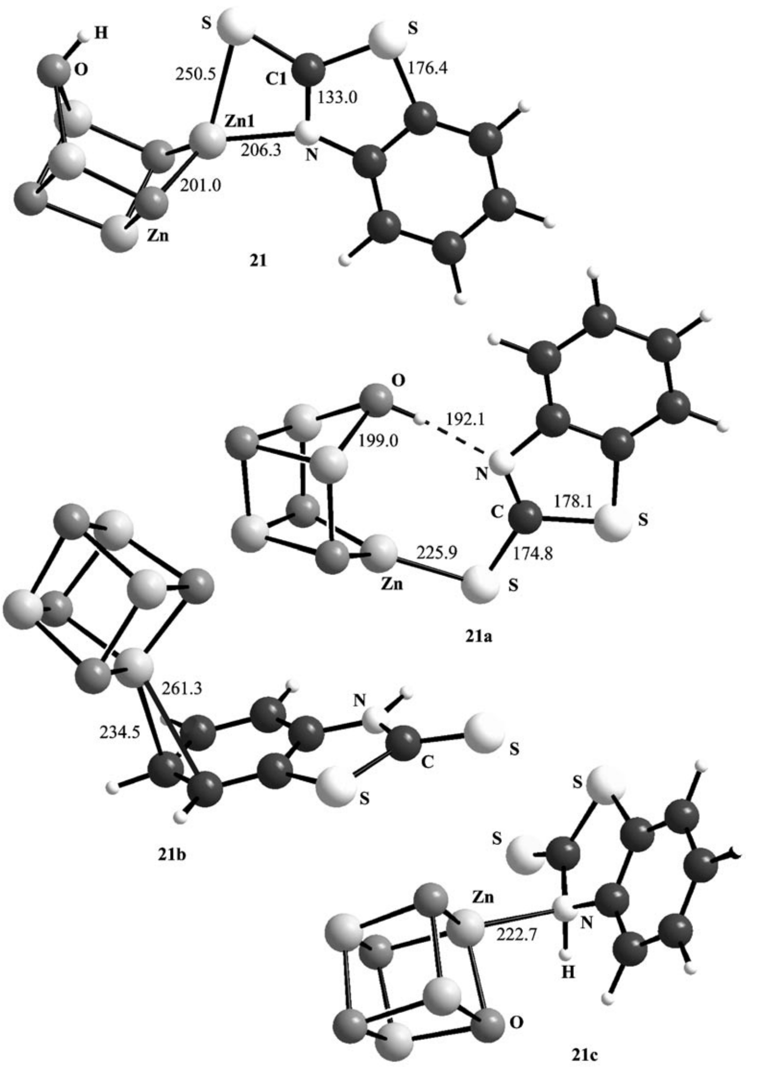


Figure 8. Structures of the accelerator complex [$Zn_4O_3(OH)(SBt)$] (**21**) and its less stable isomers **21a–c**. Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

drogen-bonded to the nitrogen atoms of the two BtS^- ions (N···H–O–H···N) and coordinated to the zinc atom via the oxygen atom. Thus, there are two five-membered rings of connectivity C-S-Zn-O-H-N, very similar to the corresponding local structure of complex **21a**. The Zn–S bond lengths of $[Zn(SBt)_3(OH_2)]^-$ are 234 pm.

The disulfide form of MBT lacking any NH or SH groups (MBTS or BtSSBt) is not expected to react chemically with dry zinc oxide at moderate temperatures and will just be adsorbed at the ZnO surface, primarily via one of the bridging sulfur atoms in an analogous manner to Me_2S_2 (see below) rather than through the nitrogen atoms. The sulfenamide accelerators *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) and *N*-*tert*-butylbenzothiazole-2-sulfenamide (TBBS) have been reported not to react chemically with bulk zinc oxide.[44] Therefore, we did not study these chemicals in the present work. However, the physical interaction of CBS and TBBS with Zn_4O_4 is expected to be similar to that of Me_3N (see above).

Adsorption of organic polysulfides (R_2S_n) and elemental sulfur (S_6) on Zn_4O_4: Organic polysulfides R_2S_n are intermediates in the vulcanization process. They originate from the reaction of the accelerators with elemental sulfur. Previously, we have shown that the methyl derivatives Me_2S_n with $n=2$–5 form chelate complexes with Li^+ ions.[45] In these cases the interaction energy ranges from −140 to −190 kJ mol^{-1} and the bonding has been explained by ion–dipole attraction after the metal cation induced or enhanced the dipole moment of the polysulfide ligand by polarization. A similar interaction can be expected with the positively charged zinc atoms at the surface of ZnO. We calculated the most stable structure of the adduct [$(Me_2S_2)Zn_4O_4$] (**22**) which is similar to that of [$(Me_2S)Zn_4O_4$] (**11**); see Figure 10. The binding energy of **22** is −83.2 kJ mol^{-1}, considerably less than in the case of **11** (−106.7 kJ mol^{-1}). Besides one Zn–S bond of length 240.4 pm, two O···H hydrogen bonds (214.0 and 264.3 pm) bind the Me_2S_2 ligand to the Zn_4O_4 cluster. As a consequence of these hydrogen bonds, the C-S-S-C torsion angle changes from 87.6° in the free ligand to −148.6° in **22**. The S–S bond length increases

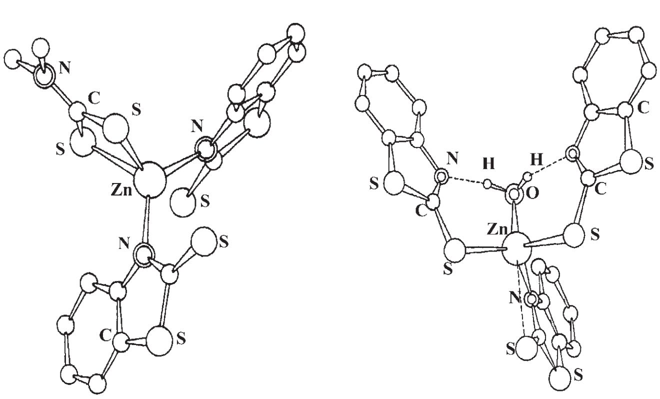
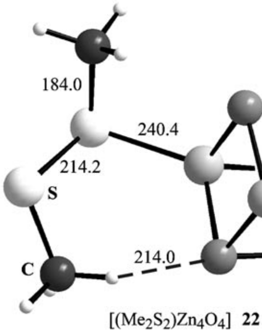
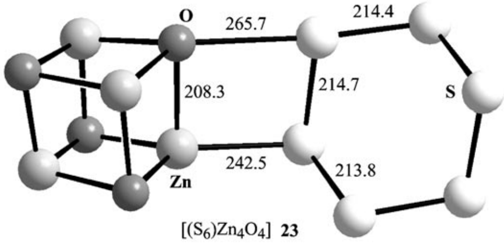


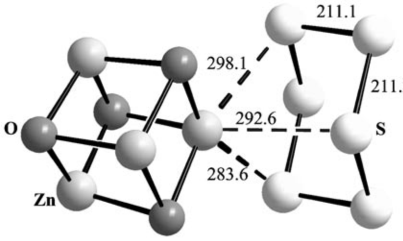
Figure 9. Structures of the anions $[Zn(SBt)_2(S_2CNMe_2)]^-$ (left) and $[Zn(SBt)_3(OH_2)]^-$ (right).[43] The mean N···O distance is 267 pm, and the countercations are nBu$_4$N$^+$.



$[(Me_2S_2)Zn_4O_4]$ **22**



$[(S_6)Zn_4O_4]$ **23**



$[(S_6)Zn_4O_4]$ TS **23a**

Figure 10. Structures of $[(Me_2S_2)Zn_4O_4]$ (**22**) and $[(\eta^2\text{-}S_6)Zn_4O_4]$ (**23**) as well as of the transition state $[(\eta^3\text{-}S_6)Zn_4O_4]$ (**23a**). Bond lengths in picometers, calculated at the B3LYP/6-31+G* level.

considerably, by 5.9 pm or 2.8 %, on coordination of Me_2S_2, while at the same time the NBO atomic charges of the sulfur atoms change only very little, from 0.07 in Me_2S_2 to 0.05 (three-coordinate) and 0.10 (two-coordinate) in **22**.

The interaction of zinc oxide with commercial elemental sulfur is expected to be relatively weak, since the S_8 molecule is of high D_{4d} symmetry and lacks any dipole moment. However, in our previous work we have shown that the sulfur homocycles S_6,[45] S_7,[46] and S_8[47] form chelate complexes of the type $[MS_n]^+$ with univalent metal cations such as Li^+, Ca^+, V^+, and Cu^+. The last three metal ions are even able to break down the S_8 molecule to form complexes with two S_4 ligands which are more stable than the isomeric S_8 complexes.[47]

To reduce the calculation time for the zinc oxide adducts we substituted S_8 by the chairlike S_6, which is also of high symmetry (D_{3d}).[48] In the case of Li^+ the most stable complex with S_6 is of C_{3v} symmetry with a binding energy of $-134\ kJ\,mol^{-1}$. For the interaction of S_6 with Zn_4O_4 two structures of very similar energy but differing hapticity were found. The most stable structure is of C_1 symmetry with an unprecedented planar four-membered ZnOSS heterocycle connecting the two components (Figure 10). In addition to a coordinative S→Zn bond there is another dative bond (O→S), evidently with delocalization of oxygen electron density into the antibonding σ* molecular orbital of the neighboring S–S bond. The length of this bond increases from 211.2 pm in free S_6 to 214.4 pm in **23**. A similar interaction can be expected with other sulfur rings such as S_7 and S_8. Thus, elemental sulfur is activated by zinc oxide both by polarization and by bond weakening [Eq. (25)].

$$Zn_4O_4 + S_6 \rightarrow [(\eta^2\text{-}S_6)Zn_4O_4]\ (\mathbf{23})\quad \Delta E_o = -60.7\ kJ\,mol^{-1} \tag{25}$$

The second S_6 adduct (**23a**) is a transition state with one negative vibrational eigenvalue and a relative energy of $4.5\ kJ\,mol^{-1}$ compared to **23**. It contains the S_6 ligand linked to one zinc atom with three Zn–S bonds of lengths 283.6, 292.6 and 298.1 pm (see Figure 10). All S···O contacts are longer than 350 pm. This geometry is analogous to that of the most stable isomer of $[LiS_6]^+$, but the low symmetry of **23a** indicates already that it is not a stable minimum structure. Only very approximately, **23a** is of C_{3v} symmetry (μ = 3.85 D).

Summary and Outlook

Small molecules related to the chemistry of rubber vulcanization by sulfur or sulfur donors are more or less strongly adsorbed on the surface of small ZnO clusters such as tetrahedral Zn_4O_4 and drum-shaped Zn_6O_6. In cases where no labile hydrogen atoms are available, the interaction is mainly due to (induced) dipole–ion attraction between the substrate and the zinc cations with very little charge transfer. The absolute adsorption energies increase from −57 to $-130\ kJ\,mol^{-1}$ in the order $CO < S_6 < H_2S < C_2H_4 < C_3H_6 < Me_2S_2 < C_5H_8 < MeSH < Me_2O < Me_2S < Me_3N$. Thus, tertiary amines and organic sulfides will drive out adsorbed olefins and elemental sulfur from the ZnO surface. In cases where proton transfer to one of the oxygen atoms of ZnO takes place, the addition reactions are strongly exothermic. This holds true for the chemical reactions of Zn_4O_4 with H_2O ($-183\ kJ\,mol^{-1}$), H_2S ($-245\ kJ\,mol^{-1}$), MeOH ($-171\ kJ\,mol^{-1}$), MeSH ($-230\ kJ\,mol^{-1}$), C_3H_6 ($-121\ kJ\,mol^{-1}$), and CH_3COOH ($-255\ kJ\,mol^{-1}$). In these cases, surface OH groups are formed on the ZnO particles. The largest absolute binding energy was obtained for addition of the acetate anion to Zn_4O_4 ($-263\ kJ\,mol^{-1}$). The vulcanization accelerator MBT (**19**) with several donor sites reacts spontaneously with the Zn_4O_4 cluster with proton transfer from nitrogen to oxygen and formation of a $>C{-}S^-$ group (thiolate anion), which interacts with a zinc atom to give a chelate complex with a binding energy of $-247\ kJ\,mol^{-1}$. This species and an isomer of almost identical energy are probably responsible for the activation of elemental sulfur during rubber vulcanization in the presence of zinc oxide, and corresponding polysulfido complexes are likely to be formed. This will be shown in Part 2 of this work. Other $[(MBT)Zn_4O_4]$ isomers are characterized by interactions of either the aromatic ring or the nitrogen atom with a zinc center, with binding energies of -52.6 kJ mol^{-1} and -36.6 kJ mol^{-1}, respectively.

The theoretical approach used in this work can be extended to study the interaction of various rubber chemicals, not only with stoichiometric zinc oxide clusters but also with oxygen-deficient clusters such as Zn_6O_5. In addition, ZnO clusters of lower symmetry may be used to simulate the effect of crystal defects at the surface of macroscopic ZnO particles. Furthermore, the omnipresent OH groups at the surface of ZnO, which result from reactions with proton donors such as water, thiols, secondary amines, acids, or MBT, can be studied with regard to their interactions with rubber chemicals. Finally, one or more of the zinc atoms may be substituted by other metal atoms to create complexes of differing reactivity, some of which may be even paramagnetic. These investigations on the role of ZnO as a template[49] for the early stages of the vulcanization process are now in progress.[50]

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