DOI: 10.1002/ejic.200700399

# Charge-Transfer Complexes between the Sulfur Molecules $SO_2$, $S_2O$, $S_3$, SONH, and $SOCl_2$ and the Amine Donors $NH_3$ and $NMe_3$ – A Theoretical Study

Ralf Steudel*[a] and Yana Steudel[a]

**Keywords:** Ab initio calculations / Donor–acceptor systems / Thermodynamics / Sulfur / Solvent effects

The formation of adducts between the acceptor molecules $SO_2$, $S_2O$, $S_3$, and $SOCl_2$ and the donor molecules ammonia and trimethylamine has been studied by high-level G3X(MP2) theory, in most cases for the first time. Minimum energy structures with a 1:1 composition and with sulfur–nitrogen bonds have been located for all complexes. The thermodynamic properties, vibrational spectra, and atomic charges of these molecules have been calculated. Of the 10 investigated complexes, only $SO_2{\cdot}NMe_3$ (**2**) and $S_2O{\cdot}NMe_3$ (**4**) are predicted to be thermodynamically stable in the gas phase under standard conditions ($\Delta G°_{298} < 0$). However, all adducts except $S_3{\cdot}NH_3$ (**5**), $SOCl_2{\cdot}NH_3$ (**7**), and $SOCl_2{\cdot}NMe_3$ (**8**) are stable thermodynamically at 77 K. In a polar continuum with a dielectric constant ($\varepsilon$) of 40, complexes **2**, **4**, and $S_3{\cdot}NMe_3$ (**6**) are stable even at 25 °C. However, if the adducts are formed in the polar continuum from the gaseous components, all adducts except $S_3{\cdot}NH_3$ are formed not only exothermally but also exergonically. Complexes **2**, **4**, and **8** are the only species known in the solid state so far. The charge transfer from donor to acceptor in the various complexes in the gas phase ranges from 0.08 to 0.39 electrostatic units and correlates inversely with the S–N bond length, which ranges from 198 to 295 pm. In general, the charge transfer weakens the bonds within the acceptor molecule, which therefore may be considered to become activated. The formation of thionyl imide (SONH) from $SOCl_2$ and $NH_3$ is exergonic in the gas phase and the interaction between SONH and $NH_3$ is very weak. In the case of $SO_2$, the 1:2 complexes $SO_2{\cdot}2NH_3$ (**1a**) and $SO_2{\cdot}2NMe_3$ (**2a**), which contain two S–N bonds, are unstable with respect to their three-component molecules both in the gas phase and in a polar medium at 25 °C, but they are stable in the polar phase with respect to the gaseous components.

## Introduction

Sulfur dioxide forms well-known charge-transfer complexes with both ammonia and trimethylamine and with the two stoichiometries 1:1 and 1:2. The ammonia complexes $SO_2{\cdot}NH_3$ (**1**) and $SO_2{\cdot}2NH_3$ (**1a**) were first discovered by equilibrium vapor pressure measurements on $SO_2/NH_3$ mixtures[1] and were subsequently characterized by matrix infrared spectroscopy[2] and quantum chemical calculations.[3,4] Both molecules have $C_s$ symmetry with sulfur–nitrogen bonds approximately perpendicular to the plane of the $SO_2$ unit.[3] The enthalpies of formation of the two solid compounds **1** and **1a** from the gaseous components were estimated from the above-mentioned vapor pressure measurements as being $-40 \pm 4$ and $-96 \pm 19$ kJ mol$^{-1}$, respectively.[1] On the other hand, ab initio calculations at the MP3/6-31+G(2d,p) level of theory have predicted that the enthalpies of formation from the separated components in the gas phase at 25 °C are only –18.8 for **1** and –31.3 kJ mol$^{-1}$ for **1a**. After correction for the basis set superposition error (BSSE), the (absolute) interaction energy between $SO_2$ and $NH_3$ in **1** was found to be smaller by 6 kJ mol$^{-1}$, at –12.8 kJ mol$^{-1}$.[3] Both **1** and **1a** are unstable at room temperature and ambient pressure.

The related adduct $SO_2{\cdot}NMe_3$ (**2**) is much more stable than **1** and was first prepared in 1943 as a colorless solid.[5] Subsequently, this compound has been extensively studied by X-ray crystallography of single crystals,[6,7] microwave spectroscopy in the vapor phase,[7] UV/Vis spectroscopy in solution,[8] vapor density measurements,[9] and ab initio MO calculations.[3,10–12] The most recent and most sophisticated theoretical study applying the MP2/6-31G* level of theory predicted S–N distances of 235.9 pm for **2** and 270.7 pm for $SO_2{\cdot}2NMe_3$ (**2a**).[3]

The preparation of the adducts $S_2O{\cdot}NMe_3$ (yellow crystals) and $SOCl_2{\cdot}NMe_3$ (colorless crystals) was reported in 1963.[13] Both compounds can be sublimed in a vacuum, probably with complete dissociation in the gas phase. However, neither spectra nor structural determinations or theoretical calculations are known for these complexes. To elucidate the structures, thermodynamics, and bonding of these

---

[a] Institut für Chemie, Technische Universität Berlin, Sekr. C2
10623 Berlin, Germany
Fax: +49-30-3142-6519
E-mail: steudel@sulfur-research.de

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

interesting adducts and of a number of related species we have carried out extensive quantum chemical calculations at the G3X(MP2) level of theory not only for **1**, **1a**, **2**, and **2a**, but also for the first time for the related complexes $S_2O·NH_3$ (**3**), $S_2O·NMe_3$ (**4**), $S_3·NH_3$ (**5**), $S_3·NMe_3$ (**6**), $SOCl_2·NH_3$ (**7**), $SOCl_2·NMe_3$ (**8**), and SONH·$NH_3$ (**9**). The Gibbs energies of formation from the separated components have also been calculated for the species **1**–**8** for the first time, both in the vapor phase and in a polar medium, to predict the thermodynamic stability of these compounds under standard and nonstandard conditions. All relative energies and enthalpies reported in the text for gas-phase species correspond to the G3X(MP2) level, while all reported structural parameters as well as the energies of solvated species correspond to the B3LYP/6-31G(2df,p) level of theory.

## Results and Discussion

### Adducts in the Gas Phase

#### *Adducts of $SO_2$*

The molecular structure of the complex $SO_2·NH_3$ (**1**) was confirmed to be of $C_s$ symmetry with a relatively long S–N bond of 266.3 pm. Other bond lengths are given in Figure 1 and bond angles are listed in Table S1 in the Supporting Information. The binding energy of **1** (–18.1 kJ mol$^{-1}$) is approximately one third that of $SO_2·NMe_3$ (see below), and the Gibbs energy for the formation reaction of **1** is even positive at 298 K (14.6 kJ mol$^{-1}$; Table 1). In other words, the gaseous complex **1** is not stable under standard conditions with respect to dissociation into the two components. However, at liquid nitrogen temperature (77 K) the Gibbs energy is negative (–10.9 kJ mol$^{-1}$), and even after a BSSE correction of +4.9 kJ mol$^{-1}$ has been applied the Gibbs energy is still –6.0 kJ mol$^{-1}$ (Table 1, last column).

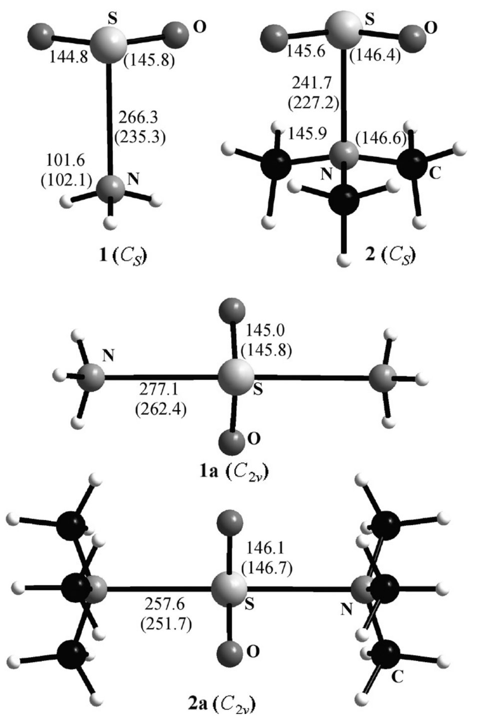

Figure 1. Structures, bond lengths (in pm), and symmetry of the complexes $SO_2·NH_3$ (**1**), $SO_2·2NH_3$ (**1a**), $SO_2·NMe_3$ (**2**), and $SO_2·2NMe_3$ (**2a**) in the gas phase. The bond lengths in a polar continuum of dielectric constant $\varepsilon$ = 40 are given in parentheses. All data calculated at the B3LYP/6-31G(2df,p) level of theory. See Table S1 (Supporting Information) for bond angles.

The S–O bonds of **1** (144.8 pm) are slightly longer than those calculated for $SO_2$ (144.3 pm). In line with this finding is the fact that the two S–O stretching vibrations are calculated to have somewhat lower wavenumbers (1162 and 1356 cm$^{-1}$) than predicted for free $SO_2$ at the same level of theory (1171 and 1381 cm$^{-1}$). The experimental values for the asymmetric SO stretching vibration of matrix-isolated **1** and of free $SO_2$ are 1338 and 1350 cm$^{-1}$,[2] respectively, in

Table 1. Reaction energies ($\Delta E_o$), enthalpies ($\Delta H°$), and Gibbs energies ($\Delta G°$) [uncorrected G3X(MP2) data in kJ mol$^{-1}$] for the formation of the gaseous donor–acceptor complexes **1**–**8** from their donor and acceptor components, as well as S–N bond lengths ($d_{SN}$) of the adducts along with the dipole moments ($\mu$, in Debye) of the sulfur component (acceptor) and of the complex, calculated at the B3LYP/6-31G(2df,p) level of theory. $\Delta e$ is the charge (in electrostatic units) transferred from the donor(s) to the acceptor on adduct formation, based on the NBO atomic charges. The BSSE correction to the reaction energy [kJ mol$^{-1}$] is given in the last-but-one column and is applied to the Gibbs energy at 77 K in the last column.

| Complex | $\Delta E_o$ | $\Delta H°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{77}$ | $\Delta G°_{77}$ | $d_{SN}$ | $\mu$ (acceptor) | $\mu$ (complex) | $\Delta e$ | BSSE correction | $\Delta G°_{77}$ corrected |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SO_2·NH_3$ (**1**) | –18.1 | –18.1 | +14.6 | –19.7 | –10.9 | 266.3 | 1.55 | 3.83 | 0.08 | +4.9 | –6.0 |
| $SO_2·2NH_3$ (**1a**) | –34.0 | –32.3 | +30.3 | –36.5 | –19.1 | 277.1 | 1.55 | 1.20 | 0.10 | +9.3 | –9.8 |
| $SO_2·NMe_3$ (**2**) | –51.5 | –50.9 | –7.3 | –53.0 | –41.1 | 241.7 | 1.55 | 4.34[a] | 0.16 | +11.8 | –29.3 |
| $SO_2·2NMe_3$ (**2a**) | –86.3 | –82.7 | +0.7 | –88.2 | –64.5 | 257.6 | 1.55 | 2.47 | 0.21 | +20.8 | –43.7 |
| $S_2O·NH_3$ (**3**) | –12.2 | –11.6 | +21.0 | –13.6 | –4.5 | 275.5 | 1.30 | 3.78 | 0.08 | +4.9 | +0.4 |
| $S_2O·NMe_3$ (**4**) | –48.4 | –47.5 | –1.3 | –49.8 | –37.1 | 246.1 | 1.30 | 4.78 | 0.20 | +12.2 | –24.9 |
| $S_3·NH_3$ (**5**) | –7.9 | –6.2 | +21.1 | –8.8 | –0.8 | 295.1 | 0.61 | 3.44 | 0.05 | +4.2 | +3.4 |
| $S_3·NMe_3$ (**6**) | –38.4 | –36.5 | +6.9 | –39.5 | –27.1 | 260.7 | 0.61 | 4.67 | 0.22 | +10.9 | –16.2 |
| $SOCl_2·NH_3$ (**7**) | +45.1 | +43.1 | +85.0 | +43.3 | +53.7 | 198.0 | 1.35 | 4.71 | 0.39 | +13.6 | +67.3 |
| $SOCl_2·NMe_3$ (**8**) | –4.8 | –3.5 | +44.8 | –5.7 | +7.0 | 214.9 | 1.35 | 6.87 | 0.39 | +19.7 | +26.7 |
| SONH·$NH_3$ (**9**) | –11.5 | –10.4 | +20.4 | – | – | 293.4 | 1.07 | 2.28 | – | – | – |

[a] Experimental value in the gas phase: 4.800(5) D;[7] estimated experimental value in benzene solution: 4.95 D.[29]

good agreement with our calculated data. As expected, the calculated O–S–O bond angle of **1** (117.7°) is slightly smaller than that calculated for $SO_2$ (119.2°) as a result of the higher coordination number at the sulfur atom. Our geometrical data are significantly different from the best previous theoretical results obtained at the MP2/6-31G* level.[3] The S–N bond, for example, is shorter (by 5.8 pm), although the overall conformation is identical. Surprisingly, the binding enthalpy calculated here is practically the same as that reported by Wong and Wiberg.[3] The absolute energies and enthalpies of complexes **1**–**9** and their components are given in Table S2.

The structure of the trimethylamine adduct **2** (Figure 1) is in agreement with previous theoretical calculations. The plane defined by the $SO_2$ unit is almost perpendicular to the $C_3$ axis of the donor $NMe_3$ (angle: 83.5°) and the shortest O···H contact is 266.4 pm. The calculated S–O bond length of 145.8 pm agrees very well with the value derived by Kuczkowski et al. from the microwave spectrum of gaseous **2** [144(1) pm] if the uncertainty of the experimental data is taken into account. These authors reported three S–N distances, depending on the type of data analysis with varying simplifications (232.8, 228.5, and 226.0 pm). The larger S–N bond length of 232.8 pm was derived from a least-squares fit of all isotopic data, although the smallest value [226(3) pm] was eventually recommended.[7] Thus, the "estimated uncertainty" of 3 pm reported by Kuczkowski et al. for the S–N distance may be just a lower limit. We obtained an S–N bond length of 239.6 pm by performing DFT calculations at the higher B3LYP/6-31+G(2df,p) level.

The agreement of the gas-phase structure of **2** with the solid-state structure is rather limited and most of the bond lengths differ considerably. In particular, our calculated S–N bond length of 241.7 pm is much larger than the reported solid state value of 204.6(4) pm.[7] This latter value may, however, be affected by packing forces and by the polar environment (see below) due to the large dipole moment (4.34 D) of this complex (Table 1). The charge transfer from the amine to the $SO_2$ unit can be calculated from the NBO atomic charges as being 0.16 electrostatic units. This value is in line with the upper limit of the charge transfer of 0.2–0.3 electrons estimated by Kuczkowski et al.[7] from the experimental dipole moment (4.80 D) and the nitrogen nuclear quadrupole coupling constants. The NBO charges on the sulfur atom (+1.64) and on the nitrogen atom (–0.50) remain practically constant during the formation of this complex, while the oxygen atoms become more negative, changing from –0.82 in $SO_2$ to –0.90 in **2**. In compensation, the nine hydrogen atoms become slightly more positively charged, changing from an average of +0.22 units in $NMe_3$ to +0.24 in **2**. Thus, the electron density moves essentially from the least electronegative atoms (H) to the most electronegative atoms (O) even though these atoms are far apart from each other. The same situation was found for the other adducts discussed below. It can be concluded from the geometry of complexes **1**–**6** that the charge transfer takes place into the π* molecular orbitals of the acceptor molecule. The binding energy is expected to result from charge delocalization as well as from mutual polarization.

The interaction energy between $SO_2$ and $NMe_3$ in the 1:1 complex **2** was first estimated by Grundnes and Christian in 1968 using the concentration- and temperature-dependence of the optical absorption of this charge-transfer complex near 275 nm in the temperature range 39–60 °C.[14] On the assumption that only a 1:1 complex is formed, even with the large excess of $NMe_3$ used in these experiments, the reaction enthalpy in the gas phase was determined as $-40.6 \pm 1.7$ kJ mol$^{-1}$. Our calculations, which include a BSSE correction, gave a $\Delta H^\circ_{298}$ value of $-50.9 + 11.8 = -39.1$ kJ mol$^{-1}$ for complex **2** and –61.9 kJ mol$^{-1}$ for the formation of the 1:2 complex **2a** from the three components (Table 1). The agreement between experiment and theory is therefore excellent.

In principle, the structures of **1**, **1a**, **2**, and **2a** are models not only for the nucleophilic attack of an amine on an $SO_2$ molecule but also more generally for the solvation of $SO_2$ by Lewis bases in solution and in the solid state. The calculated structures of the 1:2 adducts $SO_2{\cdot}2NH_3$ (**1a**) and $SO_2{\cdot}2NMe_3$ (**2a**) are shown in Figure 1, and bond angles are given in Table S1. These structures are in agreement with previous predictions.[3] No experimental structures of these species are known. The structure of **1a** ($C_{2v}$ symmetry) is characterized by two rather long S–N bonds (277.1 pm). The coordination sphere at the sulfur atom is pseudo-trigonal-bipyramidal, with the oxygen atoms and the assumed lone pair in the equatorial positions. The two axial S–N bonds are bent slightly towards the formal lone pair position with an N–S–N angle of 174.8°. An analogous structure is predicted for the related complex $SO_2{\cdot}2NMe_3$ (**2a**), which is also of $C_{2v}$ symmetry (Figure 1 and Table S1). The thermodynamic data of **1a** and **2a** are given in Table 1. The corrected Gibbs energies of formation of **1a** and **2a** from the components at 298 K are positive (39.6 and 21.5 kJ mol$^{-1}$, respectively), but the corresponding values at 77 K are negative (–9.8 and –43.7 kJ mol$^{-1}$, respectively). Both complexes are therefore predicted to be stable species in the gas phase only at temperatures well below 0 °C or in the presence of a large excess of the amine donor. The dipole moments of these two species are much smaller than those of the corresponding 1:1 complexes (Table 1).

### *Adducts of $S_2O$*

In the gas phase, disulfur monoxide is most conveniently prepared from thionyl chloride and silver sulfide at low pressures [Equation (1)]:[15]

$$SOCl_2 + Ag_2S \rightarrow S{=}S{=}O + 2\,AgCl \qquad (1)$$

This molecule was the first example of a compound containing a formal double bond between heavier main group elements to be isolated in a pure form at 20 °C. Gaseous $S_2O$ is stable for a few days at room temperature at pressures of less than 1 mbar.[16] On condensation, even at liquid nitrogen temperatures, immediate exothermic disproportionation and polymerization takes place, with the primary decomposition products being $S_3$ and $SO_2$ [Equation (2)]:[17]

$$2\ S_2O \rightarrow SO_2 + S_3 \qquad (2)$$

$$\Delta H^\circ_{298} = -49.5\ \mathrm{kJ\,mol^{-1}},\ \Delta G^\circ_{298} = -47.8\ \mathrm{kJ\,mol^{-1}}$$

We have investigated the structure and properties of the hypothetical adduct $S_2O{\cdot}NH_3$ (**3**), which is predicted to be $C_1$-symmetric with a structure analogous to that of $SO_2{\cdot}NH_3$ (**1**; see Figure 2). Due to the lower positive NBO charge on the central sulfur atom of $S_2O$ (+1.01) compared to $SO_2$ (+1.64), the interaction with Lewis bases is expected to be weaker. Thus, it is not surprising that the S–N bond of **3** is longer (275.5 pm) than that of **1** (266.3 pm). Interestingly, the length of the rather polar S=S bond of free $S_2O$ (190.8 pm) changes only slightly on complex formation with $NH_3$ (by +1.1 pm). The (uncorrected) dissociation enthalpy of **3** is only 11.6 kJ mol$^{-1}$ (Table 1). As a consequence of this weak interaction, the standard Gibbs energy of formation from the two components is positive (21.0 kJ mol$^{-1}$), which means that gaseous **3** is not a stable compound at room temperature.

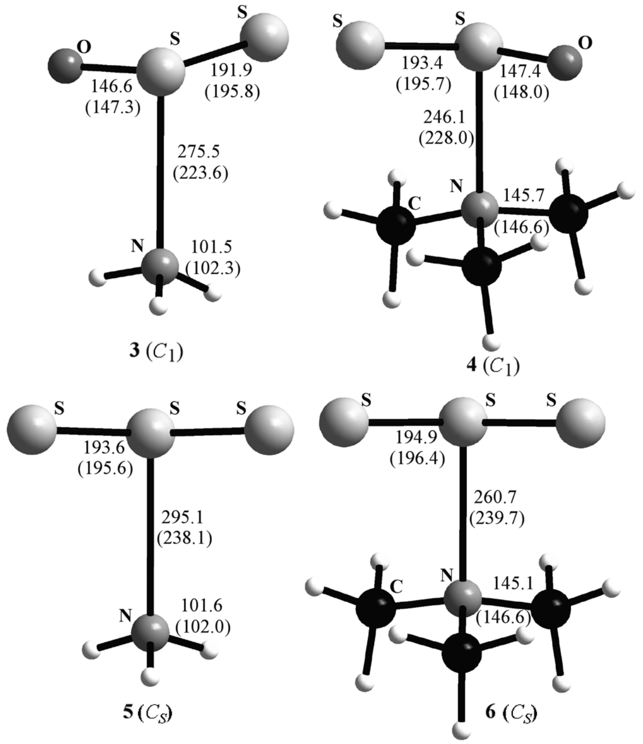

Figure 2. Structures, bond lengths (in pm), and symmetry of the complexes $S_2O{\cdot}NH_3$ (**3**), $S_2O{\cdot}NMe_3$ (**4**), $S_3{\cdot}NH_3$ (**5**), and $S_3{\cdot}NMe_3$ (**6**) in the gas phase. The bond lengths in a polar continuum of dielectric constant $\varepsilon = 40$ are given in parentheses. All data calculated at the B3LYP/6-31G(2df,p) level of theory. See Table S1 (Supporting Information) for bond angles.

The adduct $S_2O{\cdot}NMe_3$ (**4**) was prepared as yellow crystals that are stable only below –30 °C by co-condensation of $S_2O$ and $NMe_3$; its structure is unknown.[15] The calculated structure of **4** is shown in Figure 2 and bond angles are given in Table S1. The S–N bond (246.1 pm) is almost as short as that in $SO_2{\cdot}NMe_3$ (241.7 pm), therefore the interaction is clearly stronger than in the corresponding ammonia complex **3**. As a consequence, the S–S bond length increases by 2.6 pm compared to free $S_2O$ while the S–O bond length increases by only 0.9 pm. Interestingly, the S–N bond dissociation enthalpy of **4** (47.5 kJ mol$^{-1}$) is almost as large as that of the corresponding $SO_2$ adduct **2** (50.9 kJ mol$^{-1}$), whereas the standard Gibbs energy of the dissociation reaction is close to zero (–1.3 kJ mol$^{-1}$) and even becomes positive if a BSSE correction is applied (10.9 kJ mol$^{-1}$). This result explains the reported dissociation of **4** on sublimation in a vacuum. However, the Gibbs energy at 77 K is negative and **4** is expected to be a stable gas-phase species (Table 1).

### *Adducts of $S_3$*

The highly reactive molecule $S_3$ is a component of high-temperature sulfur vapors,[18] although $S_3$ has been isolated in inert matrices at low temperatures and characterized by vibrational and UV/Vis spectroscopy.[19] The structure of $S_3$ has been determined by microwave spectroscopy.[20] As mentioned above, $S_3$ is the primary disproportionation product of $S_2O$. Due to the small positive charge on the central atom of $S_3$ (NBO value: +0.33), adduct formation with $NH_3$ and $NMe_3$ is expected to be relatively weak. However, the structures of the corresponding complexes are analogous to those discussed above. Accordingly, the S–N bond of $S_3{\cdot}NH_3$ (**5**) is much longer (295.1 pm) than in any other adduct investigated in this work (see Table 1 and Figure 2). With the stronger base $NMe_3$, the S–N bond length decreases to 260.7 pm in $S_3{\cdot}NMe_3$ (**6**) (Figure 2). These structural properties are also reflected in the BSSE-corrected S–N bond-dissociation enthalpies, which are only 2.0 kJ mol$^{-1}$ for **5** and 25.6 kJ mol$^{-1}$ for **6** (Table 1). The Gibbs reaction energies for both **5** and **6** are positive at 298 K but negative for **6** at 77 K. In other words, $S_3$ may be stabilized by complex formation with $NMe_3$ at 77 K, in analogy to $S_2O$ (see above). One way to make **6** may be by disproportionation of **4**, in analogy to the reaction shown in Equation (3):

$$2S_2O{\cdot}NMe_3\ (\mathbf{4}) \rightarrow SO_2{\cdot}NMe_3\ (\mathbf{2}) + S_3{\cdot}NMe_3\ (\mathbf{6}) \qquad (3)$$

This reaction is predicted to be exothermic in the gas-phase by $\Delta H^\circ_{298} = -41.9$ kJ mol$^{-1}$ ($\Delta G^\circ_{298} = -45.7$ kJ mol$^{-1}$). It will be shown below that complex **6** is even more stable than in the gas phase at 77 K in a polar continuum.

### *Adducts of $SOCl_2$*

Thionyl chloride vapor reacts violently with gaseous ammonia with elimination of HCl and formation of thionyl imide [OSNH; Equation (4)]:[21]

$$SOCl_2 + 3NH_3 \rightarrow O{=}S{=}NH + 2NH_4Cl \qquad (4)$$

The reaction of $SOCl_2$ with $NH_3$ in solution produces $NH_4Cl$, $S_4N_4$, $NH_4(S_4N_4O)$, and other products.[22] The formation of the adduct $SOCl_2{\cdot}NH_3$ (**7**; Figure 3) may be the first step in these reactions. According to our calculations, this hypothetical molecule adopts an unusual pseudo-trigonal-bipyramidal structure with the chlorine atoms in axial positions. The S–N bond (198.0 pm) is shorter than in any of the other adducts studied in this work. Most remarkable, however, is the fact that the two chlorine atoms are bent towards the two nearest hydrogen atoms with a nonbonding Cl···H contact of just 254.7 pm and a Cl–S–Cl bond angle of 154.0° compared to 98.0° in free $SOCl_2$. Thus, the elimination of two molecules of HCl and formation of OSNH is already pre-organized in the structure of **7**, which has $C_s$ symmetry. Unexpectedly, the S–O bond of **7** is slightly shorter (143.8 pm) than calculated for free $SOCl_2$ (144.3 pm), and the SO stretching wavenumber of **7** is predicted to be larger (1285 $cm^{-1}$) than calculated for $SOCl_2$ (1271 $cm^{-1}$). The shortest O···H contact is 290.7 pm. Evidently, the considerable positive charge on the sulfur atom of $SOCl_2$ (+1.28) and the large negative charge on the nitrogen atom of $NH_3$ (–1.13) are responsible for the formation of a very short and very polar covalent S–N bond.

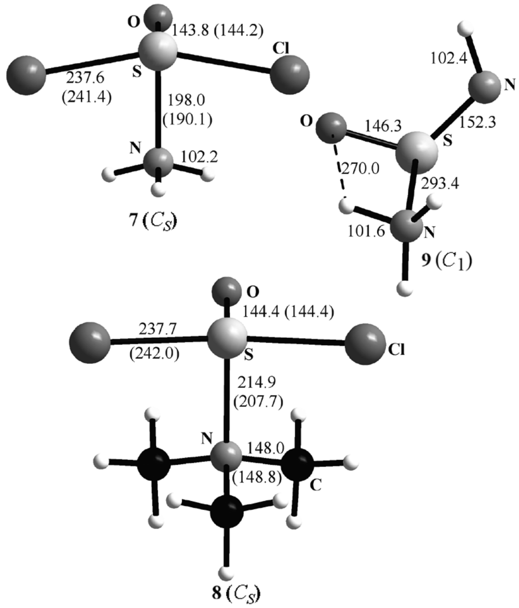

Figure 3. Structures, bond lengths (in pm), and symmetry of the complexes $SOCl_2·NH_3$ (**7**), $SOCl_2·NMe_3$ (**8**), and $SONH·NH_3$ (**9**) in the gas phase. The bond lengths of **7** and **8** in a polar continuum of dielectric constant $\varepsilon = 40$ are given in parentheses. All structures calculated at the B3LYP/6-31G(2df,p) level of theory. See Table S3 (Supporting Information) for bond angles.

However, **7** is not a stable species in the gas phase at 298 K since the binding energy is positive, as is the Gibbs energy of formation from the two components. The energy gained on S–N bond formation is evidently overcompensated by the simultaneous weakening of the two S–Cl bonds, which increase dramatically in length from 212.2 pm in $SOCl_2$ to 237.6 pm in **7**. On the other hand, the NH bond lengths increase by only 0.5 pm. The bond angles of **7** are listed in Table S2.

The formation of gaseous SONH via the hypothetical intermediate $Cl–SO–NH_2$ is exergonic, as shown by the data in Equations (5), (6), and (7):

$$SOCl_2 + NH_3 \rightarrow Cl–SO–NH_2 + HCl \qquad (5)$$
$$\Delta H^\circ_{298} = -10.2\ \text{kJ mol}^{-1},\ \Delta G^\circ_{298} = -4.7\ \text{kJ mol}^{-1}$$

$$Cl–SO–NH_2 \rightarrow O{=}S{=}NH + HCl \qquad (6)$$
$$\Delta H^\circ_{298} = +20.1\ \text{kJ mol}^{-1},\ \Delta G^\circ_{298} = -21.2\ \text{kJ mol}^{-1}$$

$$SOCl_2 + NH_3 \rightarrow O{=}S{=}NH + 2\ HCl \qquad (7)$$
$$\Delta H^\circ_{298} = +9.9\ \text{kJ mol}^{-1},\ \Delta G^\circ_{298} = -25.9\ \text{kJ mol}^{-1}$$

For comparison, the formation of SONH from $SO_2$ is predicted to be strongly endothermic and endergonic [Equation (8)]:

$$SO_2 + NH_3 \rightarrow O{=}S{=}NH + H_2O \qquad (8)$$
$$\Delta H^\circ_{298} = +50.5\ \text{kJ mol}^{-1},\ \Delta G^\circ_{298} = +51.6\ \text{kJ mol}^{-1}$$

In contrast to the hypothetical $SOCl_2·NH_3$, a compound of composition $SOCl_2·NMe_3$ (**8**) has been prepared[15] but its structure is unknown. The predicted structure of gaseous **8** is similar to that of **7** and is also of $C_s$ symmetry (Figure 3; see Table S3 for bond angles). The S–Cl bonds are again quite long (237.7 pm) but the S–N bond (214.9 pm) is considerably longer than in **7** (198.0 pm). The charge difference between N (–0.43) and S (+1.40) is 1.83 units in **8**, which results in a large dipole moment of 6.87 D (Table 1). One can therefore expect this structure to change considerably in a polar environment (see below). All fundamental vibrations of **8** are strongly coupled with other modes. The wavenumber of the S–O stretching mode is predicted to be 1262 $cm^{-1}$, compared to 1271 $cm^{-1}$ calculated for free $SOCl_2$.

Gaseous $SOCl_2·NMe_3$ seems to be unstable under standard conditions since the Gibbs energy of the formation reaction is positive. This also holds for a temperature of 77 K if the BSSE correction is taken into account (Table 1). We will show below, however, that the formation of **8** is more favorable in a polar medium.

### *Adduct of SONH*

We have also investigated the structure of a 1:1 adduct of thionyl imide with ammonia, namely $SONH·NH_3$ (**9**; see Figure 3). The very long S–N bond (293.4 pm) and the rather small (uncorrected) dissociation enthalpy of 10.4 kJ $mol^{-1}$ are surprising since there is an additional O···H bonding interaction between the sulfinyl group and one of the hydrogen atoms of $NH_3$, as can be deduced from the close contact distance of 270.0 pm. This additional interaction can be interpreted as a Coulomb attraction between the positively charged H atom and the π electrons of the almost planar OSNH molecule (O=S=N–H torsion angle: 3.5°) with an H–N–S=O torsion angle of 2.5°. On the other hand, this type of interaction is also known as hyperconjugation between the π electrons of the sulfinyl group and the antibonding σ orbital of the NH bond. The $NH_3$ group is tilted with respect to the S–N single bond as a consequence of this O···H attraction but the N–H bond lengths within the ammonia molecule are all identical (101.6 pm). Because of the small interaction energy of **9** we did not analyze this species any further (see Tables 1 and S2 for more details). Compound **9** may exist as $[NH_4][SON]$ in the solid state.

### *General Considerations*

Analysis of the data in Table 1 reveals that there is an inverse relationship between the formation enthalpies ($\Delta H°_{298}$) of adducts **1**–**8** and the S–N bond lengths, although there is a considerable scattering of the data. No such relationship exists between $\Delta H°_{298}$ and the dipole moments of the acceptors. This is not surprising since the dipole moment vectors of donor and acceptor are almost perpendicular to each other in adducts **1**–**6**. In other words, the dipole–dipole attraction can only be a minor contribution to the interaction energy in these complexes. On the other hand, the charge transfer, $\Delta e$, from donor to acceptor is clearly related to the dissociation enthalpy – a higher $\Delta e$ gives a more negative $\Delta H°_{298}$ (Table 1).

Adduct formation becomes more favorable at low temperatures due to a decrease of the reaction entropy. To study this effect we chose a temperature of 77 K as liquid nitrogen is normally used for cold traps in preparative experiments. The Gibbs energies for the adduct-formation reactions are provided for this temperature in Table 1, assuming all reactants and products still to be gaseous. The data corrected for the BSSE indicate that all adducts except $S_3{\cdot}NH_3$, $SOCl_2{\cdot}NH_3$, and $SOCl_2{\cdot}NMe_3$ are stable at this temperature in the gas phase ($\Delta G°_{77} < 0$).

## Adducts in a Polar Continuum

As outlined above, the transfer of the highly polar adducts **1**–**8** into a polar continuum is expected to result in their stabilization and considerable structural changes, although the polar components are also stabilized in this kind of continuum. Our thermodynamic data calculated at the B3LYP/6-31G(2df,p) level of theory using the polar continuum model (PCM) are summarized in Table 2. The results reveal that all ammonia complexes, with the exception of $SOCl_2{\cdot}NH_3$ (**7**), are expected to be less stable at $\varepsilon = 40$ while all the trimethylamine complexes are predicted to be more stable than in the gas phase. Definitely negative Gibbs energies of formation are predicted at 298 K only for $SO_2{\cdot}NMe_3$ and $S_2O{\cdot}NMe_3$, and these two species do in fact exist as crystalline solids. The reported compound of composition $SOCl_2{\cdot}NMe_3$[15] may therefore have a different structure than assumed in this work. An alternative to the donor–acceptor adduct would be an ionic solid $[Me_3NSOCl]^+Cl^–$ containing a pyramidal coordinated sulfur atom as in $SOCl_2$.

The standard Gibbs energy of formation in the case of $S_3{\cdot}NMe_3$ is close to zero (–0.8 kJ mol$^{–1}$), which means that this adduct may exist at temperatures considerably lower than 25 °C. This prediction is more convincing if one uses the energies of formation of the complexes in the polar continuum but with respect to the *gaseous* components. The corresponding data are presented in Table 3. All complexes except $S_2O{\cdot}NH_3$ and $S_3{\cdot}NH_3$ are thermodynamically stable under standard conditions and with respect to their components, even $SOCl_2{\cdot}NMe_3$. Experimental data are available for the two ammonia complexes of $SO_2$. The reaction enthalpies of the solid adducts from the gaseous components have been determined as –40 ± 4 kJ mol$^{–1}$ for **1** and –96 ± 19 kJ mol$^{–1}$ for **1a** from equilibrium vapor measurements.[1] Our calculations of the reaction enthalpies in the polar continuum but from the gaseous components resulted in enthalpy values of –57.1 and –81.7 kJ mol$^{–1}$, respectively (Table 3), in fair agreement with experiment, especially if the BBSE correction is applied qualitatively.

Table 3. Reaction energies ($\Delta E_o$), enthalpies ($\Delta H°_{298}$), and Gibbs energies ($\Delta G°_{298}$) [G3X(MP2) in kJ mol$^{–1}$] for the formation of the solvated donor–acceptor complexes **1**–**8** in a polar continuum of dielectric constant $\varepsilon = 40$, but from the gaseous components.

| Complex | $\Delta E_o$ (solv-gas) | $\Delta H°_{298}$ (solv-gas) | $\Delta G°_{298}$ (solv-gas) |
|---|---|---|---|
| $SO_2{\cdot}NH_3$ (**1**) | –55.7 | –57.1 | –21.3 |
| $SO_2{\cdot}2NH_3$ (**1a**) | –82.5 | –81.7 | –23.3 |
| $SO_2{\cdot}NMe_3$ (**2**) | –85.6 | –85.5 | –40.0 |
| $SO_2{\cdot}2NMe_3$ (**2a**) | –114.9 | –111.6 | –26.6 |
| $S_2O{\cdot}NH_3$ (**3**) | –37.4 | –39.2 | +2.1 |
| $S_2O{\cdot}NMe_3$ (**4**) | –79.7 | –79.2 | –30.9 |
| $S_3{\cdot}NH_3$ (**5**) | –16.5 | –17.3 | +21.5 |
| $S_3{\cdot}NMe_3$ (**6**) | –62.5 | –61.0 | –15.0 |
| $SOCl_2{\cdot}NH_3$ (**7**) | –44.4 | –46.2 | –4.3 |
| $SOCl_2{\cdot}NMe_3$ (**8**) | –54.0 | –51.6 | –10.6 |

Table 2. Reaction energies, enthalpies, and Gibbs energies [kJ mol$^{–1}$] for the formation of the solvated donor–acceptor complexes **1**–**8** from their components in the gas phase ($\Delta E_o$ only) and in a polar continuum of dielectric constant $\varepsilon = 40$, as well as S–N bond lengths [pm] and dipole moments [D] of the solvated adducts, all calculated at the B3LYP/6-31G(2df,p) level of theory.

| Complex | $\Delta E_o$ (gas) | $\Delta E_o$ (solv) | $\Delta H°_{298}$ (solv) | $\Delta G°_{298}$ (solv) | $d_{SN}$ (solv) | $\mu$ (solv) |
|---|---|---|---|---|---|---|
| $SO_2{\cdot}NH_3$ (**1**) | –31.2 | –15.0 | –16.5 | +21.2 | 235.3 | 6.28 |
| $SO_2{\cdot}2NH_3$ (**1a**) | –50.7 | –21.7 | –20.9 | +39.2 | 262.4 | 3.71 |
| $SO_2{\cdot}NMe_3$ (**2**) | –47.9 | –56.8 | –56.5 | –9.5 | 227.2 | 6.54 |
| $SO_2{\cdot}2NMe_3$ (**2a**) | –73.3 | –77.8 | –74.3 | +12.0 | 251.7 | 3.46 |
| $S_2O{\cdot}NH_3$ (**3**) | –24.1 | –5.2 | –5.3 | +36.1 | 223.6 | 7.71 |
| $S_2O{\cdot}NMe_3$ (**4**) | –42.8 | –57.5 | –57.0 | –8.9 | 228.0 | 7.81 |
| $S_3{\cdot}NH_3$ (**5**) | –15.7 | +9.5 | +8.7 | +47.6 | 238.3 | 7.10 |
| $S_3{\cdot}NMe_3$ (**6**) | –32.0 | –48.2 | –46.8 | –0.8 | 239.7 | 7.90 |
| $SOCl_2{\cdot}NH_3$ (**7**) | +18.3 | –11.8 | –13.9 | +28.5 | 190.1 | 7.20 |
| $SOCl_2{\cdot}NMe_3$ (**8**) | +7.7 | –33.3 | –31.1 | +10.2 | 207.5 | 9.66 |

Table 4. Selected fundamental modes of the gaseous adducts **1**–**4** and **6** (wavenumbers in cm$^{-1}$), calculated at the B3LYP/6-31G(2df,p) level of theory (X, Y, Z = O, S). Wavenumbers for the polar continuum of dielectric constant 40 are given in parentheses (ν: stretching mode; δ: bending mode).

| Mode | $SO_2 \cdot NH_3$ (**1**) | $SO_2 \cdot NMe_3$ (**2**) | $S_2O \cdot NH_3$ (**3**) | $S_2O \cdot NMe_3$ (**4**) | $S_3 \cdot NMe_3$ (**6**) |
|---|---|---|---|---|---|
| $\nu_{SO}$ | 1166/1356 (1134/1275) | 1137/1319 (1099/1249) | 1194 (1149) | 1160 (1118) | – |
| $\nu_{SS}$ | – | – | 671 (630) | 652 (607) | 582/655 (562/599) |
| $\nu_{SN}$ | 131 (165) | 128 (149) | 161 (174) | 133/283[a](155/317)[a] | 97 (121) |
| $\nu_{NC}$ (symm.) | – | 819 (809) | – | 817 (805) | 819 (806) |
| $\delta_{XYZ}$ | 528 (551) | 529 (533) | 385 (365) | 381 (379) | 267 (280) |

[a] Splitting due to coupling with other modes.

The structural changes on transfer of the gaseous complexes into a medium of dielectric constant $\varepsilon = 40$ mainly concern the S–N bonds, which shorten dramatically in adducts **1**–**6** but much less so in the $SOCl_2$ complexes **7** and **8**. Accordingly, the calculated structure of $SO_2 \cdot NMe_3$ (**2**) at $\varepsilon = 40$ is in much better agreement with the X-ray structure of this complex than the structure predicted for the gas phase. For instance, the calculated S–N bond length decreases from 241.7 pm in the gas phase to 227.2 pm at $\varepsilon = 40$ (a value of 204.6 pm has been derived crystallographically).[7] The O–S–O, O–S–S, and S–S–S bond angles of species **2** all decrease by about 2° in the polar medium (Table S1), and the symmetry of some complexes (e.g., **1**, **1a**, and **8**) is lower in the polar medium ($C_1$) than in the gas phase.

The vibrational spectra also reflect the structural changes of the adducts between the gas phase and the polar continuum. In general, the fundamental modes are strongly coupled due to the low symmetry of the complexes, although a few assignments can be made. The most important vibrations of the acceptor parts of the molecules are given for both phases in Table 4. Thus, while the S–O and S–S stretching vibrations are shifted to lower wavenumbers in the polar continuum, the S–N stretching modes are predicted to appear at higher wavenumbers in the polar phase. For example, the two S–O stretching vibrations of $SO_2$ vary from 1171/1381 cm$^{-1}$ for gaseous $SO_2$, via 1166/1356 cm$^{-1}$ for gaseous $SO_2 \cdot NH_3$ and 1137/1319 cm$^{-1}$ for gaseous $SO_2 \cdot NMe_3$, to 1099/1249 cm$^{-1}$ for $SO_2 \cdot NMe_3$ in the polar continuum. The vibrations of the $NMe_3$ units in complexes **2**, **4**, and **6**, however, are much less affected. For example, the symmetrical stretching mode of the $NC_3$ skeleton always occurs at $818 \pm 1$ cm$^{-1}$ in the gas phase and at $807 \pm 2$ cm$^{-1}$ in the polar continuum, whereas the bending modes of the acceptors do not show any uniform shift on transfer of the gaseous complexes into the polar continuum.

## Conclusions

According to our G3X(MP2) calculations, the structures of the adducts $SO_2 \cdot NH_3$ (**1**), $SO_2 \cdot 2NH_3$ (**1a**), $SO_2 \cdot NMe_3$ (**2**), $SO_2 \cdot 2NMe_3$ (**2a**), $S_2O \cdot NH_3$ (**3**), $S_2O \cdot NMe_3$ (**4**), $S_3 \cdot NH_3$ (**5**), $S_3 \cdot NMe_3$ (**6**), $SOCl_2 \cdot NH_3$ (**7**), $SOCl_2 \cdot NMe_3$ (**8**), and $SONH \cdot NH_3$ (**9**) correspond to energy minima on the corresponding potential hypersurfaces. However, only **2** and **4** are thermodynamically stable in the gas phase under standard conditions with respect to their acceptor and donor components ($\Delta G°_{298} < 0$). The latter two complexes have, in fact, been prepared as solid materials. Species **2**, **4**, and **6** are predicted to be stable in a polar continuum of dielectric constant $\varepsilon = 40$. Thus, the preparation of $S_3 \cdot NMe_3$ can be expected in the future. All species except **3** and **5** are thermodynamically stable if the equilibrium between the gaseous components and the adduct in the polar continuum is analyzed. The structures of complexes **3**–**9** have been calculated for the first time. The structural changes on complex formation as well as the vibrational spectra indicate a weakening of the bonds in the acceptor molecule, in particular in the polar continuum. On the other hand, the donor–acceptor interaction is stronger in the polar environment than in the gas phase and, as a consequence, the S–N bond lengths are shorter under such circumstances.

## Computational Details

The structures and energies of the various complexes were examined according to G3X(MP2) theory[23] using the GAUSSIAN 03[24] program package. This composite method corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy calculations together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2) [25] theory with three important changes: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large basis set for the second-row atoms at the Hartree–Fock level. All three features are particularly important for the correct description of the sulfur-containing species examined in this work. Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real. A charge density analysis was performed for all investigated species using the natural bond orbital (NBO) approach based on the B3LYP/6-31G(2df,p) wavefunction.[26] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[27] As far as gas-phase species are concerned, all relative energies and enthalpies reported in the text correspond to the G3X(MP2) level, while all reported structural parameters correspond to the B3LYP/6-31G(2df,p) level. The correction to the basis set superposition error (BSSE) was calculated at the MP2/GTMP2Large level using the counterpoise method of the GAUSSIAN 03 program. Since this correction is calculated with fixed monomer geometries, taken from the complexes, the obtained data must be considered as upper limits, especially if there is a strong deformation, as is the case for the thionyl chloride complexes.

The investigated complexes are characterized by large dipole moments, therefore it is to be expected that the thermodynamics of formation of such species in the solid state and in polar solvents will be quite different from that in the gas phase. Calculations according to Tomasi's polar continuum model (PCM)[28] were carried out at the B3LYP/6-31G(2df,p) level to study the influence of a polar environment. This method of studying the electrostatic solute/solvent interaction has proven to be very successful in reproducing solvent effects as the solvent is represented by a continuous dielectric, characterized by a given dielectric constant ($\varepsilon$), and the solute is assumed to be embedded in a cavity in the medium. The permanent dipole of the solute induces a dipole in the medium, which in turn interacts with the molecular dipole leading to stabilization. A dielectric constant of 40.0 was used for the PCM calculations to represent the polar medium. No such calculations on complexes **1**–**8** have been reported so far.

**Supporting Information** (see footnote on the first page of this article): Absolute energies, bond angles, and atomic coordinates of compounds **1**–**8**.

## Acknowledgments

We appreciate invaluable advice from Prof. Ming Wah Wong (Richard), Singapore, and support from the Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen (HLRN).

---

[1] R. Landreth, R. G. de Pena, J. Heicklen, *J. Phys. Chem.* **1974**, *78*, 1378. Earlier work (W. D. Scott, D. Lamb, *J. Am. Chem. Soc.* **1970**, *92*, 3943) seems to be in error since the derived enthalpies of dissociation are much too large.
[2] C. S. Cass, B. S. Ault, *J. Phys. Chem.* **1984**, *88*, 432.
[3] M. W. Wong, K. B. Wiberg, *J. Am. Chem. Soc.* **1992**, *114*, 7527.
[4] For older theoretical calculations, see: a) R. R. Lucchese, K. Haber, H. F. Schaefer, *J. Am. Chem. Soc.* **1976**, *98*, 7617; b) J. E. Douglas, P. A. Kollman, *J. Am. Chem. Soc.* **1978**, *100*, 5226. The theoretical levels in these investigations are much lower and in some cases rigid geometries based on experimental data were used for the components of the complexes.
[5] A. B. Burg, *J. Am. Chem. Soc.* **1943**, *65*, 1629.
[6] D. van der Helm, J. D. Childs, S. D. Christian, *J. Chem. Soc. C* **1969**, 887.
[7] J. J. Oh, M. S. LaBarge, J. Matos, J. W. Kampf, K. W. Hillig, R. L. Kuczkowski, *J. Am. Chem. Soc.* **1991**, *113*, 4732.
[8] J. Grundnes, S. D. Christian, *J. Am. Chem. Soc.* **1968**, *90*, 2239.
[9] J. Grundnes, S. C. Christian, V. Cheam, S. B. Farnham, *J. Am. Chem. Soc.* **1971**, *93*, 20.
[10] R. R. Lucchese, K. Haber, H. F. Schaefer, *J. Am. Chem. Soc.* **1976**, *98*, 7617.
[11] J. E. Douglas, P. A. Kollman, *J. Am. Chem. Soc.* **1978**, *100*, 5226.
[12] S. Sakaki, H. Sato, Y. Imai, K. Morokuma, K. Ohkubo, *Inorg. Chem.* **1985**, *24*, 4538.
[13] a) P. W. Schenk, R. Steudel, *Z. Anorg. Allg. Chem.* **1966**, *342*, 265; b) P. W. Schenk, R. Steudel, *Angew. Chem.* **1963**, *75*, 793; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 685.
[14] J. Grundnes, S. D. Christian, *J. Am. Chem. Soc.* **1968**, *90*, 2239.
[15] a) P. W. Schenk, R. Steudel, *Z. Anorg. Allg. Chem.* **1966**, *342*, 253; b) P. W. Schenk, R. Steudel, *Angew. Chem.* **1964**, *76*, 97; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 61.
[16] Review: R. Steudel, *Top. Curr. Chem.* **2003**, *231*, 203.
[17] a) R. Steudel, *Eur. J. Inorg. Chem.* **2004**, 3513; b) J. Nakayama, S. Aoki, J. Takayama, A. Sakamoto, Y. Sugihara, A. Ishi, *J. Am. Chem. Soc.* **2004**, *126*, 9085.
[18] Review: R. Steudel, Y. Steudel, M. W. Wong, *Top. Curr. Chem.* **2003**, *230*, 117.
[19] Review: B. Eckert, R. Steudel, *Top. Curr. Chem.* **2003**, *231*, 31.
[20] M. C. McCarthy, S. Thorwirth, C. A. Gottlieb, P. Thaddeus, *J. Am. Chem. Soc.* **2004**, *126*, 4096.
[21] P. W. Schenk, *Ber. Detsch. Chem. Ges.* **1942**, *75B*, 94.
[22] a) R. Steudel, *Z. Naturforsch. Teil B* **1969**, *24*, 934; b) R. Steudel, P. Luger, H. Bradaczek, *Angew. Chem.* **1973**, *85*, 307; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 316.
[23] L. A. Curtiss, P. C. Redfern, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **2001**, *114*, 108.
[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN 98*, Gaussian Inc., Pittsburgh, PA, **1998**.
[25] L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1999**, *110*, 4703.
[26] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[27] M. Messerschmidt, A. Wagner, M. W. Wong, P. Luger, *J. Am. Chem. Soc.* **2002**, *124*, 732.
[28] a) S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117; b) S. Miertus, J. Tomasi, *Chem. Phys.* **1982**, *65*, 239; c) M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327.
[29] J. A. Moede, C. Curran, *J. Am. Chem. Soc.* **1949**, *71*, 852.

Received: April 11, 2007