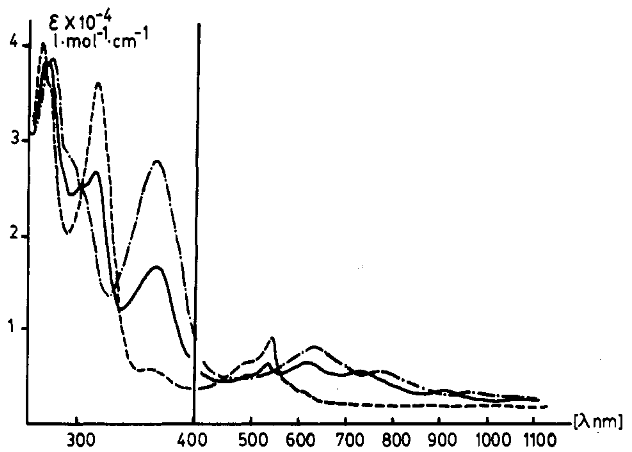

Figure 6. Absorption spectra of $[Fe(terpy)_2]^{2+/+/0}$ in DMF-TBABF$_4$ solution at 25 °C (V vs ferrocene/ferrocenium): (---) parent; (—) singly reduced species at −1.527 V; (−·−) doubly reduced species at −1.711 V.

difference between these two bands being approximately 5000 cm^{-1} (0.63 eV). The band at 31 400 cm^{-1} has slightly shifted to lower energies and has lost about half its intensity on going to the reduced species. The loss of intensity in this absorption band is due to the loss of neutral terpy function. The new band at 27 000 cm^{-1} in singly reduced IV then correlates with the 26 500 cm^{-1} band of free [terpy]$^-$. Another $\pi \rightarrow \pi^*$ transition of [terpy]$^-$ appears at 35 200 cm^{-1}. The band at 17 800 cm^{-1} of IV, assigned as MLCT, is apparently moved slightly to higher energy and loses intensity when the complex becomes singly reduced. More $\pi^* \rightarrow \pi^*$ transitions appear at around 16 800, 13 200, and 10 700 cm^{-1} and shift to lower energy on going to the doubly reduced species. The spectra of IV$^-$ shows $\pi \rightarrow \pi^*$ transitions of both neutral terpy and [terpy]$^-$ ligands in the same complex ion. This shows that when the IV is singly reduced, the added electron is localized (on the UV timescale) on one of the coordinated terpy ligands. Similar results have been reported[2e] for $[Ru(terpy)_2]^{2+}$, but the extension to IV, with its smaller central metal ion, is not obvious.

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Registry No. I, 15025-74-8; I$^+$, 18661-69-3; I$^-$, 51383-17-6; I^{2-}, 15388-61-1; I^{3-}, 19709-86-5; II, 70529-75-8; II$^+$, 96042-46-5; II$^-$, 138355-71-2; II^{2-}, 138355-72-3; II^{3-}, 138355-73-4; III, 14708-99-7; III$^+$, 13479-49-7; III$^-$, 134587-89-6; III^{2-}, 15187-23-2; III^{3-}, 134961-06-1; IV, 17455-70-8; IV$^+$, 47779-99-7; IV$^-$, 75324-87-7; IV^{2-}, 20515-11-1; DMF, 68-12-2; TBA(BF$_4$), 429-42-5; terpy, 1148-79-4; [terpy]$^{\bullet-}$, 138384-34-6; bpy, 366-18-7; bpym, 34671-83-5.

Contribution from the Department of Chemistry, University of Leipzig, O-7010 Leipzig, Germany, and Humboldt University, O-1040 Berlin, Germany

Influence of Coligands on the η^1-Coordination Mode of SO_2 in L_3NiSO_2 Complexes. A Pseudopotential ab Initio Study

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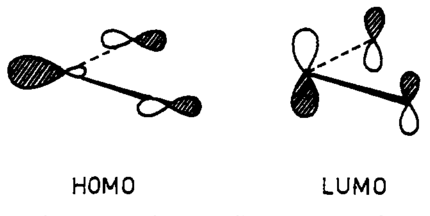
In tris(phosphine)(sulfur dioxide)nickel(0) complexes the mode of η^1-coordination of SO$_2$ depends in a very sensitive way on the nature of the phosphine coligands, i.e., their electronic and steric influences. MO calculations on the pseudopotential ab initio level show that the experimental structure (η^1-pyramidal vs η^1-coplanar coordination of SO$_2$) is a consequence of various different and partially counteracting influences of the coligands. The recently found unusual η^1-pyramidal mode as compared to the usual η^1-coplanar one can be expected to be obtained by coligands which are small and have strong donor power as well.

Introduction

In recent years the coordination chemistry of sulfur dioxide has received considerable attention. Due to the growing environmental problems the need for detailed knowledge of all aspects of SO$_2$ chemistry is obvious. In addition, however, the investigation of structure and bonding of transition-metal sulfur dioxide complexes is a fascinating topic of modern coordination chemistry. SO$_2$ seems to be the ligand with the greatest variety of coordination modes. Due to its ability to behave either as a Lewis base or as a Lewis acid, it can attain η^1-coplanar, η^1-pyramidal or η^2-bonding to transition-metal fragments. Moreover, there exist various polynuclear SO$_2$-bridged species. Reviews about the coordination variety have been published by Ryan et al.[1] and Schenk.[2]

Depending on its coordinate bond nature, the SO$_2$ ligand is more or less activated and shows a different reaction behavior. As an important example the oxidation of the d^{10}-metal complexes L_3NiSO_2 with O$_2$ leading to bidentate coordinated sulfate seems to be typical for the η^1-pyramidal coordination mode, whereas in the case of η^1-coplanar SO$_2$ an unspecific destruction of the complex moiety is observed.[1,3] In general, in the case of M = Ni the coplanar coordination is preferred, and in the case of M = Pd and Pt, the pyramidal coordination is preferred.

Chart I



The frontier orbitals of sulfur dioxide are shown in Chart I. Sakaki et al.[4] have extensively investigated the bonding in d^{10}-metal sulfur dioxide complexes using ab initio molecular orbital methods. They found for $(PH_3)_3NiSO_2$ that due to electronic reasons the η^1-pyramidal structure should be favored (see Chart II). In the coplanar coordination mode the SO$_2$ lone-pair orbital strongly overlaps with the occupied d$_\sigma$ orbital of the d^{10} transition metal to cause a large four-electron destabilization. In the pyramidal mode the lone-pair orbital overlaps with a Ni d$_\pi$ orbital, causing

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[†] University of Leipzig.
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(1) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding* **1981**, *46*, 48.
(2) Schenk, W. A. *Angew. Chem.* **1987**, *99*, 101.
(3) Mehandru, S. P.; Anderson, A. B. *Inorg. Chem.* **1985**, *24*, 2570.
(4) Sakaki, S.; Sato, H.; Imai, Y.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1985**, *24*, 4538.

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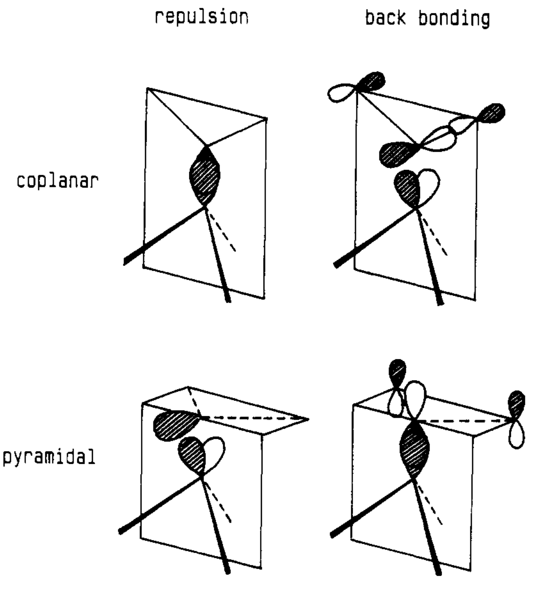
Chart II



a smaller four-electron destabilization. The π-back-donation from the Ni d_π orbital to the LUMO (π^*) of SO_2 is of a moderate amount in the coplanar structure, whereas in the pyramidal one a larger σ type back-donation from the Ni d_σ orbital to the SO_2 occurs. On the other hand, however, the steric repulsion between SO_2 and bulky PR_3 ligands is considerably larger in the η^1-pyramidal structure than in the coplanar structure. Consequently, the determining cause for coplanar coordination mode, experimentally observed in complexes $(PR_3)_3NiSO_2$, should be the smaller steric repulsion in this structure.

From the experimental fact that $(PPh_3)_3NiSO_2$ shows a coplanar coordination mode and from Sakaki's work that even for the very small coligands PH_3 the same structure should be expected, it could have been concluded that for all phosphine coligands the steric factor overcomes the electronic one. Recently, however, the complex $(PPhMe_2)_3NiSO_2$ has been synthesized[5] and investigated by X-ray diffraction.[6] It has turned out that SO_2 shows a strongly bent structure. Since $(PPhMe_2)_3NiSO_2$ can be oxidized with O_2 to a sulfato complex,[5] it represents the first example of a (phosphine)(sulfur dioxide)nickel complex with the η^1-pyramidal coordination mode of SO_2. From all these facts it must be concluded that the structure of the coordinated SO_2 is influenced in a very sensible way by the coligands in the complex. Preliminary quantum chemical investigations concerning this influence have been performed.[8] In the present work nonempirical MO calculations are carried out on the complex system $(PH_3)_3NiSO_2$. By suitable simulation of the phosphine ligands, the influence of the electronic and steric properties of the coligands on the coordination structure of SO_2 is investigated.

Computational Details

Closed-shell calculations at the SCF level were carried out with the PSHONDO program,[9] which includes the adaptation of the general ab initio pseudopotentials of Durand and Barthelat.[10,11] For nickel a pseudopotential and a double-ζ valence basis set[12] augmented by p polarization functions[13] [21/11/41] were used. This basis set yields a d^{10} configuration for the nickel atom in the complex investigated. For phosphorus and oxygen pseudopotentials and valence functions of single-ζ quality were taken from ref 14. The minimal STO-3G basis was used for hydrogen. For the sulfur donor atom, which realizes the bonding interaction with nickel, a more flexible basis was employed. We tried to determine a basis set not too large but as good as possible to reproduce the geometry of the SO_2 molecule. This is of special importance because the change of this geometry due to the coordination was just under study. It turned out that a valence split basis set [31/31][15] is necessary, which was augmented by one d orbital. With a d exponent of 0.406 the optimized values R_{S-O} = 143.5 pm and $\angle OSO$ = 116.1° are obtained (experimental values 143.08 pm and 119.32°, respectively). The pseudopotential for sulfur was also taken from ref 15.

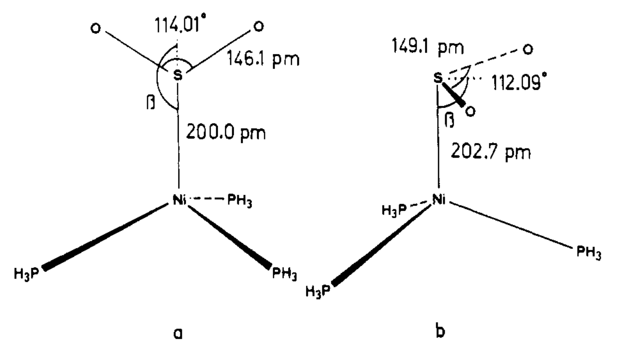


Figure 1. Optimized structural parameters for $(PH_3)_3NiSO_2$ with η^1-coplanar (β = 180°) and η^1-pyramidal (β = 90°) SO_2 coordination.

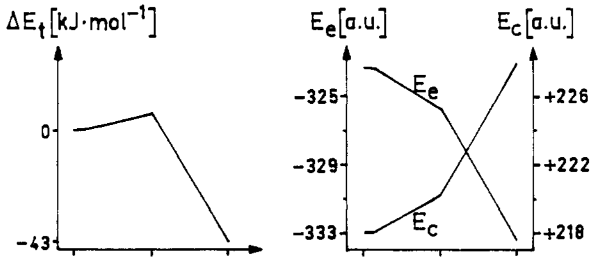


Figure 2. Total energy E_t, electronic energy E_e, and core repulsion E_c during the transition from η^1-coplanar (β = 180°) to η^1-pyramidal (β = 90°) SO_2 coordination.

Geometry optimization was limited to the parameters of importance: the Ni–S bond length and the internal SO_2 geometry. The fragment $(PH_3)_3Ni$ was not optimized but fixed to have a geometrical mean from experimental bond lengths and angles for various complexes $(PR_3)_3NiSO_2$. We used a regular trigonal structure with R_{Ni-P} = 226.0 pm, $\angle PNiP$ = 109.5°, R_{P-H} = 142.0 pm, and $\angle HPH$ = 93.5°.

Results and Discussion

η^1-Coplanar versus η^1-Pyramidal Coordination. The optimized geometry parameters for the η^1-coplanar coordination mode (β = 180°) are shown in Figure 1a. The sulfur dioxide is activated due to coordination (optimized values for the free ligand R_{S-O} = 143.5 pm and $\angle OSO$ = 116.1°), which corresponds to the decrease of the SO_2 stretch frequencies. This is an expected result because of the π-back donation to the LUMO of the SO_2, which behaves S–O antibonding and O–O bonding (see Chart I). Rotation of the SO_2 about 90° around the symmetry axis of the $(PH_3)_3Ni$ fragment yields a total energy gain of only 0.16 kJ/mol and gives unchanged geometry parameters. For a detailed discussion of the coplanar coordination mode, we therefore decided to use the SO_2 orientation shown in Figure 1a, because this one is considered to be the starting point for the bending of the SO_2.

To examine the transition from the coplanar to the pyramidal mode, a hypothetical structure midway between the two characteristic cases has been calculated (β = 135°) with the geometry parameters fixed at the values optimized for the coplanar ar-

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(5) Wenschuh, E.; Hoffmann, Th.; Handtke, K. *Z. Chem.* **1986**, *26*, 212.

(6) Sieler, J.; Peters, K.; Wenschuh, E.; Hoffmann, Th. *Z. Anorg. Allg. Chem.* **1987**, *549*, 171. Selected structural data (lengths in pm; angles in degrees) are as follows: Ni–S = 200.1 (3), S–O = 145.1 (8); O–S–O = 92.6 (6), β = 142.6 (β denotes the angle between the SO_2 plane and the Ni–S bond). The corresponding data for the well-known $(PPh_3)_3NiSO_2$ are as follows:[7] Ni–S = 203.8 (4), S–O = 144.5 (7), 145.0 (6); O–S–O = 113.4 (4), β = 166.9.

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(9) Program PSHONDO: Dupuis, M.; Rys, J.; King, H. F. *QCPE 338*; Indiana University: Bloomington, Indiana. Pseudopotential version: Daudey, J. P., University Paul Sabatier, Toulouse, France.

(10) Durand, Ph.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283.

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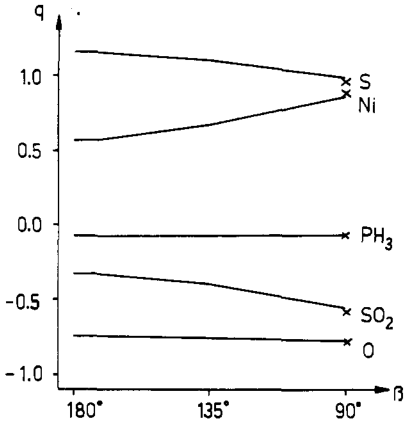

Figure 3. Charge distribution in $(PH_3)_3NiSO_2$ for various angles β. The values for the pyramidal arrangement (β = 90°) with optimized structural parameters are marked separately.

rangement. This should give at least a qualitative picture of the changes in electronic, nuclear and total energy (Figure 2). In agreement with the results of Sakaki et al. there is a large gain in electronic energy and a considerable increase in steric repulsion for decreasing β. In contrast, the total energy has been found to be lower for the pyramidal structure than for the coplanar one.

Due to the strongly bent SO_2 in L_3NiSO_2 with the bulky coligands L = $PPhMe_2$,[6] we conclude that for L = PH_3 a pyramidal SO_2 coordination should occur. The result of Sakaki et al., that the η^1-coplanar coordination yields the most stable structure, seems to be a consequence of calculational details (geometry, basis set, etc.), underestimating the acceptor ability of SO_2. One should note that the energy difference they calculated between the coplanar and the pyramidal structures is very small (only 1.5 kcal/mol). Our results show a reversal of the total energy, which is in our opinion more realistic, but the energy difference we have found (more than 43 kJ/mol, see Figure 2) is certainly too large. Obviously the calculational scheme we have adopted overestimates the pyramidal structure, possibly a consequence of the basis set superposition error. We point out, however, that it was not our aim to calculate the correct energy difference between the two structures. This would have required much higher computational efforts. The discussion following in this paper focuses only on the change of the optimized structural papameters (Figure 1) and the corresponding energies in case the electronic and steric properties of the coligands are varied.

The optimization of the η^1-pyramidal coordination structure (β = 90°) results in the geometry parameters shown in Figure 1b. Due to the electronic reasons the Ni–S bond length should decrease in the pyramidal coordination mode, because of the smaller four-electron destabilization and the stronger back-donation to SO_2. The stronger steric repulsion between SO_2 and the phosphine ligands, however, forces the calculated Ni–S bond length to increase. From this fact it can be concluded that the shorter experimental Ni–S bond length in L_3NiSO_2 with L = $PPhMe_2$ compared to L = PPh_3[6] is caused as much by electronic reasons as by the smaller steric repulsion in case of the smaller phosphine ligands.

Figure 3 shows the change of the charge distribution during the bending process. The pyramidal coordinated SO_2 turns out to be the stronger Lewis acid than the coplanar one. This confirms Sakaki's argument that the back-donation to the SO_2 is more effective from the Ni d_σ orbital than from the d_π orbital (see Chart II). The stronger charge transfer to SO_2 originates almost solely from the nickel atom. The coligands remain unchanged.

The accepting orbital for back-donation is the π^* orbital of the sulfur dioxide, which is S–O antibonding and O–O bonding. As a consequence, the S–O bond length increases for the pyramidal coordination mode. Furthermore, the OSO bond angle decreases, as experimentally found.[6] Therefore we may conclude that for the pyramidal-coordinated SO_2 no rehybridization at the sulfur atom from sp^2 to sp^3 should be assumed as is usually done.[1] The back-donation seems to go into the π^* orbital of sulfur dioxide; i.e., the sp^2 hybridization will be retained.

Table I. Selected Charges (Averaged Value of $q(H')$), Orbital Populations, and Frontier Orbital Energies (in au) for the Complex Fragment $(PH'_3)_3Ni$ with H′ = H, Ph, and Me

	H′ = H	H′ = Ph	H′ = Me
$q(P)$	−0.347	−0.623	−0.923
$q(H')$	0.072	0.170	0.276
$q(Ni)$	0.394	0.339	0.283
$POP(Ni_\sigma)$	2.004	2.019	2.039
$POP(Ni_\pi)$	3.932	3.970	4.008
$POP(Ni_\delta)$	3.670	3.672	3.670
$\epsilon(d_\sigma)$	−0.238	−0.202	−0.169
$\epsilon(d_\pi)$	−0.238	−0.205	−0.177
$\epsilon(d_\delta)$	−0.219	−0.181	−0.146

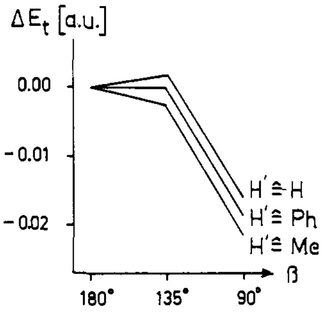

Figure 4. Turn of the total energy of $(PH'_3)_3NiSO_2$ for H′ = H, Ph, and Me during the bending of the SO_2 plane.

Coligands with Higher Basicity. We have examined how a higher basicity of the coligands influences the coordination geometry of sulfur dioxide. In order to reduce the computational effort we could only simulate the phosphine ligands by model ligands PH'_3, H′ denoting pseudo-hydrogen atoms. Trial calculations for a variety of molecules PR_3 were first carried out to find out a suitable measure for the phosphine basicity.[16] It turned out that either the P lone-pair orbital energy or the proton affinity of the molecules can serve as a measure in this case, whereas the charge distribution cannot. We decided to apply the following strategy. Subsequently, we varied the orbital exponent of the H′ pseudo-hydrogen atoms until PH'_3 has the same proton affinity as the original PR_3 molecule.[16] In the present study, we compare the ligands PPh_3 and PMe_3 with PH_3, by adapting their proton affinity to PH'_3 models.

Surely, this is only a crude method for simulating the different phosphine basicity. Improvements would be possible, but would necessitate a higher numerical effort. Table I demonstrates that our model ligands PH'_3 have those properties that we expected. The donor ability of the corresponding models PH'_3 against the nickel atom in a $(PH'_3)_3Ni$ fragment rises with increasing order of basicity $PH_3 < PPh_3 < PMe_3$. The populations of the σ and π orbitals increase as well as the energies of the corresponding occupied nickel σ and π frontier orbitals. Consequently, in the case of a coordinating SO_2 molecule, the four-electron destabilization and the back-bonding to SO_2 should be increased.

Table II shows optimized geometry parameters and atomic charges for the model complexes $(PH'_3)_3NiSO_2$. Indeed, the charge transfer from the fragment to the SO_2 increases with increasing basicity of the coligands. This results in larger S–O bond lengths and a smaller bond angle. In the coplanar coordination mode the stronger four-electron destabilization overcomes backbonding. Accordingly, the elongation of the Ni–S bond length is larger for the more basic coligands. Within the η^1-pyramidal coordination a reverse behavior is considered due to the very effective overlap between the Ni d_σ orbital and the SO_2 lone-pair orbital. This leads to a shortening of the Ni–S bond length (201.8 pm for H′ = Me compared to 202.7 pm for H′ = H).

Coligands with stronger basicity increase the four-electron destabilization as well the back-donation to SO_2. Both effects

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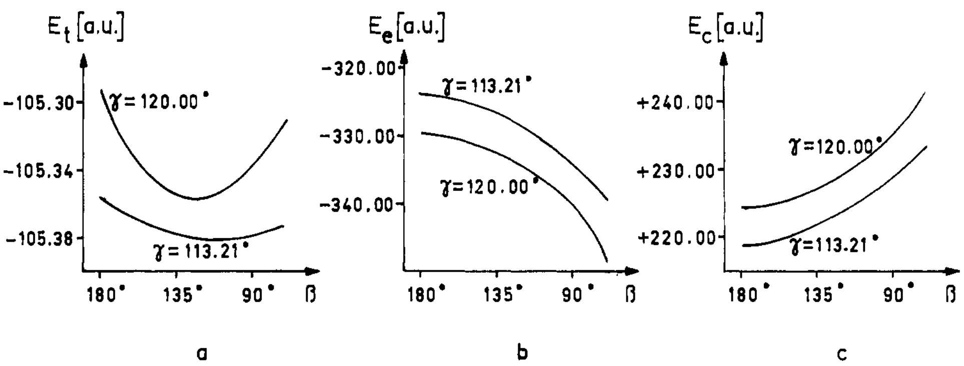

Figure 5. Qualitative changes of E_t, E_e, and E_c of $(PH_3)_3NiSO_2$ during the variation of the angle β for different angles γ (∠PNiP).

Table II. Change of SO_2 Coordination Geometry and Charge Distribution (Averaged Value of $q(PH'_3)$) in $(PH'_3)_3NiSO_2$ within the η^1-Coplanar and the η^1-Pyramidal Arrangements by Simulation of Coligands with Various σ-Donor Abilities (Bond Lengths in pm; Angles in deg)

β	H' = H 180	H' = Ph 180	H' = Me 180	H' = H 90	H' = Me 90
R(Ni–S)	200.0	200.3	200.7	202.7	201.8
R(S–O)	146.1	146.6	147.1	149.1	150.1
∠OSO	114.01	113.57	113.24	112.09	111.94
q(Ni)	0.587	0.597	0.619	0.859	0.887
q(S)	1.146	1.110	1.066	0.950	0.885
q(O)	−0.738	−0.751	−0.766	−0.773	−0.793
$q(SO_2)$	−0.330	−0.392	−0.466	−0.596	−0.701
$q(PH'_3)$	−0.086	−0.068	−0.051	−0.088	−0.062

favor the pyramidal coordination mode. Figure 4 shows the larger stabilization for the bending. Even the barrier can vanish.

The further decrease of the OSO angle in the pyramidal mode in the case of stronger donating coligands (see Table II) is again understandable due to the O–O bonding character of the π^*-acceptor orbital of SO_2 (Chart I). However, we concede that the extremely small angle of 92.6° experimentally found in $(PPhMe_2)_3NiSO_2$[6] cannot be explained merely by this argument.[17] There must be further reasons.

Coligands with Larger Steric Influence. By means of pseudo-hydrogen atoms H' one can simulate various substituents R in the phosphine ligands only in an electronic sense, i.e. in their donor/acceptor ability. To examine the influence of the stronger steric repulsion of bulky phosphines PR_3 the PNiP angle γ in the complex $(PH_3)_3NiSO_2$ was systematically increased. This artifice simulates the effect of phosphines with larger cone angles.[18]

By starting from the optimized geometry parameters of the coplanar coordination mode, we varied the angle β from 180 to 70° for γ = 113.2° (averaged experimental value for $(PPh_3)_3NiSO_2$[7]) and γ = 120.0° (planar arrangement of $(PH_3)_3Ni$). Again, we have calculated the energy quantities for only three values of β. Fitting of the calculated data results in the qualitative energy behavior shown in Figure 5. It was found that for larger angles γ the minimum of the total energy is shifted to β angles larger than 90° (see Figure 5a). This was expected because of the increasing steric repulsion for larger β (see Figure 5c). From Figure 5b, however, it follows that the electronic consequences of increasing the angle γ result in an even greater tendency toward the pyramidal mode. This can be explained by comparing the fragments $(PH_3)_3Ni$ with a single PR_3. For the latter the increase of the cone angle raises the energy of the phosphorus lone-pair orbital and in turn the donor ability. In the fragment $(PH_3)_3Ni$ one has to consider two orbitals of a_1 symmetry, the formally empty sp_σ hybrid orbital and the occupied d_σ orbital. Both orbitals, however, mix if the bond to SO_2 is formed. Thus, with increasing PNiP angle the donor ability of the fragment increases and in turn the four-electron destabilization with the sulfur lone-pair and the charge transfer to SO_2 increase. Consequently, bulkier phosphine coligands favor the coplanar SO_2 coordination only in a sterical sense. In an electronic sense they would prefer the pyramidal coordination mode.

Conclusions

In complexes of the type L_3NiSO_2, coligands L with higher basicity favor the η^1-pyramidal coordination mode of SO_2. Coligands with a larger steric factor have, on the one hand, a similar electronic effect. On the other hand, the stronger steric repulsion with the SO_2 oxygen atoms argues against the bent SO_2 structure. Consequently, in complexes L_3NiSO_2 the pyramidal coordination structure can be expected to be obtained by coligands which are small and have strong donor power. To summarize, the coordination mode of SO_2, experimentally found in the complexes is a consequence of various different and partially counteracting influences of the coligands.

Acknowledgment. We thank Dr. Carlo Mealli, Florence, for helpful discussions.

Registry No. $(PH_3)_3NiSO_2$, 98976-49-9.

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