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Synthesis and Structural Characterization of a Sulfur Dioxide Complex of Nickel with Tris(2-(diphenylphosphino)ethyl)amine

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By reaction of gaseous sulfur dioxide with the complex [NiBr(np$_3$)]BPh$_4$ (np$_3$ = tris(2-(diphenylphosphino)ethyl)amine, N(CH$_2$CH$_2$PPh$_2$)$_3$), in the presence of the reducing agent NaBH$_4$, a complex of formula [Ni(np$_3$)SO$_2$] is obtained. This compound has been characterized by the usual techniques including a single-crystal X-ray analysis. The compound crystallizes in the space group $P6_3$ with a = 13.493 (5) Å, c = 11.936 (4) Å, and Z = 2. The structure has been refined by least-squares methods to the R and R_w values of 0.037 and 0.043, respectively. The nickel atom is five-coordinated with a SO$_2$ group linked to the metal in a bent mode. The Ni–S bond distance is 2.336 (3) Å. Both structure and bonding of the compound are discussed.

Introduction

Transition-metal complexes with a SO$_2$ ligand have, over the past few years, been the subject of wide interest. In particular, the binding mode (coplanar vs. bent) of the SO$_2$ group to the metal has been widely investigated for its theoretical implications.[1]

In previous research from this laboratory several transition-metal complexes with the tripod-like tri(tertiary phosphines) 1,1,1-tris(diphenylphosphinomethyl)ethane, p$_3$, and tris(2-(diphenylphosphino)ethyl)amine, np$_3$, have been prepared and characterized. These phosphines, by acting as ancillary ligands, favor the coordination of small molecules or ions such as CO,[2] NO,[3] BH$_4$,[4] OH,[5] SR,[6] SO$_4$,[7] and SeO$_4$[7] to the metal. In particular, the compound [Ni(p$_3$)SO$_2$] has been obtained[4] by reaction of gaseous SO$_2$ and the p$_3$ ligand with nickel(II) salts with poorly coordinating ions. An X-ray diffraction study has shown that the geometry about d^{10} nickel is tetrahedral with the four atoms of the Ni–SO$_2$ fragment coplanar.

If the ligand np$_3$ in alcohol solution is used in place of p$_3$, (alkyl sulfito)metal complexes of formula [M(np$_3$)(SO$_3$R)]Y, where M = Co or Ni, R = CH$_3$ or C$_2$H$_5$, and Y = BF$_4$ or BPh$_4$, are formed.[8] In order to obtain the simple SO$_2$ adduct of np$_3$ metal complexes, it is necessary to add the reducing agent NaBH$_4$ to the ethanol solution. In this manner a compound with the formula [Ni(np$_3$)SO$_2$] is obtained, which has been characterized with the usual chemical–physical measurements. A complete X-ray analysis has also been performed.

Experimental Section

Physical Measurements. Magnetic, conductometric, and spectrometric measurements (both visible and infrared) were carried out using methods already described.[9] Oxygen microanalyses are by Mikroanalytisches Laboratorium, Bonn, West Germany.

[Ni(np$_3$)SO$_2$]. [NiBr(np$_3$)]BPh$_4$[10] was dissolved in dry tetrahydrofuran (40 mL). Then SO$_2$ was bubbled through the solution while adding NaBH$_4$ (0.5 mmol) dissolved in ethanol (10 mL). The solution turned brown. The red-brown crystals obtained were filtered, washed with tetrahydrofuran and petroleum ether, and dried. The results of the elemental analysis agree with the formula [Ni(np$_3$)SO$_2$]. Anal. Calcd for [Ni(np$_3$)SO$_2$], C$_{42}$H$_{42}$NNiO$_2$P$_3$S: C, 65.0; H, 5.4; N, 1.8; Ni, 7.6; O, 4.1; P, 12.0; S, 4.1. Found: C, 65.0; H, 5.5; N, 1.8; Ni, 7.5; O, 4.0; P, 11.9; S, 3.9.

Collection and Reduction of the X-ray Data. The crystal used for data collection was a hexagonal prism elongated along the sixfold axis, with dimensions 0.11 × 0.14 × 0.36 mm. The lattice constants were determined at room temperature from a least-squares refinement of the angular settings of 20 reflections, carefully centered on a Philips PW 1100 diffractometer. The hexagonal unit cell dimensions are a = 13.493 (5) Å, c = 11.936 (4) Å, and V = 1881.94 Å^3. The observed density of 1.36 g cm^{-3} measured by flotation in toluene–carbon tetrachloride agrees with the value of 1.370 g cm^{-3} calculated for two formula units of [Ni(np$_3$)SO$_2$] per cell. The observed extinction 00l for $l = 2n + 1$ is consistent either with the centrosymmetric space group $P6_3/m$ or with the acentric space group $P6_3$ of the Laue group $6/m$. The acentric $P6_3$ space group was chosen because its symmetry is the one most consistent with the formula of the compound. This choice was confirmed by the solution and successful refinement of the structure.

Data collection was carried out using Cu Kα (λ 1.5418 Å) radiation, monochromatized with a flat graphite crystal. Reflections within $2\theta \leq 160°$ were collected using the ω–2θ scan technique. The scan speed was 0.05°/s. The scan width calculated according to the formula $a + b \tan \theta$ varied from 0.82 to 1.50. Stationary-background measurements were taken before and after each scan for a time equal to half the scan time. The intensity of three standard reflections measured every 120 readings showed no systematic trend. Of 1371 total reflections 836 were considered observed with $I \geq 3\sigma(I)$. The intensities were corrected for background, and values of $\sigma(I)$ were derived, as previously described,[11] using a value for p of 0.03. The data were then corrected for Lorentz–polarization effects and for absorption using the program AGNOST.[12] The eight faces of the crystal were of the form {100}, {001}. The calculated transmission factors ranged from 0.651 to 0.823 (μ(Cu Kα) = 27.54 cm^{-1}).

Scattering factors for neutral atoms (Ni, S, P, N, C) were taken from the compilation of Cromer and Waber[13] and were modified for both the real and imaginary components of anomalous dispersion for Ni, S, and P atoms.[14] Scattering factors for hydrogen atoms were taken from ref 15.

Solution and Refinement of the Structure. The nickel atom was set in the special position $^1/_3$, $^2/_3$, 0. The positions of the sulfur and of the phosphorus atoms were obtained from the first three-dimensional Fourier synthesis. A subsequent Fourier synthesis, phased by these three atoms, led to the location of all nonhydrogen atoms. A cycle of least-squares refinement, using isotropic temperature factors for all of the atoms, was followed by cycles with anisotropic temperature factors assigned to all noncarbon atoms. At this stage the hydrogen atoms were included as a fixed-atom contribution in calculated positions (C–H = 0.95 Å) with temperature factors equal to those of the carbon atoms to which they were attached. Finally, additional cycles of refinement using anisotropic thermal parameters for all nonhydrogen atoms were carried out. The function minimized in the least-squares calculation was $\sum w(|F_o| - |F_c|)^2$, where w is taken as $w = 1/\sigma^2(F_o)$.

Owing to the polar nature of the acentric $P6_3$ space group, the absolute configuration of the structure was determined by applying the anomalous dispersion correction. The two possible orientations of the structure that must be considered are x, y, z and $x, y, \bar{z}$. Least-squares refinement on the two possible configurations, the second being obtained by changing the sign of the z coordinate of all atoms, gave R values of 0.039 (for x, y, z) and 0.037 (for $x, y, \bar{z}$). An analysis of the standard deviations of the parameters together with Hamilton's test[16] confirmed that the $x, y, \bar{z}$ structure was the correct one. Final positional and thermal parameters are listed in Table I. A list of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The [Ni(np$_3$)SO$_2$] complex, obtained by reaction of sulfur dioxide with [NiX(np$_3$)]BPh$_4$ in the presence of NaBH$_4$, is

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Table I. Atomic[a] Parameters for the Structure of [Ni(np$_3$)SO$_2$] (All Quantities × 10^5)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	6667	3333	0	450	450	511 (13)	225 (3)	0	0
S(1)	6667	3333	−1957 (3)	379	379	433 (19)	189 (5)	0	0
P(1)	6319 (1)	1531 (1)	205 (2)	488 (9)	445 (8)	523 (10)	250 (8)	66 (10)	−31 (10)
O(1)	7603 (8)	3340 (7)	−2269 (8)	1694 (92)	744 (55)	586 (53)	345 (66)	266 (61)	−63 (47)
N(1)	6667	3333	1940 (8)	665	665	453 (65)	333 (24)	0	0
C(1)	6166 (7)	2145 (7)	2345 (7)	1034 (67)	765 (56)	500 (46)	472 (51)	96 (44)	−132 (44)
C(2)	6631 (7)	1493 (7)	1715 (8)	788 (54)	646 (49)	706 (51)	369 (42)	274 (44)	−28 (44)
C(3)	4843 (5)	337 (4)	69 (6)	544 (33)	446 (31)	460 (39)	280 (27)	−81 (41)	−54 (39)
C(4)	4085 (5)	490 (5)	−598 (6)	569 (40)	423 (34)	631 (46)	278 (32)	54 (33)	−15 (31)
C(5)	2970 (6)	−407 (6)	−728 (7)	522 (38)	596 (42)	771 (59)	346 (35)	102 (38)	117 (40)
C(6)	2601 (5)	−1426 (6)	−221 (7)	476 (38)	499 (39)	848 (60)	234 (33)	−52 (39)	−20 (39)
C(7)	3351 (6)	−1580 (6)	440 (7)	646 (45)	513 (39)	679 (51)	236 (36)	−138 (40)	−169 (39)
C(8)	4471 (5)	−713 (5)	566 (6)	574 (41)	450 (36)	580 (42)	274 (34)	−19 (33)	−94 (32)
C(9)	7082 (6)	901 (5)	−501 (7)	381 (35)	411 (38)	944 (62)	204 (31)	−4 (36)	−98 (37)
C(10)	6916 (7)	719 (7)	−1648 (8)	882 (62)	701 (54)	754 (62)	517 (50)	−57 (50)	−49 (45)
C(11)	7488 (8)	270 (7)	−2250 (9)	1037 (72)	774 (58)	1211 (83)	661 (58)	−348 (67)	−133 (59)
C(12)	8224 (9)	22 (8)	−1722 (13)	806 (73)	672 (63)	1717 (128)	415 (55)	−379 (83)	−83 (82)
C(13)	8403 (7)	194 (8)	−599 (13)	461 (47)	654 (54)	1930 (128)	356 (43)	75 (62)	−54 (66)
C(14)	7837 (6)	639 (6)	6 (10)	570 (41)	593 (41)	1185 (74)	319 (36)	255 (56)	80 (61)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + ...))$. F (relative scale factor) = 7785.

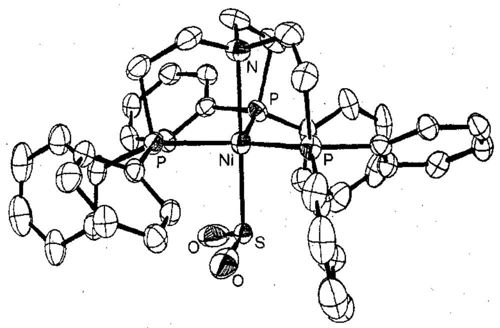

Figure 1. Perspective view of the [Ni(np$_3$)SO$_2$] complex (ORTEP diagram showing 30% probability ellipsoids).

Table II. Bond Lengths (Å) and Bond Angles (deg) with Their Estimated Standard Deviations as Obtained from Final Least-Squares Parameters

	Bond Lengths		
Ni–S	2.336 (3)	C(5)–C(6)	1.349 (11)
Ni–P	2.248 (2)	C(6)–C(7)	1.378 (12)
Ni–N	2.315 (10)	C(7)–C(8)	1.381 (8)
S–O	1.312 (12)	C(8)–C(3)	1.378 (9)
P–C(2)	1.856 (9)	C(9)–C(10)	1.390 (13)
P–C(3)	1.839 (5)	C(10)–C(11)	1.395 (17)
P–C(9)	1.836 (9)	C(11)–C(12)	1.352 (19)
N–C(1)	1.476 (9)	C(12)–C(13)	1.361 (21)
C(1)–C(2)	1.511 (15)	C(13)–C(14)	1.387 (17)
C(3)–C(4)	1.390 (11)	C(14)–C(9)	1.373 (14)
C(4)–C(5)	1.389 (8)		
	Bond Angles		
S–Ni–P	96.25 (7)	P–C(2)–C(1)	107.6 (7)
S–Ni–N	180.0	P–C(3)–C(4)	118.4 (4)
P–Ni–N	83.75 (7)	P–C(3)–C(8)	122.7 (6)
P–Ni–P′	118.83 (5)	C(3)–C(4)–C(5)	119.4 (6)
Ni–S–O	106.5 (4)	C(4)–C(5)–C(6)	121.7 (8)
O–S–O′	112.3 (5)	C(5)–C(6)–C(7)	119.0 (6)
Ni–P–C(2)	102.0 (3)	C(6)–C(7)–C(8)	120.7 (7)
Ni–P–C(3)	119.1 (3)	C(7)–C(8)–C(3)	120.3 (7)
Ni–P–C(9)	126.1 (2)	P–C(9)–C(10)	117.1 (7)
C(2)–P–C(3)	102.9 (3)	P–C(9)–C(14)	125.2 (7)
C(2)–P–C(9)	104.2 (5)	C(9)–C(10)–C(11)	120.6 (10)
C(3)–P–C(9)	99.6 (3)	C(10)–C(11)–C(12)	120.1 (11)
Ni–N–C(1)	109.1 (5)	C(11)–C(12)–C(13)	120.4 (13)
C(1)–N–C(1)′	109.8 (6)	C(12)–C(13)–C(14)	119.8 (12)
N–C(1)–C(2)	111.8 (7)	C(13)–C(14)–C(9)	121.4 (11)

Table III. Bond Lengths (Å) and Bond Angles (deg) Corrected for Thermal Motion

	Bond Lengths		
Ni–S	2.341	Ni–N	2.320
Ni–P	2.251	S–O	1.314
	Bond Angles		
S–Ni–P	96.25	P–Ni–P′	118.83
S–Ni–N	180.0	Ni–S–O	106.49
P–Ni–N	83.75	O–S–O′	112.29

diamagnetic, air-stable in the solid state, and practically insoluble in common organic solvents. In the solid state this compound neither reacts with molecular oxygen nor loses sulfur dioxide at room temperature. The presence of the reducing agent is necessary to prevent the formation of the alkyl sulfito derivative.[8] On the basis of a direct comparison of the IR spectrum of the complex with that of the isomorphous complex [Ni(np$_3$)I], the two strong bands at 1115 and 1005 cm^{-1} and the band of medium intensity at 600 cm^{-1} can be undoubtedly assigned to SO$_2$ vibration modes. These bands are assigned respectively to the asymmetric stretching, to the symmetric stretching, and to the bending vibrations of the coordinated SO$_2$ molecule. The frequencies of the stretching modes are appreciably lower than the values found for the uncoordinated solid sulfur dioxide (ν_{asym} 1330, 1308 cm^{-1}; ν_{sym} 1147 cm^{-1})[17] as well as the values found in other compounds bearing a coordinated SO$_2$ molecule.[18]

The structure of the compound consists of mononuclear units of [Ni(np$_3$)SO$_2$]. The bond lengths and angles with their estimated standard deviations are summarized in Tables II and III. Figure 1 shows a perspective view of the molecule. In this compound the nickel atom is five-coordinate with a trigonal-bipyramidal geometry given by the four donor atoms of the tripod ligand np$_3$ and by a sulfur atom. The molecule possesses a crystallographic threefold axis passing through the nitrogen, nickel, and sulfur atoms. Three equivalent peaks, related to each other through the threefold axis, were found in the asymmetric unit at a S–O bond distance from the sulfur atom. This initially suggested the existence of three oxygen atoms bound to the sulfur atom. However, this was not consistent with the chemical knowledge of this compound. In addition, a least-squares refinement assuming a whole SO$_3$ group leads to physically unreasonable results, such as unusually high values for the thermal parameters. Also, some large differences between observed and calculated structure factors could not be justified. A chemically reasonable model assuming a disordered SO$_2$ group distributed over three possible symmetrical orientations in the cell was then used, where each oxygen atom was assigned a population parameter of $^2/_3$. By assuming this SO$_2$ model, a better fit of F_c to F_o's is obtained. This interpretation of a SO$_2$ molecule consistent with a ternary symmetry is not novel; a recent reexamination of the structure of $Pt(PPh_3)_3SO_2$ has shown that the disordered SO_2 group is best interpreted as having a bent configuration with a threefold disorder of the oxygen atoms in the $Pt-SO_2$ group.[19] Incidentally, both Pt and Ni compounds belong to the same space group, $P6_3$.

A rigid-body thermal motion analysis was performed.[12] The resulting corrections to be applied to the coordinates were almost insignificant. This fact also suggests that the origin of the high thermal motion parameters of the oxygen atoms, as well as the unusually short S–O bond distance (1.312 (12) Å),[20] are not to be ascribed to thermal effects but, instead, mostly to disorder. The Ni–P bond distance of 2.248 (2) Å compares well with other TBP Ni complexes containing the np_3 ligand.[21] The long Ni–N bond distance of 2.315 (10) Å suggests a distortion of the trigonal bipyramid toward tetrahedral geometry. Also, the 0.24-Å displacement of the nickel out of the plane defined by the phosphorus atoms in the direction toward the sulfur atom may support this tendency toward tetrahedral distortion of the TBP geometry. Finally, the Ni–S distance of 2.336 (3) Å, although the shortest, is close to the range of values reported[1] for a bent SO_2 group linked to a transition metal.

Both the electronic distribution and the binding mode of $M-SO_2$ moieties in metal complexes can be elucidated using a MO approach as proposed by Ryan and Eller[1] which is analogous to that developed for nitrosyl complexes.[22] According to this, the SO_2 molecule possesses two molecular orbitals close enough in energy to interact with each other upon bending of the SO_2 group to give stabilized and destabilized molecular orbitals. In particular, by adopting the molecular orbital scheme proposed for the trigonal-bipyramidal geometry[23] and filling it with the 10 d electrons of the nickel, the HFMO will be the orbital (π^*, xz) predicting a bent geometry of the SO_2 group.

Moreover, the observed tetrahedral distortion of the ideal trigonal-bipyramidal geometry about the Ni atom S–Ni–P angle of 96.25 (7)°, intermediate between 90 and 109.5°, stabilizes the d_{z^2} orbital and reduces the energy gap between the two sets of orbitals (σ^* and π^*) and facilitates their interactions and the bending of the $M-SO_2$ group.

The bent geometry of the $Ni-SO_2$ group can also be explained by using a simple valence-bond treatment where the $Ni(np_3)$ moiety can be considered to be a base which denotes an axial lone pair of electrons from the nickel atom to the SO_2 molecule, thus lowering the formal electron configuration on nickel to d^8. In this manner the compound can be considered a sulfoxylo (SO_2^{2-}) complex of nickel(II). The low IR absorption energies of the SO_2 molecule may well be consistent with the assumption of a charge transfer from the metal to the sulfur atom. However, such a transfer effect upon the bending of a SO_2 moiety undoubtedly is greatly influenced by rules more subtle than those simply based on the geometries of the $M-SO_2$ moieties.

A comparison of the present SO_2 complex with the analogous nitrosyl complex, $[Ni(np_3)NO]^+$, is quite interesting since both the SO_2 and NO ligands can be considered formally to be linked to a d^{10} nickel atom, surrounded by the same np_3 ligand. In spite of the similarity previously suggested between the SO_2 and NO molecules, the overall geometry of the nitrosyl complex is remarkably different. In fact, the NO molecule is almost linearly bound to the nickel while the np_3 ligand distorts, causing the apical nitrogen atom to move from the metal. In this case, although the σ^* and π^* orbitals of nitrosyl have the correct symmetry for second-order Jahn–Teller interactions,[19] their energies are not close enough to allow them. The present comparison confirms that the tendency to bend is greater for $M-SO_2$ complexes than for M–NO complexes, a consequence of the smaller energy separation between the σ^* and π^* orbitals in the SO_2 molecule.

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Registry No. $Ni(np_3)SO_2$, 67338-09-4; $[NiBr(np_3)]BPh_4$, 15051-07-7.

Supplementary Material Available: A listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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