cm^{-1}. The spectrum has some similarity with that of the GaI_4^- ion (143 (vs), 214 (w), 235 (w) cm^{-1}) and would therefore be formulated $Ga(diox)_2^+\ GaI_4^-$ as was first proposed by Brewer et al.[3] However, the presence of a higher weak band at 306 cm^{-1} suggests that the structure may also be metal–metal bonded. There is strong chemical evidence to support this view.

First, the complex readily reacts with tetramethylammonium iodide as in eq 1, indicating that the gallium–gallium bond

$$2(CH_3)_4NI + Ga_2I_4{\cdot}2(diox) \rightarrow ((CH_3)_4N)_2^+Ga_2I_6^{2-} + 2(diox) \quad (1)$$

is retained on substitution of the iodide ion. Second, the ligand-replacement reaction shown in eq 2 occurs with pyridine. If an ionic complex, as proposed by Brewer et al.,[3] is

$$Ga_2I_4{\cdot}2(diox) + 2(py) \rightarrow Ga_2I_4{\cdot}2(py) + 2(diox) \quad (2)$$

present, then it would be expected that four pyridine molecules would displace bidentate dioxane. In both reactions the products were confirmed by chemical analysis and Raman spectra. The shift in the frequency of the very strong band in $Ga_2I_6^{2-}$ (118 cm^{-1}) to 143 cm^{-1} in $Ga_2I_4{\cdot}2(diox)$ is not surprising in view of the work of Taylor[9] on mixed-halide species $Ga_2X_{6-r}Y_r^{2-}$ (r = 0–6). He found that in these species the frequency of the in-phase A_1 mode changes appreciably on halide-ion replacement and appears to be mainly associated with mass change. Thus, in $Ga_2I_4Cl_2^{2-}$, the intense band occurs at 145 cm^{-1}.

In summary, this investigation shows conclusively that the $Ga_2Cl_4{\cdot}2(diox)$ complex is a discrete molecule containing a gallium–gallium band and is the first example of a neutral complex of the unknown Cl_2–Ga–Ga–Cl_2. It also provides a rare example of dioxane behaving as a monodentate ligand toward a metal.

Spectroscopic and other evidence strongly suggest that the structure of analogous bromide and iodide complexes are similar.

Registry No. $Ga_2Cl_4{\cdot}2(diox)$, 68317-88-4; $Ga_2Br_4{\cdot}2(diox)$, 68317-89-5; $Ga_2I_4{\cdot}2(diox)$, 68317-90-8.

Supplementary Material Available: A listing of observed and calculated structure factors (18 pages). Ordering information is given on any current mast head page.

References and Notes

(1) S. M. Ali, F. M. Brewer, J. Chadwick, and G. Garton, *J. Inorg. Nucl. Chem.*, **9**, 124 (1959).
(2) F. M. Brewer, J. R. Chadwick, and G. Garton, *J. Inorg. Nucl. Chem.*, **23**, 45 (1961).
(3) F. M. Brewer, G. S. Reddy, and P. L. Goggin, *J. Indian Chem. Soc.*, **44**, 179 (1967).
(4) *Struct. Rep.*, **26**, 693 (1961).
(5) C. A. Evans, K. H. Tan, S. P. Tapper, and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 988 (1973).
(6) G. M. Sheldrick, "SHELX 76. A Program for Crystal Structure Determination", University of Cambridge, 1976.
(7) D. T. Cromer and J. T. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(8) K. L. Brown and D. Hall, *J. Chem. Soc., Dalton Trans.*, 1843 (1973).
(9) K. H. Tan and M. J. Taylor, *Inorg. Nucl. Chem. Lett.*, **10**, 267 (1974).
(10) J. C. Beamish, M. Wilkinson, and I. J. Worrall, *Inorg. Chem.*, in press.

Contribution from Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87545

Structures of (Sulfur dioxide)tris(triphenylphosphine)nickel(0), $Ni(SO_2)(PPh_3)_3$, and Bis(sulfur dioxide)bis(triphenylphosphine)nickel(0), $Ni(SO_2)_2(PPh_3)_2$[1]

D. C. MOODY and R. R. RYAN*

Received June 20, 1978

The structures of $Ni(SO_2)(PPh_3)_3$ (I) and $Ni(SO_2)_2(PPh_3)_2$ (II) have been determined by three-dimensional X-ray diffraction techniques. Complex I crystallized in the space group $P2_1/n$ with lattice constants of a = 11.39 (2) Å, b = 31.01 (3) Å, c = 13.11 (2) Å, and β = 95.34 (9)° and was refined to an unweighted R value of 0.080 for 3635 reflections for which $I \geq 2\sigma(I)$. Complex II crystallized in the space group $P2_1/c$ with lattice constants of a = 19.427 (6) Å, b = 10.370 (6) Å, c = 17.702 (6) Å, β = 112.62 (2)°, and Z = 4 (Mo $K\alpha_1$ radiation, λ 0.7093 Å) and was refined to an unweighted R value of 0.078 for 1483 reflections for which $I \geq 3\sigma(I)$. The sulfur dioxide groups are S bonded in both complexes and are coplanar with their respective Ni–S bonds. For complex II, the two SO_2 groups are nearly coplanar with each other, the dihedral angle between them being 23.5°. The angles about the nickel atoms are nearly tetrahedral in both complexes with NiS distances of 2.06 (1) and 2.08 (1) Å for II and 2.038 (4) Å for I. Complex I exhibits an average S–O distance of 1.448 (5) Å and an O–S–O angle of 113.4 (4)° while the values for II are 1.39 (1) Å and 115.5 (1)°. The significance of these structures relative to the isoelectronic complexes $Pt(SO_2)(PPh_3)_3$ and $Pt(SO_2)_2(PPh_3)_2$, which exhibit pyramidal geometry at the sulfur atom, is discussed.

Introduction

The amphoteric nature of sulfur dioxide with respect to its interaction with transition-metal centers, although structurally illustrated several years ago,[2–4] has recently been a subject of renewed interest. This is due, at least in part, to the recent suggestion[5] that while the bonding principles which govern this behavior for sulfur dioxide are similar to those for nitrosyl complexes,[4] the differences are sufficient to make a thorough study of SO_2 systems worthwhile. It was indicated, on the basis of extended Hückel calculations[5,6] (see especially ref 6), that for the four-coordinate d^{10} transition-metal systems the M–SO_2 bonding should be more sensitive to the basicity of the transition-metal center (and, therefore, the nature of the ancillary ligands) than for other electronic configurations and coordination types.[5] The structural evidence tends to support this view, and there now exist four complexes of this type, two of which ($Pt(SO_2)(PPh_3)_3$[6] and $Pt(SO_2)_2(PPh_3)_2$[7]) exhibit pyramidal geometry at the sulfur atoms and two of which ($Ni(SO_2)p_3$[8] [p_3 = 1,1,1-tris((diphenylphosphino)methyl)ethane] and $Co(NO)(SO_2)(PPh_3)_2$[9]) contain coplanar M–SO_2 groups. A third possibility which was unexpected and as yet not fully understood, i.e., the η^2 type of bonding, in which the sulfur–metal and one of the oxygen–metal distances are nearly equal, was discovered in the $Rh(NO)(SO_2)(PPh_3)_2$[10] complex and has subsequently been shown to exist in the complexes $RuCl(NO)(SO_2)(PPh_3)_2$,[11] $Mo(SO_2)(CO)_3(phen)$,[12] and $Mo(SO_2)_2(CO)_2(bpy)$.[12]

The question as to whether the difference between the modes of bonding, when the SO_2 is bound solely through the sulfur atom, is due primarily to inherent differences in metal basicity is not answered by the available structural data. The p_3 ligand, for example, constrains the P–Ni–P angles to be somewhat

0020-1669/79/1318-0223$01.00/0

less than the tetrahedral angle and, therefore, makes the fourth coordination site more favorable toward Ni–S π-bonding interactions, thereby increasing the tendency for the coplanar $Ni(SO_2)$ geometry in $Ni(SO_2)p_3$, as does the presence of the nitrosyl ligand in the Co complex.

We report here the chemistry and structures of two complexes, $Ni(SO_2)(PPh_3)_3$ and $Ni(SO_2)_2(PPh_3)_2$, which may be compared directly with the analogous Pt complexes.

Experimental Section

Reagents. All solvents used were reagent grade and were degassed prior to use. $Ni(CO)_2(PPh_3)_2$ was obtained from the Ventron Corp., and $Ni(PPh_3)_4$ was prepared by literature procedures.[13]

Syntheses and Reactions of $Ni(SO_2)_2(PPh_3)_2$. The yellow crystalline compound $Ni(CO)_2(PPh_3)_2$ was dissolved in 50 mL of benzene and was subjected to a rapid stream of sulfur dioxide gas. Although the solution appeared to darken immediately, only unreacted $Ni(CO)_2(PPh_3)_2$ was recovered upon addition of heptane.

In a similar experiment, 0.13 g (0.2 mmol) of $Ni(CO)_2(PPh_3)_2$ and 0.10 g (0.4 mmol) of PPh_3 were dissolved in 50 mL of benzene, and the solution was flushed with a rapid stream of sulfur dioxide. The solution slowly turned purple over a period of 3 h. Heptane (50 mL) addition resulted in the isolation of the purple-red crystalline product $Ni(SO_2)_2(PPh_3)_2$. The infrared spectrum (Nujol mull) contained no residual $\nu(CO)$, and the $\nu(SO_2)$ occurred at 1288, 1278, 1120, and 1113 cm^{-1}. The complex slowly loses SO_2 upon heating to 100 °C, while rapid decomposition occurs at 140 °C. Elemental analyses were low in sulfur but generally support the formulation above. Anal. Calcd for $NiS_2O_4P_2C_{36}H_{30}$: C, 60.78; H, 4.25; P, 8.71; S, 9.01. Found: C, 60.52; H, 4.70; P, 8.22; S, 5.65.

A 30 mL benzene solution of 0.2 g (0.18 mmol) of $Ni(PPh_3)_4$ was flushed with gaseous sulfur dioxide for 3 h. Addition of heptane resulted in the precipitation of a purple crystalline compound which proved to be the same bis(sulfur dioxide) complex isolated above. This $Ni(SO_2)_2(PPh_3)_2$ complex was also obtained from a similar experiment where 1.8 g (6.9 mmol) of PPh_3 was added to the benzene solution prior to precipitation with heptane. Reaction of a benzene solution of 0.2 g of $Ni(PPh_3)_4$ and 1.8 g of PPh_3 with ~3 mmol of gaseous SO_2, instead of saturation of the solution with a SO_2 flush, resulted in the formation of a blue solution. Heptane addition (50 mL) resulted in the precipitation of a blue crystalline solid, $Ni(SO_2)(PPh_3)_3$. Anal. Calcd for $NiSO_2P_3C_{54}H_{45}$: C, 71.30; H, 4.99; S, 3.52; P, 10.21. Found: C, 71.11; H, 5.00; S, 3.34; P, 10.07. The infrared spectrum (Nujol mull) revealed $\nu(SO_2)$ at 1205 and 1055 cm^{-1}. Thermogravimetric analyses revealed that decomposition of the sample occurs above 110 °C. If a large excess of SO_2 is added to the system above prior to precipitation of the product, a color change to purple is observed. However, the blue color slowly returned upon flushing the system with nitrogen. Addition of heptane at the purple stage results in crystallization of pure $Ni(SO_2)_2(PPh_3)_2$, while addition of heptane at the blue stage precipitates pure $Ni(SO_2)(PPh_3)_3$.

Both products react with air in the solid state or in solution to yield pale yellow products. These appear to contain appreciable triphenylphosphine oxide, but no peaks suggestive of $NiSO_4$ products were observed in their infrared spectra.

X-ray Measurements and Refinement. Pertinent information concerning the cell, absorption correction, and intensity measurements is given in Table I. For each crystal, two standards were measured after every 50 reflections. For $Ni(SO_2)(PPh_3)_3$ (I) a decrease of about 10% was observed over the period of the data collection; no detectable change occurred for the $Ni(SO_2)_2(PPh_3)_2$ crystal. A correction curve was estimated for structure I by least-squares refinement of a polynomial to the standards and applied to the data. Assignment of weights and the correction of the calculated structure factors were handled as usual.[9]

Structure I was solved using MULTAN followed by difference Fourier methods and refined to an unweighted *R* value of 0.080. Structure II was solved by Patterson and difference Fourier methods and refined to an unweighted *R* value of 0.078. Both structures were refined with anisotropic thermal parameters for all atoms heavier than carbon, and secondary extinction parameters were refined. No attempt was made to account for hydrogen atoms. Peaks which appeared in the final difference Fourier maps could either be reasonably assigned as hydrogen or could not be interpreted in terms of an additional structural feature.

Table I. Crystal Data and Collection Methods

	A. For $Ni(SO_2)(PPh_3)_3$
space group	$P2_1/n$
cell parameters	$a = 11.39$ (2), $b = 31.01$ (3), $c = 13.11$ (2) Å $\beta = 95.34$ (9)°
counting techniques	stationary crystal, stationary counter; 20 s on the peak, 10-s symmetric backgrounds to 40° 2θ
intensities	4301; 3635 for which $I \geqslant 2\sigma(I)$
cryst morphology	{100}, 0.24 mm; {010}, 0.10 mm; {011}, 0.14 mm
abs coeff	6.1 cm^{-1}
transmission	0.86–0.89
	B. For $Ni(SO_2)_2(PPh_3)_2$
space group	$P2_1/c$
cell parameters	$a = 19.427$ (6), $b = 10.370$ (6), $c = 17.702$ (6) Å $\beta = 112.62$ (2)°
diffractometer and counting technique	Picker FACS-I, P. G. Lenhert's Disk Operating System,[14] Wang encoders, graphite monochromator, 3.5° takeoff angle, (1.5° + dispersion) continuous scans, 20-s symmetric background counts, Mo Kα radiation (λ 0.709 30 Å)
intensities	3062 after averaging equivalent reflections; 1483 for which $I \geqslant 3\sigma(I)$
cryst morphology	{100}, 0.062 mm (distance from the origin); $\{10\bar{1}\}$, 0.060 mm; {011}, 0.13 mm
abs coeff	5.1 cm^{-1}
transmission[15]	0.92–0.94
	C. For Both Compounds
cell refinement	12 high-order reflections
ω scans	$\leqslant$0.3° at half-height on all three axes
scattering factors	neutral atom scattering factors[16]

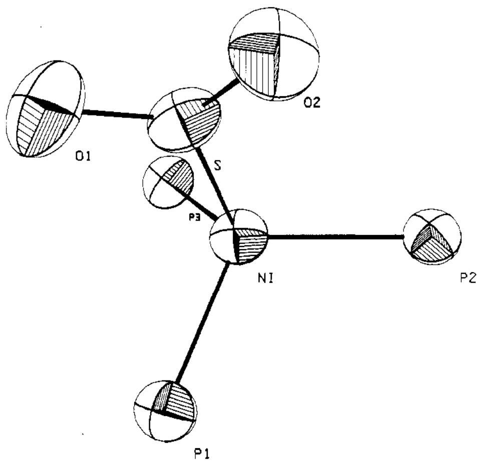

Figure 1. Nickel coordination geometry in $Ni(SO_2)(PPh_3)_3$.

Parameters and selected distances and angles are shown in Tables II–V.

Discussion

Stereoviews and projections of structures I and II are shown in Figures 1–4.

The coordination about the Ni atom in structure I is nearly tetrahedral with S–Ni–P angles which are slightly less than tetrahedral while the P–Ni–P angles are slightly larger. The $NiSO_2$ moiety is nearly coplanar, the angle between the Ni–S bond and the sum of the SO_2 vectors being 166.9°. This distortion, while small, is clearly significant and represents the largest deviation from coplanarity observed to date except for those complexes for which this angle is approximately 120°. When compared to the isoelectronic complex $Pt(SO_2)(PPh_3)_3$,[6] which exhibits pyramidal geometry at the sulfur atom, the near coplanarity of the Ni complex directly attests to the importance of the relative basicity of Pt compared to Ni in similar environments in determining the geometry of the M–SO_2 group.

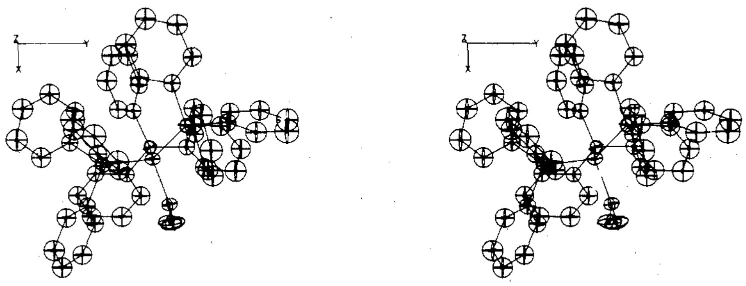

Figure 2. Stereoview of $Ni(SO_2)(PPh_3)_3$.

Table II. Fractional Coordinates and Thermal Parameters for (Sulfur dioxide)tris(triphenylphosphine)nickel[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0.82799 (10)	0.39835 (4)	0.28889 (9)	2.7 (1)	4.6 (1)	5.2 (1)	−0.2 (1)	0.7 (1)	0.0 (1)
S(1)	−0.00266 (22)	0.42031 (8)	0.30098 (21)	3.0 (2)	5.4 (2)	6.7 (2)	−0.9 (3)	0.6 (3)	−1.1 (3)
O(1)	0.06576 (56)	0.42671 (24)	0.21427 (50)	5.0 (5)	11.6 (6)	7.6 (5)	−3.9 (9)	4.8 (8)	1.2 (9)
O(2)	0.06841 (55)	0.41888 (23)	0.39813 (52)	3.8 (4)	11.1 (6)	7.9 (5)	−1.0 (8)	−1.2 (8)	−3.4 (9)
P(1)	0.76688 (22)	0.39758 (8)	0.11880 (18)	3.7 (2)	4.9 (2)	4.9 (2)	−0.7 (3)	0.7 (3)	0.6 (3)
P(2)	0.85531 (22)	0.33197 (8)	0.35119 (19)	3.8 (2)	4.8 (2)	5.6 (2)	0.1 (3)	0.1 (3)	0.9 (3)
P(3)	0.71710 (22)	0.44077 (8)	0.38473 (19)	3.3 (2)	5.1 (2)	5.1 (2)	0.5 (3)	0.7 (3)	−0.7 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.6211 (8)	0.3750 (3)	0.0734 (7)	4.0 (2)	C(2)	0.3976 (10)	0.6458 (3)	0.0206 (8)	5.6 (3)
C(3)	0.5300 (9)	0.3825 (3)	0.1350 (7)	4.8 (2)	C(4)	0.4119 (10)	0.3673 (3)	0.1022 (8)	6.3 (3)
C(5)	0.3962 (11)	0.3452 (4)	0.0092 (9)	6.9 (3)	C(6)	0.5158 (11)	0.6618 (4)	0.0518 (9)	6.9 (3)
C(7)	0.7591 (9)	0.4498 (3)	0.0517 (7)	4.2 (2)	C(8)	0.3348 (9)	0.5391 (3)	0.0184 (7)	4.9 (2)
C(9)	0.3350 (10)	0.4975 (4)	0.0668 (8)	6.3 (3)	C(10)	0.2416 (11)	0.4698 (4)	0.0450 (9)	6.8 (3)
C(11)	0.8521 (11)	0.5197 (4)	0.0233 (10)	7.9 (3)	C(12)	0.8534 (10)	0.4786 (4)	0.0764 (8)	6.5 (3)
C(13)	0.8655 (8)	0.3650 (3)	0.0444 (7)	3.8 (2)	C(14)	0.0542 (10)	0.6145 (3)	0.0161 (8)	5.9 (3)
C(15)	0.9723 (11)	0.6418 (4)	0.0633 (9)	6.9 (3)	C(16)	0.9734 (10)	0.6860 (4)	0.0506 (8)	6.2 (3)
C(17)	0.0540 (10)	0.7056 (3)	−0.0068 (8)	5.7 (3)	C(18)	0.8632 (9)	0.3207 (3)	0.0560 (7)	4.6 (2)
C(19)	0.8295 (8)	0.3254 (3)	0.4865 (7)	4.2 (2)	C(20)	0.2528 (10)	0.7045 (3)	0.4833 (8)	5.8 (3)
C(21)	0.2731 (11)	0.7047 (4)	0.3731 (9)	7.5 (3)	C(22)	0.2097 (11)	0.6780 (4)	0.3077 (9)	6.9 (3)
C(23)	0.1262 (10)	0.6499 (4)	0.3369 (8)	6.3 (3)	C(24)	0.1080 (9)	0.6477 (3)	0.4449 (8)	5.1 (2)
C(25)	0.7684 (9)	0.2874 (3)	0.2895 (7)	4.1 (2)	C(26)	0.6477 (9)	0.2951 (3)	0.2635 (7)	5.0 (2)
C(27)	0.9227 (10)	0.7602 (4)	0.2840 (8)	6.3 (3)	C(28)	0.8694 (11)	0.7222 (4)	0.3021 (8)	6.9 (3)
C(29)	0.7501 (12)	0.7144 (4)	0.2810 (9)	7.5 (3)	C(30)	0.6783 (10)	0.7482 (4)	0.2297 (8)	6.0 (3)
C(31)	0.0067 (8)	0.3106 (3)	0.3502 (7)	4.1 (2)	C(32)	0.0538 (9)	0.2838 (3)	0.4311 (8)	5.3 (2)
C(33)	0.3291 (10)	0.7669 (4)	0.0751 (8)	6.3 (3)	C(34)	0.2315 (10)	0.2761 (3)	0.3401 (8)	5.9 (3)
C(35)	0.1843 (9)	0.3021 (3)	0.2615 (8)	5.6 (3)	C(36)	0.0678 (9)	0.3204 (3)	0.2648 (7)	4.5 (2)
C(37)	0.5642 (8)	0.4230 (3)	0.3886 (7)	4.2 (2)	C(38)	0.4664 (9)	0.4499 (3)	0.3603 (7)	4.9 (2)
C(39)	0.3502 (10)	0.4313 (4)	0.3598 (8)	6.1 (3)	C(40)	0.3367 (10)	0.3892 (4)	0.3915 (8)	6.4 (3)
C(41)	0.4342 (11)	0.3634 (4)	0.4231 (8)	6.3 (3)	C(42)	0.5510 (9)	0.3803 (3)	0.4205 (7)	4.8 (2)
C(43)	0.2346 (8)	0.5514 (3)	0.4781 (6)	3.7 (2)	C(44)	0.3149 (9)	0.5551 (3)	0.4041 (7)	4.8 (2)
C(45)	0.2760 (10)	0.5487 (3)	0.2989 (8)	6.1 (3)	C(46)	0.1559 (10)	0.5380 (3)	0.2720 (8)	6.1 (3)
C(47)	0.0771 (9)	0.5338 (3)	0.3466 (8)	5.5 (2)	C(48)	0.1159 (8)	0.5414 (3)	0.4514 (7)	4.2 (2)
C(49)	0.7013 (8)	0.4967 (3)	0.3394 (7)	4.2 (2)	C(50)	0.6506 (9)	0.5037 (3)	0.2395 (8)	5.3 (2)
C(51)	0.6388 (10)	0.5460 (4)	0.2004 (8)	6.2 (3)	C(52)	0.6823 (11)	0.5803 (4)	0.2590 (9)	7.6 (3)
C(53)	0.7362 (12)	0.5739 (4)	0.3587 (10)	8.7 (4)	C(54)	0.7452 (10)	0.5315 (4)	0.4021 (8)	6.4 (3)

[a] Anisotropic thermal motion is defined by $\exp[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + U'_{12}hk + U'_{13}hl + U'_{23}kl)]$ where $U'_{ij} = U_{ij}B_iB_j$ and U_{ij} is multiplied by 100 in the table.

Table III. Selected Distances (Å) and Angles (deg) for $Ni(SO_2)(PPh_3)_3$

Ni-S	2.038 (4)	S-O(1)	1.450 (6)
Ni-P(1)	2.273 (4)	S-O(2)	1.445 (7)
Ni-P(2)	2.226 (3)	O(1)-S-O(2)	113.4 (4)
Ni-P(3)	2.280 (4)	C-C[a]	1.407 (1.366, 1.457)
S-Ni-P(1)	106.3 (1)	C-C-C[a]	120.0 (117.2, 124.51)
S-Ni-P(2)	100.5 (1)	P-C[a]	1.843 (1.832, 1.854)
S-Ni-P(3)	109.5 (1)	C-P-C[a]	101.86 (100.22, 103.43)
P(1)-Ni-P(2)	111.7 (1)		
P(1)-Ni-P(3)	114.3 (1)		
P(2)-Ni-P(3)	113.4 (1)		

[a] Average value followed by (minimum, maximum).

The influence of geometric constraints on the ancillary ligands (see Introduction) is clearly demonstrated by comparison with $Ni(SO_2)P_3$[8] in which the $NiSO_2$ group is coplanar within experimental error, the sum of the angles about the sulfur atom being 360.0°.

An interesting feature of the structure is the rotational (about the Ni–S bond) orientation of the SO_2 plane with respect to the $Ni(PPh_3)_3$ fragment; i.e., the oxygen atoms are displaced 0.19 Å in the same direction from the plane defined by S, Ni, and P(2) in a manner reminiscent of the direction

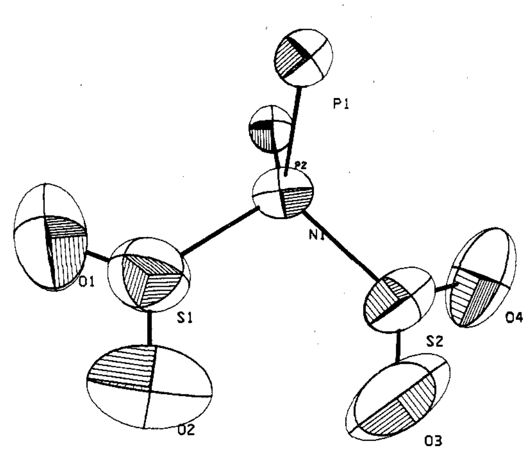

Figure 3. Nickel coordination geometry in $Ni(SO_2)_2(PPh_3)_2$.

Table IV. Fractional Coordinates and Thermal Parameters for Bis(sulfur dioxide)bis(triphenylphosphine)nickel

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0.7388 (2)	0.1132 (3)	0.9278 (2)	6.1 (2)	4.8 (2)	4.1 (2)	−0.6 (4)	2.6 (3)	−0.1 (4)
S(1)	0.6405 (5)	0.2136 (10)	0.8983 (5)	11.6 (8)	9.9 (9)	11.4 (7)	2.6 (15)	9.3 (12)	3.0 (12)
O(1)	0.5771 (13)	0.1671 (26)	0.8974 (20)	11.9 (20)	20.6 (32)	52.3 (52)	6.3 (42)	30.8 (54)	18.7 (59)
O(2)	0.6350 (16)	0.3471 (28)	0.8777 (24)	28.3 (37)	11.9 (27)	67.8 (71)	7.7 (51)	42.4 (79)	12.2 (70)
S(2)	0.8177 (5)	0.2512 (9)	0.9324 (5)	10.0 (7)	7.9 (6)	9.4 (6)	−5.5 (13)	8.5 (11)	−0.9 (11)
O(3)	0.7968 (13)	0.3660 (24)	0.8894 (17)	16.1 (22)	15.5 (26)	37.3 (38)	−7.7 (40)	18.6 (46)	22.8 (52)
O(4)	0.8939 (10)	0.2278 (22)	0.9782 (11)	8.0 (14)	19.6 (24)	15.2 (19)	−12.8 (34)	7.4 (28)	−3.4 (35)
P(1)	0.7193 (3)	−0.0413 (6)	0.8340 (3)	5.1 (4)	5.0 (5)	3.7 (4)	−1.0 (8)	3.6 (7)	−0.1 (7)
P(2)	0.7744 (3)	0.0226 (6)	1.0530 (3)	4.4 (4)	5.3 (5)	3.8 (4)	−0.5 (8)	3.0 (6)	−1.5 (7)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.673 (1)	0.006 (2)	0.727 (1)	3.2 (5)	C(2)	0.644 (1)	−0.091 (2)	0.668 (1)	4.0 (5)
C(3)	0.609 (1)	−0.056 (2)	0.584 (1)	4.5 (5)	C(4)	0.600 (1)	0.072 (2)	0.563 (1)	3.7 (5)
C(5)	0.630 (1)	0.170 (2)	0.620 (1)	4.4 (5)	C(6)	0.668 (1)	0.137 (2)	0.703 (1)	3.7 (5)
C(7)	0.656 (1)	−0.164 (2)	0.844 (1)	4.0 (5)	C(8)	0.577 (1)	−0.138 (2)	0.806 (1)	5.1 (6)
C(9)	0.528 (1)	−0.233 (2)	0.817 (1)	5.6 (6)	C(10)	0.557 (1)	−0.342 (2)	0.863 (1)	5.5 (6)
C(11)	0.633 (1)	−0.365 (2)	0.899 (1)	4.8 (6)	C(12)	0.685 (1)	−0.277 (2)	0.893 (1)	3.7 (5)
C(13)	0.803 (1)	−0.128 (2)	0.834 (1)	3.5 (5)	C(14)	0.800 (1)	−0.257 (2)	0.812 (1)	5.4 (6)
C(15)	0.868 (1)	−0.319 (2)	0.816 (1)	6.9 (7)	C(16)	0.935 (1)	−0.245 (3)	0.842 (1)	6.0 (6)
C(17)	0.934 (1)	−0.119 (2)	0.861 (1)	5.4 (6)	C(18)	0.868 (1)	−0.056 (2)	0.861 (1)	5.1 (6)
C(19)	0.700 (1)	−0.003 (2)	1.092 (1)	3.4 (5)	C(20)	0.714 (1)	0.025 (2)	1.174 (1)	3.8 (5)
C(21)	0.656 (1)	−0.003 (2)	1.203 (1)	4.5 (6)	C(22)	0.591 (1)	−0.059 (2)	1.149 (1)	4.5 (5)
C(23)	0.576 (1)	−0.086 (2)	1.067 (1)	4.1 (5)	C(24)	0.632 (1)	−0.057 (2)	1.038 (1)	3.7 (5)
C(25)	0.842 (1)	0.117 (2)	1.137 (1)	3.6 (5)	C(26)	0.904 (1)	0.059 (2)	1.194 (1)	3.1 (5)
C(27)	0.952 (1)	0.136 (2)	1.260 (1)	4.3 (5)	C(28)	0.936 (1)	0.266 (2)	1.266 (1)	5.4 (6)
C(29)	0.873 (1)	0.323 (2)	1.204 (1)	4.9 (6)	C(30)	0.824 (1)	0.248 (2)	1.136 (1)	4.2 (5)
C(31)	0.818 (1)	−0.142 (2)	1.064 (1)	3.3 (5)	C(32)	0.786 (1)	−0.244 (2)	1.091 (1)	4.5 (5)
C(33)	0.818 (1)	−0.367 (2)	1.089 (1)	5.8 (6)	C(34)	0.875 (1)	−0.379 (2)	1.061 (1)	4.9 (5)
C(35)	0.909 (1)	−0.276 (2)	1.039 (1)	4.4 (5)	C(36)	0.879 (1)	−0.148 (2)	1.039 (1)	3.4 (5)

Table V. Selected Distances (Å) and Angles (deg) for $Ni(SO_2)_2(PPh_3)_2$

Ni–S(1)	2.058 (9)	P–C[a]	1.859 (1.829, 1.884)
Ni–S(2)	2.076 (8)		
Ni–P(1)	2.233 (6)	C–P–C[a]	103.1 (100.9, 106.5)
Ni–P(2)	2.257 (6)		
S(1)–Ni–S(2)	105.1 (4)	S(1)–O(1)	1.32 (2)
P(1)–Ni–P(2)	109.4 (3)	S(1)–O(2)	1.42 (2)
S(1)–Ni–P(1)	107.4 (3)	O(1)–S(1)–O(2)	112 (2)
S(1)–Ni–P(2)	111.3 (3)		
S(2)–Ni–P(1)	115.8 (3)	S(2)–O(3)	1.39 (2)
S(2)–Ni–P(2)	107.8 (3)	S(2)–O(4)	1.41 (2)
C–C[a]	1.408 (1.352, 1.449)	O(3)–S(2)–O(4)	119 (2)
C–C–C[a]	120.0 (113.4, 127.54)		

[a] Average value followed by (minimum, maximum).

Table VI. SO_2 Infrared Frequencies (cm^{-1})

$Pt(SO_2)_2(PPh_3)_2$	1182, 1149, 1035[a]
$Pt(SO_2)(PPh_3)_3$	1201, 1053[b]
$Ni(SO_2)(P_3)$	1190, 1055, 1045[c]
$Ni(SO_2)(PPh_3)_3$	1205, 1055
$Ni(SO_2)_2(PPh_3)_2$	1288, 1278, 1120, 1113

[a] C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, 89, 3066 (1967). [b] J. J. Levison and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 2013 (1972). [c] Reference 8.

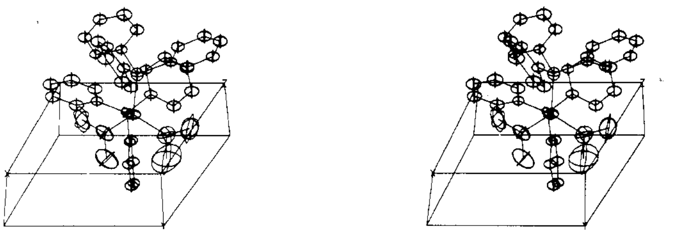

Figure 4. Stereoview of $Ni(SO_2)_2(PPh_3)_2$.

of bending in the Pt complex (see Figure 2, ref 6). Inspection of the stereoview in Figure 2 shows no obvious steric hindrance to an alternate conformation in which a Ni–P bond bisects the O–S–O angle, suggesting an inherent electronic preference for the conformation observed, perhaps due to a π interaction involving the SO_2 and a phosphine ligand.

It should be noted that the S–Ni–P angles, while less than tetrahedral, are larger than those displayed by the analogous Pt complex (S–Pt–P = 96.4 (1), 93.3 (1), and 99.6 (1)°) in accord with the increased M–S π interaction in the Ni complex.[17] The directional nature of this effect is clearly demonstrated by this structure; the S–Ni–P(2) angle is significantly less than the remaining two analogous angles. Also consistent with this observation is the shorter Ni–P(2) distance (2.226 Å as compared to 2.273 and 2.280 Å for P(1) and P(3)) attesting to the lack of competition for π bonding in the P(2)–Ni–S plane.

A further point is that the vibrational frequencies of the SO_2 ligand in $Ni(SO_2)(PPh_3)_3$ as well as those of $Ni(SO_2)P_3$ are in the range established for those complexes which contain the pyramidal SO_2 geometry (see Table VI). These frequencies, the slight bending of the SO_2 in the triphenylphosphine complex, and the large thermal motion perpendicular to the SO_2 plane reported for the tripod complex[8] lead us to believe that these complexes are borderline cases and that substitution of the phosphine by more basic ligands may induce the pyramidal geometry for the Ni complexes. These complexes emphasize the danger of using the vibrational frequencies alone to establish the binding mode for the SO_2. As has been suggested previously,[6,7] the factors which dictate the amount of charge transfer to the ligand, and therefore the vibrational frequencies, are more subtle than those which determine the $M–SO_2$ geometry. These complexes do not, however, undergo the sulfato reaction, and it has been suggested by Kubas[18] that the available data indicate the absence of this reaction generally suffices to establish coplanarity.

Structure II exhibits tetrahedral geometry about the metal atom and contains two coplanar $M–SO_2$ groups. Not only do the M–S bonds lie in the plane of their respective SO_2 ligands, but also the SO_2 planes are nearly coplanar with respect to each other, the dihedral angle between them being 23.5°. (The O(2)···O(3) distance between ligands is 3.07 Å.) The near-coplanarity of the two ligands is suggestive of a synergetic interaction reminiscent of the situation in $Co(NO)(SO_2)(PPh_3)_2$[9] which contains a coplanar Co–SO_2 group, the plane of which also contains the linear Co–NO moiety, and is also reminiscent of the interaction between ethylene and SO_2 in the complex $CpRh(C_2H_4)(SO_2)$[19] in which the C–C bond of the ethylene is bisected by the SO_2 plane in a way which maximizes π–π interaction perpendicular to this plane and stabilizes the coplanar M–SO_2 geometry.

We note also that the S–Ni–S angle is the smallest angle in the coordination sphere for the complex, emphasizing the role of intraplane π–π interaction in determining this angle.

Again, this structure gains added interest when compared with that of $Pt(SO_2)_2(PPh_2)_2$[7] which contains two pyramidal SO_2 groups and exhibits S–Pt–S and P–Pt–P angles of 106.3 (1) and 158.6 (1)°, respectively.

The differences in chemistry between $Ni(SO_2)_2(PPh_3)_2$ and $Pt(SO_2)_2(PPh_3)_2$ also make an interesting comparison. The nickel system is characterized by a general lack of ligand lability. Although one SO_2 can be replaced by PPh_3 under forcing conditions to yield $Ni(SO_2)(PPh_3)_3$, excess SO_2 readily causes reconversion back to $Ni(SO_2)_2(PPh_3)_2$. The platinum system, however, is characterized by an extreme lability of both SO_2 ligands.[20] Addition of PPh_3 irreversibly converts $Pt(SO_2)_2(PPh_3)_2$ to $Pt(SO_2)(PPh_3)_3$ even in the presence of a large excess of SO_2. Similarly the CO/SO_2 equilibrium which exists for the platinum system (see ref 20, Figure 3), appears to be absent in the nickel case. Reaction with molecular oxygen to form the bidentate sulfate, which readily occurs for $Pt(SO_2)_2(PPh_3)_2$, also appears to be absent for $Ni(SO_2)_2(PPh_3)_2$.

Acknowledgment. The authors express their appreciation to Kenneth V. Salazar for his assistance in this endeavor.

Registry No. I, 68438-44-8; II, 68438-45-9; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Ni(PPh_3)_4$, 15133-82-1.

Supplementary Material Available: Listings of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work performed under the auspices of the U.S. Department of Energy, Division of Basic Energy Sciences.
(2) (a) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **8**, 1921 (1969); (b) S. J. La Placa and J. A. Ibers, *ibid.*, **5**, 405 (1966).
(3) C. Barbeau and R. J. Dubey, *Can. J. Chem.*, **51**, 3684 (1973).
(4) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).
(5) R. R. Ryan and P. G. Eller, *Inorg. Chem.*, **15**, 494 (1976).
(6) P. G. Eller, R. R. Ryan, and D. C. Moody, *Inorg. Chem.*, **15**, 2442 (1976).
(7) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, **15**, 1823 (1976).
(8) P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, **15**, 2768 (1976).
(9) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, following paper in this issue.
(10) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, **16**, 2473 (1977).
(11) R. D. Wilson and J. A. Ibers, *Inorg. Chem.*, **17**, 2134 (1978).
(12) G. J. Kubas and R. R. Ryan, to be submitted for publication in *Inorg. Chem.*
(13) R. A. Schunn, *Inorg. Synth.*, **13**, 124 (1972).
(14) P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).
(15) P. Coppens, J. deMeulenaer, and H. Tompa, *Acta Crystallogr.*, **22**, 601 (1967), using a recent modification by Dr. L. Templeton (private communication).
(16) D. T. Cromer, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England.
(17) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(18) G. J. Kubas, *Inorg. Chem.*, in press.
(19) R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, **15**, 797 (1976).
(20) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, **16**, 1052 (1977).

Contribution from Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87545

Structure of Nitrosyl(sulfur dioxide)bis(triphenylphosphine)cobalt[1]

D. C. MOODY, R. R. RYAN,* and A. C. LARSON

Received June 20, 1978

The structure of nitrosyl(sulfur dioxide)bis(triphenylphosphine)cobalt has been determined by single-crystal X-ray techniques. The coordination about the cobalt atom is approximately tetrahedral, with coplanar, sulfur-bound M–SO_2 geometry and a linear nitrosyl group. In contrast, the isoelectronic complex $Rh(NO)(SO_2)(PPh_3)_2$ exhibits a bent nitrosyl group and an η^2-SO_2 coordination in which the sulfur and one oxygen are approximately equidistant from the rhodium atom. The difference between these two complexes may be attributed to differences in metal basicity. The title complex crystallizes in the space group $P2_1/c$ with lattice parameters of $a = 20.494$ (13) Å, $b = 10.146$ (6) Å, $c = 17.693$ (11) Å, and $\beta = 119.78$ (4)° with $Z = 4$. The Co–S distance is 2.021 (8) Å while the Co–N distance is 1.68 (1) Å. The M–N–O angle is 169 (2)°. The dihedral angle between the plane defined by the Ni, S, and N atoms and that defined by the SO_2 is 20.1°.

Introduction

The recent characterization of a four-coordinate tetrahedral complex,[2] $Rh(NO)(SO_2)(PPh_3)_2$ (I), which exhibits η^2-SO_2 coordination has been quickly followed by the addition of two new examples of this type of coordination: a five-coordinate trigonal-bipyramidal complex,[3] $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ (II), in which the S–O bond is contained in the equatorial plane and a six-coordinate complex,[4] $Mo(phen)(CO)_3(\eta^2\text{-}SO_2)$ (III). Although the stereochemical factors and/or characteristics of the metal center which facilitate the η^2 type of bonding are yet to be determined, several questions come to mind whose answers could help to limit the possibilities. For example, structure III clearly makes the point that the presence of the nitrosyl ligand is not a necessary condition for the η^2-type SO_2 bonding, but its sufficiency is left open by structures I and II. In addition, the basicity of the transition-metal center may play an important role, a factor which may be controlled by appropriate choice of the ancillary ligands as well as choice of transition metal.

In order to define the role of some of these parameters we have prepared and structurally characterized $Co(NO)(SO_2)(PPh_3)_2$.

Experimental Section

Synthesis of $Co(NO)(SO_2)(PPh_3)_2$. Nitrosyltris(triphenylphosphine)cobalt was prepared by literature procedures[5] and was reacted with excess gaseous SO_2 in benzene solution. Addition of heptane resulted in the precipitation of the brown-red crystalline solid $Co(NO)(SO_2)(PPh_3)_2$. The infrared spectrum (Nujol mull) revealed $\nu(SO_2)$ peaks at 1250 and 1085 cm^{-1} which suggested coplanar MSO_2 coordination. Similarly no SO_2 was evolved upon heating the sample to 80 °C in vacuo. Although crystals of $Co(NO)(SO_2)(PPh_3)_2$ decomposed slowly in air, a rapid reaction was observed with air in solution. The products of this oxidation appear to contain no $\nu(SO_4)$ peaks by infrared analysis, but substantial PPh_3O does appear to be present.