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 $\pi$–$\pi$ 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 $\pi$–$\pi$ 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.

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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 $\eta^2$-$SO_2$ 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 $\eta^2$-$SO_2$ 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 $\eta^2$ 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 $\eta^2$-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.

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**Table I.** Crystal Data and Collection Methods

| | |
|---|---|
| space group | $P2_1/c$ |
| cell parameters | $a = 20.494$ (13), $b = 10.146$ (6),<br>$c = 17.693$ (11) Å<br>$\beta = 119.78$ (4)° |
| cell refinement | 12 high-order reflections |
| diffractometer and counting technique | Picker FACS-I, P. G. Lenhert's Disk Operating System,[12] 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) |
| ω scans | ≤0.3° at half-height on all three axes |
| intensities | 2976 after averaging equivalent reflections; 1624 for which $I \geq 3\sigma(I)$ |
| cryst morphology | {100}, 0.053 mm (distance from the origin);<br>{011}, 0.13 mm |
| abs coeff | 7.6 cm$^{-1}$ |
| transmission (max, min) | 0.93, 0.85[13] |
| scattering factors | neutral atom scattering factors for all atoms[14] |

**X-ray Measurements and Refinement.** Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections, measured after every 50 measurements, decreased by approximately 5% over the period of the data collection process. A correction curve for this decrease was estimated by least-squares refinement of a polynomial to the standards and applied to the data. The variance for $\overline{F^2}$ was computed from $\sigma^2(\overline{F^2}) = \sigma_C{}^2(\overline{F^2}) + \sigma_N{}^2(\overline{F^2})^2$ where $\sigma_C{}^2$ is the variance due to counting statistics, $\overline{F^2}$ is the squared structure factor averaged over equivalent reflections and $\sigma_N{}^2$ is taken to be 0.015.

The function minimized in the least-squares refinements was $\sum w(F_o - F_c{}^*)^2$ where $w = 4F_o/\sigma^2(\overline{F^2})$ and

$$F_o{}^* = kF_c\bigg/\left\{1 + 2g\left[\frac{e^2}{mc^2V}\right]^2 Lp\left[\frac{(1+\cos^2 2\alpha)(\cos^2 2\alpha + \cos^4 2\theta)}{(\cos^2 2\alpha + \cos^2 2\theta)^2}\right]^2 F_c{}^2\right\}^{1/4\ 6,7}$$

where $2\alpha$ is the $2\theta$ value for the monochromator, and $k$ is a scale constant.

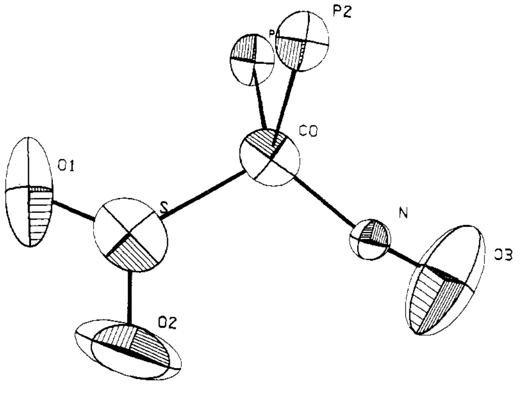

**Figure 1.** ORTEP projection of the inner coordination sphere.

**Figure 2.** Stereoview of the molecular structure.

The structure was determined by standard Patterson, Fourier, and least-squares methods using the LASL System of Crystal Structure Programs. Refinements carried out with anisotropic thermal parameters for all atoms, except the nitrogen and carbons, converged to an unweighted $R$ value of 10.1% and a weighted $R$ value of 7.6%. Attempts to refine the nitrogen atom anisotropically resulted in physically unrealizable thermal parameters. A final difference Fourier map contained several small peaks (≤0.6 e/cm$^3$) whose positions could not be interpreted in terms of any additional structural features.

The final structural parameters are given in Table II and selected distances and angles are shown in Table III.

## Discussion

A projection of the molecular structure (excluding carbons)

**Table II.** Fractional Coordinates and Thermal Parameters for Nitrosyl(sulfur dioxide)bis(triphenylphosphine)cobalt[a]

| atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co(1) | 0.7718 (2) | 0.1215 (3) | 0.1977 (2) | 6.3 (2) | 5.4 (2) | 4.1 (2) | 1.2 (4) | 7.9 (4) | 0.6 (4) |
| P(1) | 0.7272 (3) | 0.0220 (6) | 0.2776 (3) | 4.0 (4) | 5.7 (5) | 3.4 (4) | 0.4 (8) | 4.8 (7) | 0.3 (7) |
| P(2) | 0.7818 (3) | −0.0412 (6) | 0.1179 (3) | 4.0 (4) | 5.2 (4) | 3.6 (4) | 0.3 (7) | 4.3 (7) | −0.2 (7) |
| S(1) | 0.6929 (4) | 0.2559 (8) | 0.1237 (4) | 10.1 (6) | 8.2 (6) | 6.5 (5) | 3.3 (12) | 10.2 (10) | 0.3 (10) |
| O(1) | 0.6106 (8) | 0.2430 (20) | 0.0878 (9) | 6.0 (12) | 19.5 (21) | 8.0 (14) | 9.1 (30) | 0.6 (22) | 2.1 (28) |
| O(2) | 0.7169 (10) | 0.3856 (17) | 0.1103 (13) | 18.5 (21) | 5.5 (14) | 25.9 (25) | 4.6 (30) | 24.6 (38) | 11.9 (34) |
| O(3) | 0.9166 (9) | 0.2209 (20) | 0.3061 (11) | 7.7 (13) | 23.4 (24) | 10.4 (16) | −8.6 (32) | 9.1 (25) | −15.9 (32) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 0.856 (1) | 0.192 (1) | 0.258 (1) | 2.3 (4) | C(1) | 0.315 (1) | 0.355 (2) | 0.254 (1) | 2.3 (4) |
| C(2) | 0.377 (1) | 0.351 (2) | 0.339 (1) | 3.2 (5) | C(3) | 0.406 (1) | 0.279 (2) | 0.866 (1) | 4.5 (5) |
| C(4) | 0.197 (1) | 0.006 (2) | 0.607 (1) | 3.5 (5) | C(5) | 0.213 (1) | 0.982 (2) | 0.536 (1) | 4.4 (5) |
| C(6) | 0.305 (1) | 0.124 (2) | 0.967 (1) | 2.7 (4) | C(7) | 0.304 (1) | 0.254 (2) | 0.990 (1) | 4.1 (5) |
| C(8) | 0.367 (1) | 0.455 (2) | 0.504 (1) | 3.9 (5) | C(9) | 0.284 (1) | 0.250 (2) | 0.696 (1) | 3.5 (5) |
| C(10) | 0.154 (1) | 0.490 (2) | 0.953 (1) | 4.8 (6) | C(11) | 0.086 (1) | 0.438 (2) | 0.939 (1) | 4.5 (5) |
| C(12) | 0.072 (1) | 0.411 (2) | 0.008 (1) | 4.9 (5) | C(13) | 0.128 (1) | 0.441 (2) | 0.093 (1) | 3.2 (5) |
| C(14) | 0.341 (1) | 0.618 (2) | 0.207 (1) | 2.8 (4) | C(15) | 0.404 (1) | 0.553 (2) | 0.210 (1) | 2.9 (5) |
| C(16) | 0.436 (1) | 0.763 (2) | 0.169 (1) | 4.5 (5) | C(17) | 0.372 (1) | 0.824 (2) | 0.165 (1) | 4.8 (6) |
| C(18) | 0.157 (1) | 0.173 (2) | 0.811 (1) | 3.1 (5) | C(19) | 0.146 (1) | 0.096 (2) | −0.023 (1) | 3.9 (5) |
| C(20) | 0.111 (1) | 0.440 (2) | 0.526 (1) | 4.3 (5) | C(21) | 0.435 (1) | 0.239 (2) | 0.088 (1) | 5.7 (6) |
| C(22) | 0.374 (1) | 0.109 (2) | 0.316 (1) | 4.8 (5) | C(23) | 0.315 (1) | 0.122 (2) | 0.232 (1) | 5.4 (6) |
| C(24) | 0.450 (1) | 0.630 (2) | 0.191 (1) | 4.5 (5) | C(25) | 0.324 (1) | 0.748 (2) | 0.687 (1) | 4.0 (5) |
| C(26) | 0.170 (1) | 0.993 (2) | 0.947 (1) | 2.7 (4) | C(27) | 0.166 (1) | 0.641 (2) | 0.459 (1) | 3.3 (5) |
| C(28) | 0.127 (1) | 0.673 (2) | 0.506 (1) | 3.9 (5) | C(29) | 0.102 (1) | 0.925 (2) | 0.041 (1) | 4.0 (5) |
| C(30) | 0.183 (1) | 0.213 (2) | 0.293 (1) | 3.2 (5) | C(31) | 0.134 (1) | 0.116 (2) | 0.237 (1) | 4.0 (5) |
| C(32) | 0.057 (1) | 0.358 (2) | 0.699 (1) | 4.4 (5) | C(33) | 0.025 (1) | 0.258 (2) | 0.210 (1) | 4.7 (5) |
| C(34) | 0.079 (1) | 0.143 (2) | 0.770 (1) | 4.2 (5) | C(35) | 0.434 (1) | 0.107 (2) | 0.068 (1) | 5.2 (6) |
| C(36) | 0.371 (1) | 0.177 (2) | 0.550 (1) | 5.3 (6) | | | | | |

[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)

| | | | |
|---|---|---|---|
| Co-P(1) | 2.266 (6) | Co-N-O | 169 (2) |
| Co-P(2) | 2.248 (6) | Co-S-O(1) | 126 (1) |
| Co-S | 2.021 (8) | Co-S-O(2) | 119 (1) |
| Co-N | 1.68 (1) | S-O(1) | 1.48 (1) |
| P(1)-Co-P(2) | 104.8 (2) | S-O(2) | 1.47 (2) |
| P(1)-Co-S | 105.3 (3) | O(1)-S-O(2) | 114 (1) |
| P(1)-Co-N | 113.7 (5) | | |
| P(2)-Co-S | 112.4 (3) | C-C[a] | 1.408 (1.366, 1.444) |
| P(2)-Co-N | 109.0 (5) | C-C-C[a] | 120.0 (112.6, 127.5) |
| S-Co-N | 111.4 (6) | P-C[a] | 1.863 (1.836, 1.898) |
| N-O | 1.13 (2) | C-P-C[a] | 103.0 (101.1, 106.2) |

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

is shown in Figure 1, and Figure 2 contains a stereoview of the entire molecule.

The coordination geometry of the cobalt may be described as approximately tetrahedral with a nearly linear nitrosyl [∠Co–N–O = 169 (2)°] and a nearly coplanar $M–SO_2$ moiety, the angle between the M–S vector and the perpendicular to the $SO_2$ plane being 84.4°. The M–N distance of 1.68 (1) Å and the N–O distance of 1.13 (2) Å are within experimental error of those observed in recently reported $d^{10}$ four-coordinate cobalt nitrosyl structures; i.e., Co–N = 1.664 (11), 1.645 (6), 1.650 (6), and 1.698 (5) Å and N–O = 1.136 (12), 1.174 (6), 1.120 (5), and 1.164 (3) Å in $[Co(NO)_2(diphos)][PF_6]$,[8] $[Co(NO)_2(PPh_3)_2][PF_6]$,[9] $Co(NO)_2(SacSac)$,[10] and $Co(NO)(CO)_3$,[11] respectively. The average Co–P distance of 2.257 (8) Å is not significantly different from that reported for $[Co(NO)_2(PPh_3)_2][PF_6]$ (2.266 (3) Å).

The significance of this structure is apparent when compared with the isoelectronic complex $Rh(NO)(SO_2)(PPh_3)_2$ (I) which exhibits a bent nitrosyl group [140.4 (6)°] and a $\eta^2$-$SO_2$ ligand with nearly equal Rh–S [2.327 (2) Å] and Rh–O [2.342 (5) Å] distances. The only other structurally characterized[3] example of a mixed $SO_2$–NO complex (II) shows this same type of $SO_2$ binding. The question as to whether or not this type of bond is a general feature of complexes containing both nitrosyl and sulfur dioxide as ligands is therefore answered by this work. Furthermore it has been suggested[2] that a necessary condition for the $\eta^2$ bonding mode is the existence of a strongly $\pi$-bonding ligand capable of providing a perturbation of the metal d orbital in the plane of the $SO_2$ (in a hypothetical starting model) in such a way as to make possible a second-order Jahn–Teller term which couples the in-plane wagging motion of the $SO_2$ group to the resulting molecular orbital. We note, in this vein, that in the present structure the $Co–SO_2$ and Co–NO groups are nearly coplanar; the dihedral angle between the $SO_2$ plane and the plane formed by the S, Co, and N atoms is 20.1°. Since inspection of Figure 2 shows no obvious steric hindrance to rotation about the $Co–SO_2$ bond, it is reasonable to assume that the coplanarity of the groups is due to a ligand–ligand interaction. The deviation of the Co–NO angle [169 (2)°] from linearity may also be indicative of such an interaction as has been suggested for the four-coordinate dinitrosyl–transition-metal complexes (see ref 8 and references cited therein). The present structure might be considered then to represent a point on the reaction pathway to the side-on bonded geometry in which the geometric relationship between the two amphoteric ligands is such as to support our original suggestion concerning the nature of the interaction which favors the $\eta^2$ type of bonding. The difference between the two structures (Rh, Co) must be attributed to the decreased basicity of the Co center. Whether the third structurally verified mode of transition-metal $SO_2$ bonding (i.e., pyramidal geometry at the sulfur atom) will exist concurrently with the presence of the nitrosyl ligand is an interesting question which remains to be answered.

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

**Registry No.** $Co(NO)(SO_2)(PPh_3)_2$, 68457-35-2; $Co(NO)(PPh_3)_3$, 18712-92-0.

**Supplementary Material Available:** Listings of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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