Troyanov[9] has reported that the electrical conductivity of single crystal platelets of ZrCl has been found (by an unspecified method) to be about 1.5×10^{-3} ohm^{-1} cm^{-1} normal to the plate and 55 ohm^{-1} cm^{-1} within the plate.

During the course of the present investigation a structure for ZrCl was reported by Troyanov.[9] In an earlier report of the preparation of ZrCl and its powder pattern, Troyanov and Tsirel'nikov[8] had indexed the powder pattern on the basis of a rhombohedral cell with $a = 9.12$ Å, $\alpha = 21.62°$, and $Z = 2$, corresponding to the trigonal cell $a = 3.41$ Å, $c = 26.66$ Å, $Z = 6$, as found here. The reported structure was solved using film data, and the poor refinement ($R = 0.29$) was attributed to difficulties in measuring the 60 $h0l$ intensities used. Few details are provided regarding procedures and methods. Nonetheless the space group and the basic ordering of the layers were correctly deduced, although this was quite obscured by thoroughly unreasonable interlayer distances reported, viz., 2.87 Å for Zr–Zr, 2.81 Å for Cl–Cl, and 3.10 Å for Zr–Cl vs. 3.09, 3.61, and 2.63 Å, respectively, determined in the present work.

Finally a significant correspondence in metal–metal bonding is to be noted between that found here for ZrCl (and implied for HfCl according to powder data[7,28]) and that reported by Franzen and Graham[29] for Hf₂S. Generally structural similarities in metal–metal bonding between reduced transition metal chlorides and sulfides have been exceedingly small, but in this case similar double metal layers can be discerned. Indeed, the coordination polyhedra about the metal, the relative metal–metal distances, and calculated bond orders about Hf in Hf₂S are remarkably similar to those about Zr in ZrCl. However, the smaller fraction of nonmetal in the isoelectronic sulfide places only a single bridging layer of sulfur between the double metal layers, thereby greatly reducing the structural and presumably the electrical anisotropy. In contrast there seems to be no clear relationship between the structures of ZrCl and the isoelectronic NbO.

Registry No. ZrCl, 14989-34-5; ZrCl₄, 10026-11-6; zirconium, 7440-67-7.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes for ZrCl (2 pages). Ordering information is given on any current masthead page.

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Sulfur Dioxide Bonding in Four-Coordinate Complexes. Crystal and Molecular Structure of the Toluene Solvate of Bis(sulfur dioxide)bis(triphenylphosphine)platinum

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The crystal and molecular structure of the toluene solvate of bis(sulfur dioxide)bis(triphenylphosphine)platinum, Pt-(SO₂)₂(PPh₃)₂·C₇H₈, has been determined at −63 °C. The compound crystallizes in the space group $P2_1/c$ with $a = 10.858$ (3) Å, $b = 20.570$ (6) Å, $c = 19.497$ (6) Å, and $\beta = 115.62$ (2)° with $\rho_{calcd} = 1.59$ g/cm³ for $Z = 4$ (MoKα_1 radiation, λ 0.709 30 Å). The structure refined to an unweighted R value of 0.036 for 5592 reflections with $I > 3\sigma(I)$. The coordination geometry around the platinum is best described as a severely distorted tetrahedron with P1–Pt–P2 and S1–Pt–S2 angles of 158.58 (6) and 106.33 (8)°, respectively. The angles are consistent with arguments relating to the relative π-acceptor strength of the two ligands. Both sulfur dioxide groups are pyramidal with the average angle between the M–S vectors and SO₂ planes being 119° and an average M–S distance of 2.43 Å.

Introduction

The ability of terminally bound sulfur dioxide to exhibit at least two types of interactions with transition metal complexes has long been recognized. Conclusive structural evidence exists for complexes with bent MSO₂ moieties in which the geometry at the S atom is pyramidal (the angle between the M–S vector and the SO₂ plane being approximately 120°) as well as those for which the MSO₂ is planar.[1–6] It has been pointed out that SO₂ is similar to the nitrosyl ligand in this regard and that the behavior of both may be understood in terms of the number of d electrons and coordination geometry of the transition metal.[4,7–9] Thus, both ligands provide a readily observable

structural characteristic which serves as a test for bonding concepts. Conversely, of course, the sterochemistry of the complex controls the geometry, charge density, and chemistry of bound ligands making correlations between the chemistry and geometry of SO_2 containing complexes particularly useful.

It is interesting then that although the metal-catalyzed oxygenation of SO_2 to SO_4^{2-} has been extensively studied, the previous lack of structural studies in this area made it impossible to associate this reaction with either a bent or a coplanar MSO_2 geometry.

While the similarities between SO_2 and NO transition metal interactions are interesting, it is their differences which make the study of SO_2 complexes especially worthwhile. The maximum symmetry of a transition metal–sulfur dioxide complex is C_{2v}, precluding the possibility of symmetry-required degenerate electronic states. Thus, consideration of geometric distortion due to first-order Jahn–Teller effects is unnecessary and the bonding models which account for the sulfur geometry are inherently simpler. Both SO_2 and NO^+ contain a highest filled donor orbital of σ symmetry and empty acceptor orbitals of the proper energy and symmetry to produce a strong π interaction when these ligands bind to a transition metal complex. Aside from the differences in symmetry (SO_2 has only one readily accessible π-type orbital), the most obvious difference between the ligands is that, while the π orbitals are of similar energy, the σ orbital for SO_2 lies considerably higher than does its NO^+ counterpart.[8] One might then expect that the π- and σ-type antibonding orbitals will lie closer together in sulfur dioxide–transition metal complexes. If the tendency of the ligand to bend depends on the proximity of these two orbitals, as has been generally supposed, it follows that structures exhibiting the bent geometry are more likely to occur for SO_2 than for the isoelectronic nitrosyl analogues.

Four-coordinate (d^{10}) transition metal systems are of particular chemical interest due to the facility with which they undergo reactions of the bound ligands. We feel that the bonding in these systems has not been clearly understood in spite of the large body of literature attempting to correlate the observed structural features with current bonding concepts. Clearly, the SO_2-containing complexes provide a powerful adjunct to the extensive work done on the nitrosyls. We, therefore, present here the first structural description of a four-coordinate (d^{10}) bis(sulfur dioxide) complex.

Experimental Section

The toluene solvate of bis(sulfur dioxide)bis(triphenylphosphine)platinum was prepared by passing SO_2 through a solution of $Pt(C_2H_4)(PPh_3)_2$[10] and crystallized from toluene as brown-red platelets. The compound is unstable toward loss of SO_2 at room temperature; however, coating wth mineral oil slows this decomposition, as does cooling of the sample.

Room-temperature precession photographs revealed diffraction patterns consistent with the space group $P2_1/c$. A crystal of approximate dimensions $0.42 \times 0.20 \times 0.17$ mm was mounted on a glass fiber and coated with mineral oil. The crystal was placed on a Picker FACS 1 diffractometer and cooled to -63 °C in a nitrogen cold stream. The cell constants obtained from least-squares refinement of 12 high-order reflections are $a = 10.858$ (3) Å, $b = 20.570$ (6) Å, $c = 19.497$ (6) Å, and $\beta = 115.62$ (2)°, with $\rho_{calcd} = 1.59$ g/cm^3 for $Z = 4$ (Mo Kα_1 radiation, λ 0.709 30 Å).

Intensities were measured utilizing graphite-monochromatized Mo Kα radiation. A standard θ–2θ scan technique, 1.5° (plus α_1–α_2 dispersion) scan at 2°/min and 20-s background at each extreme of the scan, was utilized to collect 7585 reflections ($2\theta \leq 50°$). Of the 6957 unique reflections collected, 5592 were observed with $I > 3\sigma(I)$ (where $\sigma(I)$ was computed as usual)[11] and were used in the solution and refinement of the structure. The intensities of two standard reflections measured every 50 reflections indicated no major instability trends in the data and minor fluctuations were corrected using a polynomial determined by least-squares fitting the standard reflection curves. Absorption corrections were applied[12] ($\mu = 39.72$ cm^{-1}) assuming a crystal bounded by eight faces, {100}, {001}, and {011}.

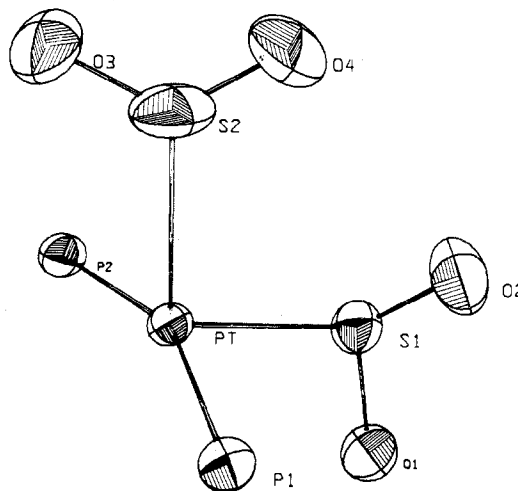**Figure 1.** Stereoview of the molecular structure including the toluene of solvation.

Figure 2. Heavy-atom structure of $Pt(SO_2)_2(PPh_3)_2$; thermal ellipsoids are drawn at the 50% probability level.

The transmission factor varied between 0.61 and 0.49.

The platinum atom was located using standard Patterson techniques and all nonhydrogen atoms were located using difference Fourier techniques. Refinement was performed as described in previous publications[11] using neutral atom scattering factors[13] and appropriate dispersion terms.[14] All atoms heavier than carbon were refined anisotropically while all carbon atoms were refined isotropically. The final refinement including a secondary extinction parameter[15,16] yielded on unweighted R value of 0.036. No attempt was made to locate or account for hydrogen atoms. Final atomic parameters are given in Table I and pertinent distances and angles are given in Table II. We offer no ready explanation for the large difference in Pt–S distances, 2.391 (2) and 2.464 (2) Å, but we do note that the discrepancy was even larger in a room-temperature data set and may be associated with the instability of the complex.

Discussion

Examination of the stereoview of the complex (Figure 1) and the platinum coordination geometry depicted in Figure 2 reveals at least three noteworthy features. (1) Both SO_2 groups are bent, the average angle between the Pt–S vector and the resultant of the two S–O vectors being 119°. (2) The P–Pt–P angle (158.6°) is noticably larger than the S–Pt–S angle (106.3°) and is the largest P–M–P angle reported for a tetrahedral d^{10} complex. (3) The two SO_2 ligands are approximately bisected by alternate Pt–P–S planes. The toluene of solvation might seem to occupy a possible fifth coordination site, but the distance from platinum to the center of the toluene phenyl fragment exceeds 4 Å. Hence, the toluene may serve to some extent to block a possible fifth coordination site but is not directly involved in the bonding.

From previous investigations, the M–S bond distance is a definitive diagnostic, distinguishing between the two structurally established alternatives for the MSO_2 geometry; the three well-characterized coplanar systems $CpMn(CO)_2SO_2$,[2] $[Ru(NH_3)_4SO_2Cl]Cl$,[1] and $CpRh(C_2H_4)SO_2$[6] contain M–S distances of 2.037 (5), 2.072 (3), and 2.096 (2) Å, respectively, while the two previously reported complexes with bent SO_2 groups $MClCO(PPh_3)_2SO_2$,[3,4] M = Ir and Rh, exhibit significantly longer distances of 2.49 (1) and 2.450 (2) Å with

Table I

<div align="center">Positional and Isotropic Thermal Parameters^a</div>

Atom	x	y	z	B, Å^2
Pt	−0.012 70 (2)	0.080 48 (1)	0.245 30 (1)	
P1	0.842 5 (2)	0.136 74 (9)	0.137 9 (1)	
P2	0.190 0 (2)	0.047 80 (9)	0.344 7 (1)	
S1	0.101 2 (2)	0.027 51 (9)	0.785 1 (1)	
S2	0.877 2 (2)	0.129 5 (1)	0.320 0 (1)	
O1	0.081 2 (5)	0.042 2 (2)	0.852 5 (3)	
O2	0.239 5 (5)	0.025 3 (3)	0.797 5 (3)	
O3	0.979 1 (6)	0.157 2 (3)	0.383 8 (4)	
O4	0.807 2 (8)	0.078 6 (5)	0.331 6 (5)	
C1	0.667 0 (7)	0.111 9 (3)	0.082 0 (4)	2.4 (1)
C2	0.586 5 (7)	0.097 5 (3)	0.118 6 (4)	3.1 (1)
C3	0.446 4 (8)	0.080 0 (4)	0.075 6 (5)	3.9 (2)
C4	0.394 4 (8)	0.076 9 (4)	−0.003 7 (4)	3.6 (1)
C5	0.476 1 (8)	0.091 4 (4)	0.959 8 (4)	3.7 (2)
C6	0.612 2 (8)	0.109 3 (4)	0.002 0 (4)	3.3 (1)
C7	0.837 3 (7)	0.218 4 (3)	0.170 3 (4)	2.6 (1)
C8	0.718 9 (7)	0.253 3 (4)	0.668 9 (4)	3.1 (1)
C9	0.727 6 (8)	0.194 1 (4)	0.706 9 (5)	3.9 (2)
C10	0.853 4 (9)	0.163 1 (4)	0.746 1 (5)	4.2 (2)
C11	0.969 7 (8)	0.191 3 (4)	0.747 5 (5)	4.4 (2)
C12	0.963 1 (7)	0.249 3 (4)	0.208 7 (4)	3.6 (2)
C13	0.918 0 (6)	0.143 3 (3)	0.071 4 (4)	2.3 (1)
C14	0.982 1 (7)	0.088 0 (4)	0.059 0 (4)	3.1 (1)
C15	0.037 7 (8)	0.090 9 (4)	1.007 1 (5)	4.0 (2)
C16	0.028 6 (8)	0.149 4 (4)	0.966 5 (5)	4.0 (2)
C17	0.965 4 (8)	0.204 3 (4)	0.978 5 (5)	4.3 (2)
C18	0.907 4 (8)	0.201 5 (4)	0.031 1 (5)	3.7 (2)
C19	0.813 1 (7)	0.021 0 (3)	0.598 1 (4)	2.6 (1)
C20	0.923 2 (8)	0.026 1 (4)	0.578 7 (4)	3.6 (2)
C21	0.925 6 (8)	0.078 1 (4)	0.532 6 (5)	4.4 (2)
C22	0.822 0 (8)	0.123 1 (4)	0.506 1 (5)	3.9 (2)
C23	0.713 6 (8)	0.119 1 (4)	0.527 1 (5)	4.1 (2)
C24	0.708 6 (7)	0.068 0 (4)	0.573 0 (4)	3.3 (1)
C25	0.269 9 (7)	0.115 0 (3)	0.410 7 (4)	2.7 (1)
C26	0.315 1 (8)	0.107 7 (4)	0.488 7 (5)	3.8 (2)
C27	0.367 7 (9)	0.163 4 (4)	0.534 3 (5)	4.9 (2)
C28	0.374 3 (9)	0.222 6 (4)	0.503 5 (5)	5.1 (2)
C29	0.330 3 (9)	0.229 8 (5)	0.426 1 (6)	5.3 (2)
C30	0.277 7 (8)	0.174 2 (4)	0.378 4 (5)	4.0 (2)
C31	0.313 9 (7)	0.026 2 (3)	0.309 1 (4)	2.7 (1)
C32	0.454 6 (7)	0.034 8 (4)	0.356 0 (4)	3.4 (2)
C33	0.452 2 (8)	−0.015 0 (4)	0.671 6 (5)	4.6 (2)
C34	0.495 6 (9)	0.010 4 (4)	0.743 5 (5)	4.6 (2)
C35	0.636 6 (8)	0.018 9 (4)	0.790 3 (5)	4.2 (2)
C36	0.732 3 (7)	−0.000 2 (4)	0.763 7 (4)	3.1 (1)
C37	0.420 7 (11)	0.190 2 (5)	0.769 9 (6)	5.9 (2)
C38	0.287 5 (11)	0.219 2 (5)	0.167 9 (6)	6.4 (3)
C39	0.480 5 (13)	0.250 2 (7)	0.783 9 (7)	8.1 (3)
C40	0.405 5 (12)	0.193 4 (6)	0.227 5 (7)	7.1 (3)
C41	0.293 0 (15)	0.176 5 (6)	0.706 1 (9)	9.1 (4)
C42	0.228 0 (16)	0.217 3 (8)	0.653 6 (10)	11.3 (4)
C43	0.590 7 (18)	0.232 3 (8)	0.344 5 (10)	13.1 (5)

<div align="center">Anisotropic Thermal Parameters (×10⁴)</div>

Atom	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Pt	45.7 (3)	12.63 (6)	12.73 (8)	0.0 (3)	20.0 (2)	−1.6 (2)
P1	57 (2)	13.2 (5)	16.1 (6)	3 (2)	25 (2)	0.3 (8)
P2	50 (2)	18.0 (5)	15.1 (6)	0 (2)	20 (2)	0.0 (9)
S1	84 (2)	14.7 (5)	22.9 (6)	−11 (2)	36 (2)	−3.8 (9)
S2	103 (3)	34.6 (8)	27.0 (8)	27 (2)	67 (2)	−5 (1)
O1	108 (7)	19 (1)	29 (2)	−13 (5)	61 (6)	−16 (3)
O2	100 (7)	25 (2)	54 (3)	−28 (6)	86 (8)	−22 (4)
O3	132 (9)	56 (3)	64 (4)	−71 (8)	131 (10)	−83 (5)
O4	242 (13)	92 (4)	94 (5)	−181 (13)	262 (15)	−111 (8)

^a With secondary extinction correction of 6 (2) × 10⁻¹ and scale factor of 0.710 (9). Carbons 1–36 are phenyl carbons of PPh₃ groups. Carbons 37–43 are toluene of solvation.

M–SO₂ angles of approximately 120°. The average Pt–S distance of 2.43 Å in the present structure is in accord with the longer distance expected for the bent geometry. On the other hand, the only other SO₂-containing Pt(0) four-coordinate complex whose structure has been reported, (Ph₃P)₃PtSO₂, exhibits a Pt–S distance of 2.40 (1) Å and the single-crystal x-ray data have been interpreted in terms of a coplanar PtSO₂ moiety.[5] We note, however, that the Pt–S bond of this complex resides on a crystallographic threefold axis and the resulting disorder of the oxygen atoms allows an alternative interpretation in terms of a bent SO₂ group. In addition, we have crystallized a triclinic form of this complex

Table II

Atoms	Dist, Å	Atoms	Angle, deg
Pt–P1	2.313 (2)	P1–Pt–P2	158.58 (6)
Pt–P2	2.316 (2)	P1–Pt–S1	101.37 (6)
Pt–S1	2.391 (2)	P1–Pt–S2	91.00 (7)
Pt–S2	2.464 (2)	P2–Pt–S1	94.15 (6)
P1–C1[a]	1.812 (7)	P2–Pt–S2	98.77 (7)
P1–C7[a]	1.804 (7)	S1–Pt–S2	106.33 (8)
P1–C13[a]	1.814 (7)	Pt–S1–O1	102.5 (2)
P2–C19[a]	1.811 (7)	Pt–S1–O2	107.2 (3)
P2–C25[a]	1.832 (7)	O1–S1–O2	114.5 (3)
P2–C31[a]	1.815 (7)	Pt–S2–O3	107.3 (3)
S1–O1	1.453 (5)	Pt–S2–O4	103.4 (3)
S1–O2	1.416 (5)	O3–S2–O4	116.9 (5)
S2–O3	1.381 (6)	(Pt–P1–P2 plane)–(Pt–S1–S2 plane)	85
S2–O4	1.368 (8)	(Pt–S1 vector)–(S1–O1–O2 plane)	118
		(Pt–S2 vector)–(S2–O3–O4 plane)	120

[a] Phenyl carbons.

and have verified the bent geometry.[17]

The large angle between the phosphine ligands and smaller S–Pt–S angle are consistent with the observed angles in other similar four-coordinate species. For the bis(nitrosyl)bis-(phosphine)(transition metal) complexes, the P–M–P angles range from 103.51 (6) to 116.3 (2)° while the N–M–N angles (linear or only slightly bent nitrosyls) range from 123.8 (4) to 157.5 (3)° depending on the metal (third-row metals generally exhibit larger angles) and to some extent on the deviations of the nitrosyl from linearity (see ref 18 and references cited therein). The complex (CO)₂Pt(PPh₂Et)₂ exhibits angles between the carbons and between the platinum–phosphine bonds of 117 (1) and 98.9 (2)°, respectively.[19] Clearly then, recognizing that in the present complex the bent SO₂ ligands indicate σ-type M–S bonds, the angles subtended at the metal can be correlated with the relative π interaction of the ligands, larger angles being associated with greater π-acceptor ability.

The structure presented here contains two SO₂ ligands bent toward opposite M–P bonds. This tendency has also been noticed in (Ph₃P)₂Os(NO)₂ where the slight bendings of the nitrosyls are distinctly toward the M–P vectors.[20] It should be emphasized that several tetrahedral bis(phosphine)–bis-(nitrosyl) structures have been determined, and all contain linear or nearly linear M–NO moieties. The present structure, then, provides the most dramatic and clear-cut example of the possible structural dissimilarities in nitrosyl and SO₂ complexes.

If one assumes, as has been done for the nitrosyls, that bending involves considerable charge transfer to the ligand, our structure is consistent with a model in which the electronic configuration at the sulfur atom can be approximately described in terms of an sp³ hybrid with a stereochemically active lone pair of electrons. The observed conformation of the two SO₂ groups with respect to one another could then be a result of the minimization of lone pair repulsions. That this argument, when carried to its logical conclusion, leads to an inconsistency is obvious from the following discussion.

It has been suggested that for {MNO}¹⁰ four-coordinate transition metal complexes there exists a clear-cut choice between (1) tetrahedral complexes with linear MNO groups and (2) square-planar complexes with strongly bent MNO groups. While this prediction (there are no known square-planar {MNO}¹⁰ complexes) has been discussed in terms of molecular orbital models, it is at least implied in these discussions that the bending of the nitrosyl would be accompanied by an effective oxidation of the metal toward a d⁸ configuration

(or even d⁶ in the case of bis(nitrosyl)metal complexes) resulting in distortion of the initially tetrahedral complex toward a square-planar geometry. If one accepts the assertion that the bonding in complexes containing SO₂ is similar to that in their nitrosyl analogues, then it follows that the same prediction must hold here. While the present compound is distinctly distorted from ideal tetrahedral geometry, the distortion is clearly not toward square planar. This observation does not, of course, preclude the possibility that a bent square-planar {MNO}¹⁰ nitrosyl or SO₂ complex will eventually emerge. It has been pointed out by Hoffmann et al.,[9] Mingos and Ibers,[21] and Enemark and Feltham[7] that the charge density transfer is no doubt greatly influenced by factors more subtle than the MNO geometry. Indeed, the result presented here makes the search for a bent {MNO}¹⁰ complex an even more intriguing challenge. Our results do, on the other hand, point to the futility of attempts to assign metal oxidation states on the basis of the ligand geometry in complexes containing amphoteric ligands and perhaps even to associate appreciable changes in metal basicities with these structural features.

Finally, we point out that the complex under discussion shows a ready reactivity toward oxygen to form (Ph₃P)₂PtSO₄ as does (Ph₃P)₃PtSO₂. All structurally characterized complexes with coplanar MSO₂ groups are, on the other hand, remarkably inert to this reaction. Notice, however, that bent SO₂ groups are associated with the chemically more basic transition metals exhibiting lower coordination numbers. While several factors may influence the mechanism and/or rate of this reaction, it is clear that it is highly correlated with a bent M–SO₂ moiety. Whether or not the bent geometry is a necessary condition for the reaction has not been established.

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