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Pyramidal Metal–Sulfur Dioxide Coordination. Chemistry of $Pt(SO_2)_2(PPh_3)_2$ and Synthesis and Molecular Structure of $Pt_3(SO_2)_3(PPh_3)_3{\cdot}C_7H_8{\cdot}SO_2$

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Slow removal of sulfur dioxide from a toluene solution of $Pt(SO_2)_2(PPh_3)_2$ yields orange crystals of $Pt_3(SO_2)_3(PPh_3)_3$, containing both toluene and SO_2 in the lattice. The compound crystallizes in the tetragonal space group $P4_2nm$ with $a = 24.272$ (7) Å, $c = 9.454$ (3) Å, and $\rho_{calcd} = 2.05$ g/cm^3 ($\rho_{measd} = 1.91$ g/cm^3) for $Z = 4$. The structure refined to an unweighted R value of 0.029 for 2321 reflections with $I \geq 3\sigma(I)$. The molecular structure consists of a triangle of platinum atoms each of which is bound to two bridging sulfur dioxide groups and a single triphenylphosphine. Rapid SO_2 removal from a $Pt(SO_2)_2(PPh_3)_2$ solution results in the formation of an orange solid of composition $Pt(SO_2)(PPh_3)_2$. Two other reactions involving displacement of labile sulfur dioxide from $Pt(SO_2)_2(PPh_3)_2$ by PPh_3 and CO have been examined and found to yield $Pt(SO_2)(PPh_3)_3$ and $Pt(CO)_2(PPh_3)_2$, respectively. The latter reaction is easily reversed by excess sulfur dioxide addition.

Introduction

The crystal structure of $Pt(SO_2)_2(PPh_3)_2$ has been determined and found to contain two pyramidal (bent) $M–SO_2$ moieties.[1] This is indeed interesting in view of the fact that all of the four-coordinate d^{10} bis(nitrosyl) complexes have essentially linear nitrosyl groups.[2] This increased tendency for SO_2 to bend relative to NO has also been confirmed in another four-coordinate platinum system, $Pt(SO_2)(PPh_3)_3$.[3] A bonding model for SO_2 complexes has been proposed which, while recognizing the similarities of the bonding for NO and SO_2, also accounts for this important difference.[4]

The pyramidal $M–SO_2$ geometry, with its longer metal–sulfur distance, might be expected to exhibit an entirely different chemistry from that of the alternative planar form. In particular it has been observed that the sulfato reaction is closely correlated with the pyramidal $M–SO_2$ geometry, as is the lability of the SO_2 ligand itself. Both of these characteristics are exhibited by $Pt(SO_2)_2(PPh_3)_2$. In the solid state a green complex, presumably $Pt(SO_2)(PPh_3)_2$, is formed on warming $Pt(SO_2)_2(PPh_3)_2$ to 50 °C.[5] Likewise, $Pt(SO_2)_2(PPh_3)_2$ readily reacts with air in solution yielding $Pt(SO_4)(PPh_3)_2$.

With a view toward expanding our understanding of SO_2 coordination chemistry, the work presented here was initiated. While attempting the preparation and crystallization of the heretofore mentioned $Pt(SO_2)(PPh_3)_2$, we unexpectedly formed crystals of $Pt_3(SO_2)_3(PPh_3)_3$. The crystal and molecular structure of this trimer is presented here, along with the chemical studies of pyramidal $M–SO_2$ groups in $Pt(SO_2)_2(PPh_3)_2$.

Experimental Section

Reagents and Chemicals. All solvents used in this study were reagent grade and used without purification. Sulfur dioxide and carbon monoxide were obtained from the Matheson Co.

$Pt_3(SO_2)_3(PPh_3)_3$. Bis(triphenylphosphine)bis(sulfur dioxide)platinum was prepared by passing SO_2 through a toluene solution of $Pt(C_2H_4)(PPh_3)_2$.[5] Over a period of 1 month, SO_2 slowly escaped through a ground-glass joint and a few orange crystals of $Pt_3(SO_2)_3(PPh_3)_3$ were formed at the surface of the solution. The yield of trimeric material was small, as the bulk of the $Pt(SO_2)_2(PPh_3)_2$ was converted to $Pt(SO_4)(PPh_3)_2$[5] by reaction with atmospheric oxygen which equilibrated over the solution as the SO_2 escaped. Attempts at preparing larger quantities of the trimer by removing SO_2 with a rapid stream of N_2 gas have instead resulted in the isolation of an orange powder (described below) with a different x-ray powder diffraction pattern and having a PPh_3:Pt ratio of 2.

$Pt(SO_2)(PPh_3)_2$. A toluene solution containing 0.18 mmol of $Pt(SO_2)_2(PPh_3)_2$ was prepared as above. Dry N_2 gas was rapidly bubbled through this solution for several hours and heptane added to precipitate 0.098 g of an orange solid (I). An infrared spectrum of I proved to be almost identical with that of the green solid previously isolated by removing SO_2 from solid $Pt(SO_2)_2(PPh_3)_2$ and formulated as $Pt(SO_2)(PPh_3)_2$.[5] Due to the fact that I has an appreciable dissociation pressure of SO_2 at room temperature, sulfur analyses were consistently low, but overall the elemental analyses are also consistent with the formulation $Pt(SO_2)(PPh_3)_2$ for this orange product (I). Anal. Calcd for $PtSO_2P_2C_{36}H_{30}$: C, 55.2; H, 3.9; S, 4.1; P, 7.9; mol wt 784.[6] Found: C, 56.2; H, 4.1; S, 2.3; P, 6.3; mol wt 930. The room-temperature ^{31}P NMR spectrum[7] of I consists of a single PPh_3 resonance at −29.6 ppm (downfield) relative to H_3PO_4 and exhibits no $^{195}Pt–^{31}P$ coupling.

$Pt(SO_2)(PPh_3)_2$ (I) in solution can be reconverted to $Pt(SO_2)_2(PPh_3)_2$ by addition of excess SO_2; however, varying amounts of impurities are present in the product depending on the time that I is allowed to stand out of solution.

Reaction of I (0.059 g, 0.075 mmol) with atmospheric O_2 in toluene solution resulted in the formation of 0.045 g (0.055 mmol) of $Pt(SO_4)(PPh_3)_2$ (73% yield), recovered by filtration and characterized by comparison of its infrared spectrum with that of an authentic sample of $Pt(SO_4)(PPh_3)_2$ prepared by reaction of $Pt(SO_2)(PPh_3)_3$ with O_2.[8]

When 0.098 g (0.13 mmol) of I was dissolved in benzene along with 0.034 g (0.13 mmole) of PPh_3, a dark brown-purple solution was obtained. Excess SO_2 was then added to allow the isolation of the product, as the expected product $Pt(SO_2)(PPh_3)_3$ is unstable toward loss of SO_2 in solution. The brown-purple solid obtained by addition of heptane to this SO_2 saturated solution was shown to be $Pt(SO_2)(PPh_3)_3$ by infrared analysis.

Reaction of $Pt(SO_2)_2(PPh_3)_2$ with PPh_3. A red-brown benzene solution of 0.1 mmol of $Pt(SO_2)_2(PPh_3)_2$ was prepared and 0.1 mmol of PPh_3 was added while gaseous SO_2 continually bubbled through the solution. An immediate color change to brownish purple was observed and the isolated product was determined to be $Pt(SO_2)(PPh_3)_3$ from infrared analysis and from x-ray precession photographs.

Reaction of $Pt(SO_2)_2(PPh_3)_2$ with CO. Carbon monoxide was bubbled through a toluene solution containing 0.2 mmol of $Pt(SO_2)_2(PPh_3)_2$ for several hours, during which the solution turned bright yellow. Heptane addition resulted in the isolation of 0.09 g (0.12 mmol) of a yellow solid with two ν_{CO} in the infrared spectrum at 1940 and 1975 cm^{-1} (Nujol mull). Elemental analysis is consistent with the formulation $Pt(CO)_2(PPh_3)_2$.[9] Anal. Calcd for $PtC_{38}P_2O_2H_{30}$: C, 58.84; H, 3.87; P, 8.0. Found: C, 58.69; H, 3.82; P, 6.80.

The above reaction has been shown to be reversible. Yellow solutions of $Pt(CO)_2(PPh_3)_2$ are readily converted back to the red-brown $Pt(SO_2)_2(PPh_3)_2$ by saturating the solutions with SO_2. Mixed SO_2/CO products have not yet been isolated from this system, however.

Crystal Structure Analysis of $Pt_3(SO_2)_3(PPh_3)_3{\cdot}C_7H_8{\cdot}SO_2$. Room-temperature precession photographs revealed a tetragonal cell (4/mmm symmetry) with conditions for nonextinction of $0kl$, $k + l = 2n$, consistent with space groups $P4_2/mnm$, $P\bar{4}n2$, and $P4_2nm$. A crystal of approximate dimensions 0.12 × 0.12 × 0.25 mm was mounted on a glass fiber and placed on a Picker FACS 1 diffractometer. The cell constants obtained from least-squares refinement of 12 high-order reflections are $a = 24.272$ (7) and $c = 9.454$ (3) Å; $\rho_{calcd} = 2.05$ g/cm^3 ($\rho_{measd} = 1.91$ g/cm^3) for $Z = 4$ (Mo Kα_1 radiation, λ 0.7093 Å).

Table I. Atomic Parameters[a]

Atom	x	y	z	B, Å^2
Pt1	0.205 85 (2)	0.284 86 (2)	0.0	*b*
Pt2	0.185 78 (2)	0.185 78 (2)	0.1180 (1)	*b*
S1	0.289 5 (2)	0.289 5 (2)	−0.1071 (7)	*b*
O1	0.328 8 (4)	0.328 8 (4)	−0.0507 (18)	*b*
O2	0.287 4 (5)	0.287 4 (5)	−0.2641 (19)	*b*
S2	0.125 2 (2)	0.257 0 (2)	0.1005 (5)	*b*
O3	0.082 0 (4)	0.250 2 (4)	0.0003 (17)	*b*
O4	0.110 9 (5)	0.282 3 (4)	0.2368 (14)	*b*
P1	0.130 0 (1)	0.130 0 (1)	0.2515 (6)	*b*
P2	0.176 8 (2)	0.371 5 (2)	−0.0626 (4)	*b*
C1	0.057 0 (6)	0.140 1 (6)	0.222 (2)	3.1 (3)
C2	0.021 6 (7)	0.159 1 (7)	0.329 (2)	4.8 (4)
C3	−0.036 4 (8)	0.165 2 (8)	0.299 (2)	5.3 (4)
C4	−0.055 3 (7)	0.157 0 (7)	0.168 (2)	5.2 (4)
C5	−0.022 7 (9)	0.141 0 (8)	0.062 (2)	6.3 (5)
C6	0.036 7 (8)	0.133 0 (8)	0.083 (2)	5.7 (5)
C7	0.140 0 (6)	0.140 0 (6)	0.442 (2)	2.5 (4)
C8	0.178 5 (6)	0.178 5 (6)	0.484 (3)	3.8 (5)
C9	0.187 5 (7)	0.187 5 (7)	0.630 (4)	4.9 (5)
C10	0.158 8 (7)	0.158 8 (7)	0.727 (3)	4.6 (5)
C11	0.118 3 (7)	0.118 3 (7)	0.684 (3)	4.2 (6)
C12	0.109 1 (6)	0.109 1 (6)	0.538 (2)	3.5 (5)
C13	0.104 0 (6)	0.387 8 (6)	−0.031 (2)	3.5 (3)
C14	0.085 9 (7)	0.396 2 (7)	0.106 (2)	4.5 (4)
C15	0.030 9 (7)	0.412 3 (7)	0.133 (3)	5.4 (4)
C16	−0.003 6 (7)	0.420 4 (7)	0.020 (3)	5.3 (4)
C17	0.012 3 (9)	0.409 0 (9)	−0.118 (2)	6.5 (5)
C18	0.068 6 (8)	0.393 0 (7)	−0.151 (2)	5.1 (4)
C19	0.184 3 (6)	0.382 0 (6)	−0.250 (2)	3.3 (3)
C20	0.168 9 (7)	0.337 9 (7)	−0.338 (2)	4.6 (4)
C21	0.171 9 (7)	0.343 8 (8)	−0.489 (3)	5.7 (4)
C22	0.191 1 (8)	0.394 3 (9)	−0.541 (2)	5.8 (5)
C23	0.205 7 (9)	0.436 2 (9)	−0.458 (3)	6.3 (5)
C24	0.204 4 (8)	0.432 1 (8)	−0.308 (2)	4.6 (4)
C25	0.210 9 (6)	0.427 7 (6)	0.031 (2)	3.4 (3)
C26	0.190 0 (7)	0.482 7 (7)	0.015 (2)	5.7 (4)
C27	0.217 9 (8)	0.524 4 (8)	0.086 (2)	6.1 (5)
C28	0.260 0 (9)	0.513 4 (9)	0.173 (2)	6.7 (5)
C29	0.280 4 (8)	0.460 7 (8)	0.190 (2)	6.5 (5)
C30	0.255 8 (6)	0.415 3 (6)	0.117 (2)	4.2 (3)
S3[c]	0.307 9 (3)	0.307 9 (3)	0.421 (1)	8.4 (3)
O5	0.345 5 (9)	0.345 5 (9)	0.378 (3)	12.6 (9)
O6	0.276 3 (9)	0.276 3 (9)	0.329 (4)	12 (1)
C31	0.500	0.500	0.986 (8)	8 (1)
C32	0.463 (1)	0.463 (1)	0.067 (4)	8 (1)
C33	0.461 (1)	0.461 (1)	0.225 (6)	12 (1)
C34	0.500	0.500	0.232 (8)	9 (2)
C35	0.500	0.500	0.863 (7)	12 (2)

Atom	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Pt1	10.57 (9)	10.35 (9)	73.8 (6)	−1.3 (2)	2.6 (7)	3.7 (7)
Pt2	10.99 (9)	10.99 (9)	59.9 (8)	−4.0 (2)	0.9 (5)	0.9 (5)
S1	12.8 (6)	12.8 (6)	119 (9)	−1 (2)	17 (4)	17 (4)
O1	18 (2)	18 (2)	173 (30)	−19 (5)	8 (10)	8 (10)
O2	23 (2)	23 (2)	101 (23)	3 (6)	24 (12)	24 (12)
S2	12.3 (7)	14.0 (8)	93 (6)	0 (1)	4 (4)	1 (4)
O3	13 (2)	23 (2)	175 (18)	−3 (3)	−12 (15)	32 (16)
O4	28 (3)	19 (3)	121 (18)	7 (4)	55 (13)	−12 (12)
P1	12.4 (6)	12.4 (6)	56 (7)	−5 (2)	2 (3)	2 (3)
P2	13.1 (8)	10.3 (7)	84 (5)	0 (1)	−5 (3)	0.0 (3)

[a] Secondary extinction correction of 2.2 (2) × 10^{-5} and scale factor of 0.3248 (5). [b] Anisotropic thermal parameters (× 10^4) are given for these atoms. [c] Atom positions following are associated with SO_2 and toluene in the lattice.

Intensities were measured utilizing graphite-monochromatized Mo Kα radiation. A standard θ–2θ scan technique, employing a 1.5° (plus α_1–α_2 dispersion) scan at 2°/min with 20-s background counts at each extreme of the scan, was utilized to collect 5536 reflections ($2\theta \leq 50°$). Of the 2730 unique reflections (after averaging equivalent observations), 2321 were observed according to the criterion $I > 3\sigma(I)$ (where $\sigma(I)$ was computed as usual)[10] 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. Minor fluctuations were corrected using a polynomial determined by least-squares fitting the standard reflection curves. Absorption corrections were applied[11] (μ = 81.48 cm^{-1}) assuming a crystal bounded by 10 faces, {100}, {001}, and {110}. The transmission factor varied between 0.44 and 0.41.

The patterson function could be interpreted in terms of an ordered structure with chemically reasonable geometry only in the space group $P4_2nm$. This interpretation established a triangle of platinum atoms coordinated by bridging SO_2 groups and terminal triphenylphosphines. Further difference maps revealed the presence of both SO_2 and toluene of solvation. Refinement was performed as described in previous publications[10] using neutral-atom scattering factors[12] and appropriate dispersion terms.[13] In the trimeric unit, atoms heavier than carbon

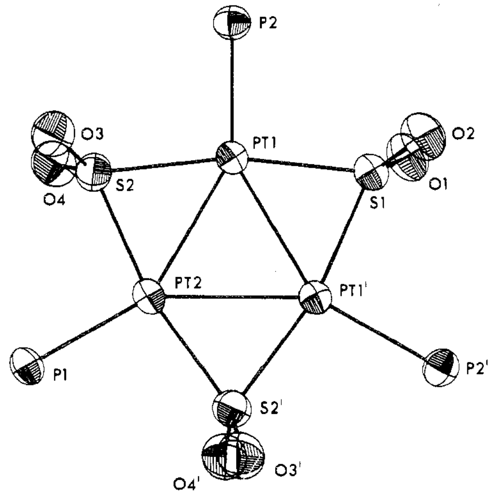

Figure 1. Molecular structure of $Pt_3(SO_2)_3(PPh_3)_3$ with carbon atoms omitted. Thermal ellipsoids are depicted at the 50% probability level.

Figure 2. Stereoview of the structure with the toluene and sulfur dioxide of solvation omitted.

were refined anisotropically while all carbon atoms were refined isotropically. Additionally, both molecules of solvation were refined isotropically. The final refinement including a secondary extinction parameter[14,15] yielded an unweighted *R* value of 0.029. Refinement of the other enantiomorphic form yielded a slightly higher *R* value. 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.

Results and Discussion

Molecular Structure of $Pt_3(SO_2)_3(PPh_3)_3$. A projection of the molecule is shown in Figure 1 and a stereoview in Figure 2. The molecule contains a mirror plane passing through Pt2, P1, S1, O1, and O2, thus relating Pt1 and Pt1′ of the metal triangle. The Pt–Pt distances of 2.695 (1) and 2.712 (1) Å observed in this structure are consistent with that expected for a single Pt–Pt bond. Each platinum atom is bound to two symmetrically bridging sulfur dioxide groups and one triphenylphosphine group. It is interesting to note that the phosphorus atoms of the terminal triphenylphosphine groups and the sulfur atoms of the bridging sulfur dioxide groups are all very nearly coplanar with the platinum triangle. The angles between the normal to the [Pt1–Pt2–Pt1′] plane and the Pt1–P2 and Pt2–P1 vectors are 90 and 86°, respectively. The dihedral angle between the [Pt1–Pt2–Pt1′] plane and the [Pt1–S1–Pt1′] plane is 3°, while that between [Pt1–Pt2–Pt1′] and [Pt1–S2–Pt2] is 2°. These dihedral angles differ drastically from those observed in $Pd_3(SO_2)_2(t\text{-BuNC})_5$, which average 48°.[16] This structure also contains a metal triangle; however, only two SO_2 groups are present. Thus two of the metal atoms are bonded to two terminal *t*-BuNC groups and one bridging SO_2, while the other is bonded to the two bridging SO_2 groups and one terminal isocyanide group. It appears likely that the differences in dihedral angles discussed above could simply be the result of steric effects associated with the bulky *t*-BuNC ligands. Although the corresponding palladium complex, $Pd_3(SO_2)_3(PPh_3)_3$, has been prepared,[17] no structural studies have been reported. The ability of SO_2 to bridge a large range of metal–metal distances should prove favorable for the formation of more such complexes.[18-21]

Table II. Distances (Å) and Angles (deg)

Distances			
Pt1–Pt1′	2.712 (1)	S1–O2	1.49 (2)
Pt1(Pt1′)–P2	2.695 (1)	S2–O3	1.42 (1)
Pt1–S1	2.271 (5)	S2–O4	1.47 (1)
Pt1–S2	2.279 (4)	P1–C1(C1′)	1.81 (1)
Pt1–P2	2.295 (4)	P1–C7	1.84 (2)
Pt2–S2(S2′)	2.275 (4)	P2–C13	1.83 (2)
P2–P1	2.292 (5)	P2–C19	1.80 (2)
S1–O1	1.45 (2)	P2–C25	1.82 (2)

Angles			
Pt1–Pt1′–Pt2	59.79 (1)	Pt1–S1–Pt1′	73.3 (2)
Pt1–Pt2–Pt1′	60.41 (3)	Pt1–S2–Pt2	72.6 (1)
Pt2–Pt1(Pt1′)–S1	112.96 (9)	Pt1–S1–O1	117.2 (6)
Pt1′–Pt1–S2	113.41 (9)	Pt1–S1–O2	114.4 (6)
Pt1′–Pt1–S1	53.34 (9)	Pt1–S2–O3	112.9 (6)
Pt2–Pt1–S2	53.64 (9)	Pt1–S2–O4	116.4 (5)
Pt1–Pt2–S2	53.8 (1)	Pt2–S2–O3	115.9 (5)
Pt1′–Pt1–P2	149.9 (1)	Pt2–S2–O4	114.0 (5)
Pt2–Pt1–P2	150.3 (1)	O1–S1–O2	114 (1)
Pt1–Pt2–P1	149.45 (3)	O3–S2–O4	117.3 (7)
S1–Pt1–S2	165.5 (1)	Pt2–P1–C1(C1′)	114.5 (5)
S2–Pt1–S2′	167.6 (2)	Pt2–P1–C7	112.7 (7)
P2–Pt1–S1	96.6 (1)	Pt1–P2–C13	116.8 (5)
P2–Pt1–S2	96.7 (1)	Pt1–P2–C19	110.6 (5)
P1–Pt1–S2	96.1 (3)	Pt1–P2–C25	114.9 (5)

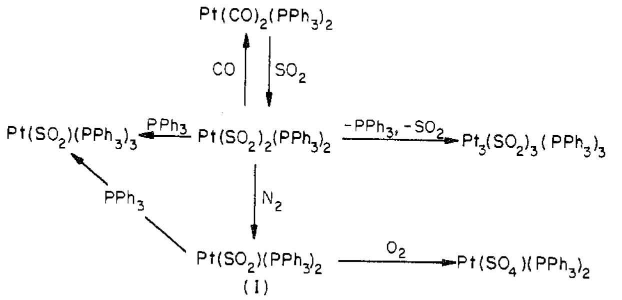

Figure 3. Reactions of $Pt(SO_2)_2(PPh_3)_2$.

Reactions of $Pt(SO_2)_2(PPh_3)_2$. A diagram depicting the various reactions studied and the products found is shown in Figure 3. Due to the instability of the product I, its formulation as $Pt(SO_2)(PPh_3)_2$ is somewhat speculative and is based mainly on the products obtained by reaction with molecular oxygen and triphenylphosphine. This product I and the previously reported product[5] of the same formulation may differ only in the extent of oligomerization. The lack of $^{195}Pt-^{31}P$ coupling in the ^{31}P NMR spectrum of I suggests that phosphine dissociation is occurring in solution. These data, coupled with the high molecular weight analysis obtained, imply that I may be an intermediate in the formation of the trimer $Pt_3(SO_2)_3(PPh_3)_3$ and that I probably exists, at least partially, as an SO_2-bridged species in solution.

The equilibrium established between $Pt(CO)_2(PPh_3)_2$ and $Pt(SO_2)_2(PPh_3)_2$ is also very interesting. Although no mixed CO/SO_2 product has been isolated, it seems likely that an intermediate such as $Pt(CO)(SO_2)(PPh_3)_2$ is involved. The further lability of the SO_2 in this proposed intermediate would seem to suggest a pyramidal MSO_2 geometry. However, it should be noted that one documented case of a coplanar MSO_2 moiety also possessing appreciable SO_2 lability has been observed.[22] It should also be noted that platinum(0) complexes are generally characterized by a large degree of ligand dissociation in solution. Thus other factors, besides pyramidal MSO_2 geometry, could be determining the lability of the SO_2 in a species like $Pt(CO)(SO_2)(PPh_3)_2$.

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Registry No. $Pt_3(SO_2)_3(PPh_3)_3\cdot C_7H_8\cdot SO_2$, 61967-09-7; I, 16009-23-7; $Pt(SO_4)(PPh_3)_2$, 12577-89-8; $Pt(SO_2)_2(PPh_3)_2$, 59187-63-2; $Pt(SO_2)(PPh_3)_3$, 15227-19-7; $Pt(CO)_2(PPh_3)_2$, 15377-00-1.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and X-Ray Structure Determination of Chromium(I) Nitrosyl Complexes with Macrocyclic Ligands

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Chromium complexes of the macrocyclic ligands *trans*-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenate(2–) ($Me_2[14]tetraenateN_4$) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]4,11\text{-}dieneN_4$) have been prepared. The nitrosyl adducts $Cr(Me_2[14]tetraenatoN_4)(NO)$ (I) and $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$ (II) have been obtained by treating the Cr(III) and Cr(II) complexes of $Me_2[14]tetraenateN_4$ and $Me_6[14]4,11\text{-}dieneN_4$, respectively, with alcoholic sodium nitrite. Infrared, conductance, mass spectral, electron spin resonance, and magnetic data indicate that the nitrosyl derivatives I and II contain Cr(I) with a linear M–NO group. Electronic spectra are strongly influenced by the NO group. The crystal and molecular structure of II ($a = 14.844$ (2) Å, $b = 19.586$ (3) Å, $c = 10.213$ (1) Å, $\beta = 127.1$ (9)°, space group $C2/c$, $Z = 4$, $R = 0.061$) confirms the linear M–NO bond. The cation and anion lie on twofold axes. The NO and NO_2 ligands are mutually trans. The hexafluorophosphate is ordered but shows librational motion.

Introduction

Chromium complexes with macrocyclic ligands[1] containing nitrogen donors have received little attention despite the large amount of data compiled for chromium complexes with nitrogen-donor ligands in general. We have now prepared chromium complexes of the macrocyclic ligands *trans*-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene ($Me_2[14]tetraeneN_4$) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]4,11\text{-}dieneN_4$). Stabilization of rare oxidation states[2] by macrocyclic ligands has recently been observed for a variety of transition metals and seemed a definite possibility for chromium. Thus, nitrosyl complexes of Cr(I) are produced when $[Cr(Me_2[14]tetraenatoN_4)(py)_2]PF_6$ or $[Cr(Me_6[14]4,11\text{-}dieneN_4)(py)](PF_6)_2$ reacts with alcoholic sodium nitrite although the starting complexes contain Cr(III) and Cr(II), respectively. Characterization of the nitrosyl complexes by the usual methods reveals that $Cr(Me_2[14]tetraenatoN_4)(NO)$ (I) is remarkably similar to the nitrosyl adducts of chromium porphyrin complexes[3] while $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$ (II) is analogous to nitrosyl–amine complexes of chromium.[4] The crystal and molecular structure of II reveals that the nitrosyl ligand is bonded linearly to the chromium and that the macrocycle adopts the typical conformation.

Experimental Section

Physical Measurements. Spectra were obtained using Cary 14R (visible) and Perkin-Elmer 337 and 457 (infrared) spectrophotometers. Magnetic susceptibilities were measured by the Faraday method[5] and corrected using Pascal's constants.[6] Elemental analyses were performed by Galbraith and Schwarzkopf Laboratories. Conductance measurements were made with an Industrial Instruments Model RC 16B conductivity bridge. The mass spectrum was obtained with an AEI MS-9 spectrometer at an ionizing potential of 70 eV. ESR spectra were obtained using a Varian V4500-10A spectrometer with diphenylpicrylhydrazyl (DPPH) as a reference.

Syntheses. All manipulations involving chromium(II) salts and metal complexes were carried out in a Vacuum Atmospheres Dry Lab unless otherwise stated. Reagent grade chemicals were employed in syntheses and physical measurements. Solvents were dried and degassed in the usual manner. Chromium metal (99%, 140 mesh) was purchased from Alfa Inorganics, Beverly, Mass.

Tetraaquochromium(II) chloride, $CrCl_2\cdot 4H_2O$, was prepared on the bench top under a blanket of nitrogen following the method of Lux and Illman.[7]

Bis(pyridine)chromium(II) chloride, $CrCl_2\cdot 2py$, was prepared by a method similar to that of Holah and Fackler.[4b]

Tetrakis(pyridine)chromium(II) trifluoromethylsulfonate, $Cr(CF_3SO_3)_2\cdot 4py$, was prepared by adding dropwise an excess of trifluoromethanesulfonic acid to a slurry of $Cr(OAc)_2$[7] (4.0 g, 11.1 mmol)