to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalysis.

Registry No. **1**, 64998-75-0; **2**, 64938-99-4; [Ni(SH)(np$_3$)], 64939-17-9; [Ni(SeH)(np$_3$)], 64939-19-1; [Ni(SCH$_3$)(np$_3$)], 64939-21-5; [Ni(H$_2$O)$_6$](BF$_4$)$_2$, 14322-78-2; [Co(SH)(np$_3$)]BPh$_4$, 61966-76-5; Ni(np$_3$), 52633-73-5; H$_2$S, 7783-06-4; H$_2$Se, 7783-07-5; HSCH$_3$, 74-93-1.

Supplementary Material Available: Listings of observed and calculated structure factors for [(p$_3$)NiSNi(p$_3$)]·1.6DMF and [(np$_3$)CoSCo(np$_3$)](BPh$_4$)$_2$·1.6DMF (15 pages). Ordering information is given on any current masthead page.

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Lability and Reactivity of Sulfur Dioxide–Transition Metal Complexes: Crystal and Molecular Structure of OsHCl(CO)[P(C$_6$H$_{11}$)$_3$]$_2$(SO$_2$)·2CHCl$_3$

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An x-ray structure determination of OsHCl(CO)(PCy$_3$)$_2$(SO$_2$)·2CHCl$_3$ (Cy = cyclohexyl) reveals octahedral coordination about the d^6 osmium(II) and a coplanar Os–SO$_2$ moiety with the hydride ligand presumably occupying the site trans to the SO$_2$. The long Os–S bond length (2.239 (3) Å) in comparison to those previously found for coplanar M–SO$_2$ groups is indicative of the strong trans influence of the hydride. The latter is also manifested by the unexpected reversibility of the metal–SO$_2$ interaction and the reaction of the complex with oxygen in solution to yield an Os(III) sulfato species, OsCl(CO)(PCy$_3$)$_2$(SO$_4$). The structure of the SO$_2$ adduct shows disorder between the chloride and carbonyl, which has been partially resolved. Important distances and angles are Os–P = 2.421 (3) and 2.425 (3) Å, Os–Cl = 2.43 (2) Å (average), Os–C = 1.93 (4) Å (average), S–O = 1.43 (1) and 1.44 (1) Å, O–S–O = 112.9 (6)°, P–Os–S = 102.9 (1) and 100.6 (1)°, and P–Os–P = 156.4 (1)°. Cell data: space group, triclinic; $Z = 2$; $a = 19.501$ (9), $b = 14.483$ (5), $c = 10.868$ (4) Å; $\alpha = 70.20$ (2), $\beta = 109.86$ (2), $\gamma = 120.96$ (2)°; $R = 0.055$ for 4450 diffractometer-collected reflections with $I \geq 3\sigma(I)$.

Introduction

A five-coordinate osmium(II) complex, OsHCl(CO)(PCy$_3$)$_2$ (Cy = cyclohexyl), has recently been synthesized and found to take up SO$_2$, presumably as a sixth ligand to the metal.[1] The reported positions of the SO infrared stretching frequencies (1284 and 1109 cm^{-1}) indicated the MSO$_2$ geometry to be coplanar by comparisons with frequencies reported for known examples of the geometry.[2] On the basis of previously reported d^6, six-coordinate complexes of transition metals containing SO$_2$ as a ligand [i.e., [Ru(NH$_3$)$_4$(SO$_2$)Cl]Cl[3] and Mn(C$_5$H$_5$)(CO)$_2$(SO$_2$)[4]] we expected[5] the present complex to contain a coplanar Os–SO$_2$ moiety with a nonlabile SO$_2$ group inert to attack by molecular oxygen (see also ref 6 and 7 concerning Rh(C$_5$H$_5$)(C$_2$H$_4$)(SO$_2$) and Ni(p$_3$)SO$_2$). Since studies of the reactivity of coordinated SO$_2$ are still in an embryonic stage, we decided to further examine the properties of this complex as part of our general investigation into the bonding of SO$_2$ to metal complexes. The results of this study, including the x-ray determination of the structure, are reported below.

Experimental Section

OsHCl(CO)(PCy$_3$)$_2$(SO$_2$)·C$_6$H$_6$ was prepared according to the published procedure.[1] Infrared spectra were recorded on a Perkin-Elmer 521 using Nujol mulls between CsBr plates. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thermogravimetric analyses were carried out on a Perkin-Elmer TGS-2 using a nitrogen purge and a heating rate of 1.25°/min.

Reversibility of the OsHCl(CO)(PCy$_3$)$_2$–SO$_2$ Interaction. OsHCl(CO)(PCy$_3$)$_2$(SO$_2$)·C$_6$H$_6$ was heated on a vacuum line to 140 °C for 1 h, during which time the color of the complex changed from yellow to red-orange. Both benzene and SO$_2$ were identified by mass spectroscopy to be present in the evolved volatiles, which were trapped at −196 °C using standard vacuum line techniques (molar ratio of volatiles/complex = 1.84). Furthermore, gaseous SO$_2$ could be readded (300 Torr, 30 min) to the red-orange residue, identified to be OsHCl(CO)(PCy$_3$)$_2$, to yield yellow OsHCl(CO)(PCy$_3$)$_2$(SO$_2$) in quantitative yield. Repetition of the SO$_2$ removal and readdition steps clearly indicated that the Os–SO$_2$ interaction is completely reversible, as had been found[8] for the M–SO$_2$ interaction in MCl(CO)(PPh$_3$)$_2$(SO$_2$) (M = Ir, Rh).

Reaction of OsHCl(CO)(PCy$_3$)$_2$(SO$_2$) with Oxygen to Give OsCl(CO)(PCy$_3$)$_2$(SO$_4$). Although the osmium–SO$_2$ adduct is air-stable in the solid state, its solutions readily air-oxidize to a sulfate complex. Saturation of a benzene solution (~20 mL) of OsHCl(CO)(PCy$_3$)$_2$(SO$_2$)·C$_6$H$_6$ (0.5 g) with oxygen resulted in slow precipitation of a light yellow solid beginning about 5 min after addition and continuing over a 3-day period. During this time the color of the supernatant solution underwent a series of dramatic color changes from yellow to gray-green to deep violet. The precipitate was collected, washed with benzene, and dried in vacuo at ambient temperature. Yield was 0.27 g (50%). The infrared spectrum of the solid revealed the presence of bidentate sulfate[9] (ν_{SO_4} 1283 (broad), 1165, 911, 890, 653, 603 cm^{-1}), carbonyl (ν_{CO} 1980 cm^{-1}), and lattice benzene ($\nu_{C_6H_6}$ 674 cm^{-1}). However, a metal–hydride stretch, which occurs at 2145 cm^{-1} for OsHCl(CO)(PCy$_3$)$_2$(SO$_2$)·C$_6$H$_6$,[1] was completely absent, indicating that the hydride ligand was displaced in the oxidation process.

The sulfate is nearly insoluble in benzene but very soluble in chloroform and was recrystallized from CHCl$_3$–hexane. CHCl$_3$ is retained in the crystal lattice very tightly (ν_{CHCl_3} 745 cm^{-1}) and cannot be completely removed even at 100 °C in vacuo. Elemental analysis revealed the empirical formula of the sulfate (dried at 100 °C) to be OsCl(CO)(PCy$_3$)$_2$(SO$_4$)·0.38CHCl$_3$. Anal. Calcd for

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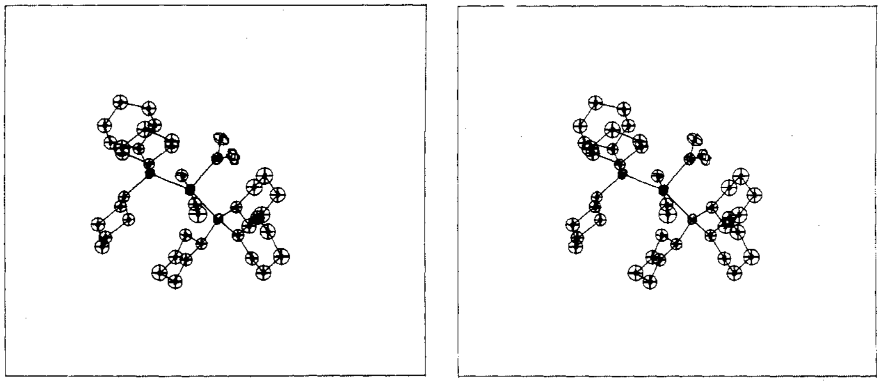

Figure 1. Stereoview of the molecular structure.

Table I. Crystal Data and Collection

Space group: Triclinic
Cell parameters: $a = 19.501$ (9) Å, $b = 14.483$ (5) Å, $c = 10.868$ (4) Å, $\alpha = 70.20$ (2)°, $\beta = 109.86$ (2)°, $\gamma = 120.96$ (2)°, $Z = 2$
Cell refinement: 12 high-order reflections
Diffractometer: Picker FACS-I, P.G. Linerts Disk Operating System,[18] 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: $\leqslant 0.3°$ at half-height on all three axes
Intensities: 4642 after averaging; 4450 for which $I \geqslant 3\sigma(I)$ and used in the refinement
Crystal morphology: {001}, 0.93 mm (distance from origin); {010}, 0.041; (100), 0.137; ($\bar{2}$01), 0.137
Linear absorption coeff: 33.2 cm^{-1}
Max, Min, transmission: 0.86, 0.70[20]

$C_{37.38}H_{66.38}O_5P_2Cl_{2.14}SOs$: C, 47.0; H, 7.0; P, 6.5; S, 3.3; Cl, 7.9. Found: C, 47.2; H, 7.3; P, 6.5; S, 3.3; Cl, 8.0.

Structure Determination. Single crystals of $OsHCl(CO)(PCy_3)_2(SO_2)\cdot 2CHCl_3$ were obtained from $CHCl_3$–ethanol solution at ambient temperature. Anal. Calcd for $C_{39}H_{69}O_3Cl_7P_2SOs$: C, 41.9; H, 6.2; P, 5.5; S, 2.9; Cl, 22.2. Found: C, 41.8; H, 6.2; P, 5.4; S, 2.8; Cl, 22.3. Thermogravimetric analysis indicated that SO_2 and $CHCl_3$ loss occurs concurrently at 90–105 °C.

Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections, measured after every 50 reflections, decreased by approximately 30% 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 and σ_N is taken to be 0.015.

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

$$F_c{}^* = kF_c/\left\{1 + 2g\left(\frac{e^2}{mc^2V}\right)^2 L \times \lambda^2\left[\frac{\cos^2 2\alpha + \cos^4 2\theta}{\cos^2 2\alpha + \cos^2 2\theta}\right]^2 F_c{}^2\right\}^{1/4}$$ [10,11]

where 2α is the 2θ value for the monochromator and k is a scale constant.

The structure was determined by standard Patterson, Fourier, and least-squares methods using the LASL System of Crystal Structure Programs. Solution and refinement of the structure in the space group $P\bar{1}$ resulted in disorder between the chloride and carbonyl groups in the osmium coordination sphere and reasonable structural and thermal parameters for the remainder of the structure. Further refinements in the noncentric space group ($P1$) were carried out in which a linear constraint was applied which maintained the centric relationship between all of the structural parameters except those of carbonyl and the chloride atom. These two groups were placed in a noncentrically related position, determined from difference maps in $P\bar{1}$, on the two crystallographically independent osmium atoms. Although this procedure resolved the "disorder" problem, inspection of the carbonyl and chloride atom distances and angles showed no improvement over those determined for the refinements in $P\bar{1}$. Therefore final refinements were done in the centric space group with neutral atom scattering factors and appropriate dispersion corrections and converged to the parameters given in Table II, with an unweighted R value of 5.5%.

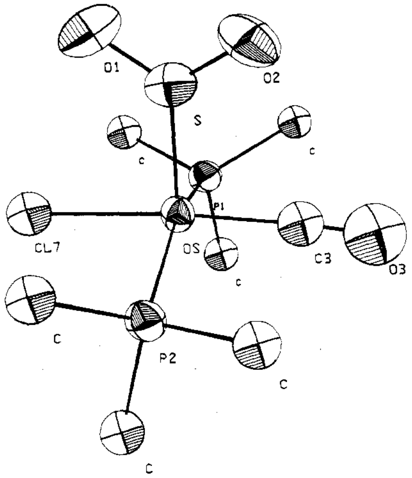

Figure 2. Projection of the Os coordination sphere.

Although a final difference map showed no alarming features, it should be noted that the C–O distance (Table III) for one of the carbonyls is less than satisfactory, presumably due to the disorder problem. In addition, the large librational motion of the chloroform has evidently resulted in bond distances and angles which are less than ideal for these molecules. No attempt was made to account for hydrogen.

Results and Discussion

Structure of $OsHCl(CO)(PCy_3)_2(SO_2)\cdot 2CHCl_3$. Inspection of the stereoviews (Figures 1 and 2) shows the six-coordination of the osmium, assuming the hydride to be trans to the sulfur atom, with trans PCy_3 groups and the carbonyl trans to the chloride. Although a survey of the literature revealed no osmium complexes containing PCy_3, we note that the Os–P distances of 2.411 (3) and 2.425 (3) Å compare well to those determined in the structures of the $Os(OH)(PPh_3)_2(NO)_2{}^+$ cation[12] (2.432 (4) and 2.436 (3) Å) and $OsCl_2(HgCl)NO(PPh_3)_2$[13] (2.40 (2) Å), while the average osmium(II)–Cl distance in the SO_2 complex (2.43 Å) is only slightly longer than that found in the latter Os(II)–HgCl complex, 2.40 Å. In spite of the aforementioned problems with the refinement, these observations and the reasonable geometry found for the SO_2 ligand (Table IV) lend credence to what we feel is the most important feature of the complex, i.e., the planarity of the M–SO_2 group and the unusually long M–S distance of 2.239 Å. If one takes into account the correction indicated by comparison of the M–Cl distances between this complex and the $[Ru(NH_3)_4(SO_2)Cl]^+$ cation[3] (Ru–Cl = 2.415 (3) Å),

Table II

Fractional Coordinates and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
C(1)	0.3755 (13)	0.6931 (18)	0.2029 (21)	9.2 (5)
Cl(1)	0.4560 (5)	0.8138 (6)	0.1312 (7)	
Cl(2)	0.3509 (4)	0.5882 (6)	0.1335 (7)	
Cl(3)	0.4150 (4)	0.6706 (9)	0.3736 (7)	
C(2)	0.1626 (15)	0.5564 (20)	0.3983 (25)	10.6 (6)
Cl(4)	0.1196 (7)	0.5123 (7)	0.2532 (9)	
Cl(5)	0.0727 (7)	0.4936 (8)	0.4672 (12)	
Cl(6)	0.2190 (6)	0.5162 (9)	0.5003 (17)	
Os(1)	0.24036 (3)	0.00559 (4)	0.05983 (5)	
S(1)	0.2405 (2)	0.8638 (3)	0.2279 (3)	
O(1)	0.2786 (6)	0.7986 (8)	0.2343 (10)	
O(2)	0.2003 (6)	0.8249 (8)	0.3365 (10)	
O(3)	0.3556 (17)	0.0003 (23)	0.9319 (28)	7.6 (9)^a
O(4)	0.1350 (18)	0.0274 (23)	0.1746 (31)	7.4 (10)^a
P(1)	0.3557 (2)	0.1625 (3)	0.1462 (3)	
P(2)	0.1232 (2)	0.9101 (3)	0.8982 (3)	
Cl(7)	0.1482 (7)	0.0256 (8)	0.1397 (11)	4.2 (2)
Cl(8)	0.3341 (8)	0.9995 (9)	0.9627 (12)	5.1 (2)
C(3)	0.3134 (21)	0.0004 (27)	0.9832 (33)	4 (1)^a
C(4)	0.1685 (27)	0.0136 (34)	0.1399 (44)	6 (1)^a
C(5)	0.4556 (7)	0.1564 (9)	0.1943 (11)	2.9 (2)
C(6)	0.5279 (8)	0.2565 (11)	0.2507 (13)	4.4 (3)
C(7)	0.6100 (9)	0.2526 (13)	0.2719 (15)	5.7 (4)^a
C(8)	0.6077 (9)	0.1444 (12)	0.3646 (15)	5.6 (3)^a
C(9)	0.5355 (8)	0.0454 (11)	0.3069 (13)	4.6 (3)
C(10)	0.4531 (8)	0.0493 (10)	0.2861 (13)	4.1 (3)
C(11)	0.3358 (7)	0.1895 (10)	0.2829 (12)	3.2 (2)
C(12)	0.3339 (8)	0.0993 (11)	0.4098 (13)	4.3 (3)
C(13)	0.7025 (9)	0.8907 (12)	0.4918 (14)	5.1 (3)
C(14)	0.6511 (9)	0.7726 (12)	0.4565 (15)	5.4 (3)
C(15)	0.3538 (9)	0.3175 (12)	0.4143 (15)	5.2 (3)
C(16)	0.3788 (7)	0.2938 (10)	0.0221 (12)	3.2 (2)
C(17)	0.5942 (7)	0.7071 (10)	0.0989 (12)	3.5 (3)
C(18)	0.5719 (8)	0.5942 (10)	0.1942 (13)	4.0 (3)
C(19)	0.6447 (9)	0.5662 (12)	0.2474 (14)	5.0 (3)
C(20)	0.6706 (9)	0.5650 (11)	0.1296 (14)	4.8 (3)
C(21)	0.6959 (8)	0.6792 (10)	0.0309 (12)	3.7 (3)
C(22)	0.9715 (8)	0.1869 (10)	0.0372 (12)	3.6 (3)
C(23)	0.0354 (10)	0.7187 (14)	0.0730 (17)	6.8 (4)
C(24)	0.9542 (11)	0.6544 (15)	0.1385 (18)	7.3 (4)
C(25)	0.8814 (10)	0.6096 (14)	0.0302 (17)	6.3 (4)
C(26)	0.1281 (11)	0.3013 (15)	0.0838 (18)	7.6 (4)
C(27)	0.0494 (9)	0.2280 (14)	0.1472 (15)	5.8 (3)
C(28)	0.8505 (7)	0.1559 (10)	0.1873 (12)	3.5 (3)
C(29)	0.9110 (8)	0.1955 (10)	0.3141 (13)	4.3 (3)
C(30)	0.8674 (9)	0.2245 (12)	0.3847 (15)	5.3 (3)
C(31)	0.8411 (10)	0.3100 (13)	0.2948 (16)	6.0 (4)
C(32)	0.7846 (9)	0.2747 (12)	0.1626 (15)	5.5 (3)
C(33)	0.8297 (8)	0.2502 (11)	0.0910 (13)	4.5 (3)
C(34)	0.9094 (7)	0.9956 (10)	0.2420 (12)	3.5 (3)
C(35)	0.9393 (8)	0.9346 (11)	0.1948 (13)	4.2 (3)
C(36)	0.9759 (9)	0.8680 (12)	0.3237 (14)	5.2 (3)
C(37)	0.9083 (10)	0.7826 (14)	0.4061 (16)	6.4 (4)
C(38)	0.8777 (9)	0.8444 (12)	0.4492 (14)	5.2 (3)
C(39)	0.8415 (8)	0.9117 (10)	0.3231 (13)	3.8 (3)
C(40)	0.3899 (8)	0.3054 (11)	0.3169 (13)	4.4 (3)

Anisotropic Thermal Parameters (× 100)^b

Atom	μ_{11}	μ_{22}	μ_{33}	μ_{12}	μ_{13}	μ_{23}
Cl(1)	22.7 (8)	13.6 (5)	17.4 (6)	9.11 (6)	7.4 (6)	−3.4 (5)
Cl(2)	15.7 (6)	15.2 (6)	16.1 (6)	7.5 (5)	1.0 (5)	−5.8 (5)
Cl(3)	12.3 (6)	37.4 (13)	10.0 (5)	6.6 (7)	0.4 (4)	−6.1 (7)
Cl(4)	32.2 (13)	15.5 (7)	17.6 (8)	5.5 (8)	4.76 (8)	−7.0 (6)
Cl(5)	30.2 (14)	20.0 (9)	30.4 (13)	8.4 (9)	10.6 (11)	−8.9 (9)
Cl(6)	14.1 (8)	23.9 (12)	55.3 (24)	4.6 (8)	−10.0 (11)	15.7 (14)
Os	2.62 (3)	3.47 (4)	3.49 (4)	1.1 (2)	0.5 (2)	−1.0 (2)
S	4.8 (2)	4.3 (2)	4.7 (2)	1.4 (2)	0.6 (2)	−0.8 (2)
O(1)	8.1 (7)	5.2 (6)	8.7 (8)	4.4 (6)	1.0 (2)	−0.2 (5)
O(2)	9.8 (8)	7.1 (7)	5.8 (7)	2.9 (6)	3.5 (6)	0.6 (6)
P(1)	2.9 (2)	3.6 (2)	3.2 (2)	1.2 (2)	0.5 (1)	−0.8 (2)
P(2)	3.0 (2)	3.8 (2)	3.8 (2)	1.2 (2)	0.4 (2)	−0.9 (2)

[a] Refined with a population factor of $^1/_2$. [b] μ_{ij}'s are defined by $\exp\{-2\pi^2[h^2\mu_{11}(a^*)^2 + k^2\mu_{22}(b^*)^2 + l^2\mu_{33}(c^*)^2 + 2hk\mu_{12}a^*b^* + 2hl\mu_{13}a^*c^* + 2kl\mu_{23}b^*c^*]\}$.

Table III. Selected Distances (Å) and Angles (deg)

	Osmium Coordination		
Os–S	2.239 (3)	Os–Cl(8)	2.45 (2)
Os–P(1)	2.421 (3)	Os–C(3)	1.92 (4)
Os–P(2)	2.425 (3)	Os–C(4)	1.95 (4)
Os–Cl(7)	2.41 (2)		
S(1)–Os–P(1)	102.9 (1)	P(2)–Os–Cl(7)	87.5 (3)
S(1)–Os–P(2)	100.6 (1)	P(2)–Os–Cl(8)	91.8 (3)
S(1)–Os–Cl(7)	92.4 (3)	P(2)–Os–C(3)	92 (1)
S(1)–Os–Cl(8)	92.8 (3)	P(2)–Os–C(4)	90 (1)
S(1)–Os–C(3)	93 (1)	Cl(7)–Os–C(3)	175 (1)
S(1)–Os–C(4)	87 (1)	Cl(8)–Os–C(4)	178 (1)
P(1)–Os–P(2)	156.4 (1)		
P(1)–Os–Cl(7)	91.3 (3)		
P(1)–Os–Cl(8)	87.4 (3)		
P(1)–Os–C(3)	88 (1)		
P(1)–Os–C(4)	91 (1)		
	Ligand Coordination		
S–O(1)	1.44 (1)	P(1)–C(11)	1.86 (1)
S–O(2)	1.43 (1)	P(1)–C(16)	1.85 (1)
C(3)–O(3)	1.14 (5)	P(2)–C(22)	1.85 (1)
C(4)–O(4)	0.98 (5)	P(2)–C(28)	1.86 (1)
P(1)–C(5)	1.88 (1)	P(2)–C(34)	1.85 (1)
O(1)–S–O(2)	112.9 (6)	Os–C(4)–O(4)	173 (4)
Os–C(3)–O(3)	177 (3)		
	Chloroform 1		
C(1)–Cl(1)	1.79 (2)	C(1)–Cl(3)	1.74 (2)
C(1)–Cl(2)	1.70 (2)		
Cl(1)–C(1)–Cl(2)	108 (1)	Cl(2)–C(1)–Cl(3)	112 (1)
Cl(1)–C(1)–Cl(3)	106 (1)		
	Chloroform 2		
C(2)–Cl(4)	1.68 (2)	C(2)–Cl(6)	1.47 (2)
C(2)–Cl(5)	1.80 (2)		
Cl(4)–C(2)–Cl(5)	99 (1)	Cl(5)–C(2)–Cl(6)	105 (2)
Cl(4)–C(2)–Cl(6)	119 (2)		

the M–S distance is approximately 0.16 Å longer than that found in the Ru complex. This can be ascribed to the strong trans effect of the hydride, which has been previously structurally documented in, for example, $OsHBr(CO)(PPh_3)_3$. The latter contains an Os–P bond trans to the hydride of length 2.56 Å, 0.22 Å longer than the other Os–P distances in the molecule.[14]

Another structural point of interest is the orientation of the SO_2 ligand in the plane containing the carbonyl, chloride, and hydride, a situation which minimizes the competition between the π^* orbitals of the SO_2 and CO for the available T_{2g} electrons of the transition metal. This can be compared to the situation in $Mn(C_5H_5)(CO)_2SO_2$ where the plane of the SO_2 bisects the two carbonyls but is in contrast to $Rh(C_5H_5)(C_2H_4)SO_2$. In the latter complex the SO_2 accepts an orientation which maximizes the $\pi^*(SO_2)$–$\pi^*(C_2H_4)$ interaction.[6]

Lability and Reactivity with Oxygen of the Coordinated SO_2. The attachment of SO_2 to $OsHCl(CO)(PCy_3)_2$ has been found to be completely reversible. Furthermore, the SO_2 adduct readily air oxidizes in solution to an Os(III)–sulfato species with the loss of hydride ligand (eq 1). The mechanism of this

$$OsHCl(CO)(PCy_3)_2(SO_2) + O_2 \xrightarrow[-H^-]{C_6H_6} OsCl(CO)(PCy_3)_2(SO_4) + \ldots \qquad (1)$$

reaction and the fate of the hydride are not yet known, but since the yield of precipitated sulfate was only 50% and the supernatant solution was highly colored, it is reasonable to assume that the displaced H^- is involved in side reactions which produce unidentified osmium complexes. The hydride loss is probably related to the preference of Os for the +3 oxidation state and the favorable coordination properties of bidentate sulfate rather than being a requisite for sulfate formation.

Table IV. Summary of the Current Structural Information[a] on $M–SO_2$ Groups (Nonbridging)

	M–S, A	Av S–O dist, Å	O–S–O, deg	Ref
Compounds with Coplanar $M–SO_2$				
$[Ru(NH_3)_4(SO_2)Cl]Cl$	2.072 (3)	1.428 (7)	113.8 (6)	3
$Mn(C_5H_5)(CO)_2SO_2$	2.037 (5)	1.404 (8)	112.6 (8)	4
$Rh(C_5H_5)(C_2H_4)SO_2$	2.096 (2)	1.436 (6)	114.4 (5)	6
$Ni(p_3)SO_2$[b]	2.013 (3)	1.365 (7)	109.1 (7)[c]	7
$OsHCl(CO)(PCy_3)_2(SO_2)$	2.239 (3)	1.435 (7)	112.9 (6)	
Compounds with Pyramidal $M–SO_2$				
$IrCl(CO)(PPh_3)_2SO_2$	2.488 (10)	1.44 (2)	117.1 (1.5)	20
$RhCl(CO)(PPh_3)_2SO_2$	2.450 (2)	1.451 (3)	113.8 (3)	21
$Pt(PPh_3)_2(SO_2)_2$	2.427 (2)	1.405 (6)	115.7 (4)	22
$Pt(PPh_3)_3SO_2$	2.368 (3)	1.440 (6)	114.2 (5)	23
$[RhCl(PPh_3)_2(SO_2)]_2$	2.369 (5)	1.45 (1)	111.5 (8)	24
Compounds with O,S-Bonded SO_2				
$Rh(NO)(PPh_3)_2(SO_2)$	2.326 (2)	1.461 (5)	115.1 (4)	16, 17

[a] Averaged over more than one SO_2 group when appropriate. [b] p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane. [c] The SO_2 oxygens show extreme thermal motion in this structure.

In view of the planar conformation found for the $Os–SO_2$ moiety, the lability of the SO_2 and its ready reactivity with oxygen to form the sulfato complex are most interesting. Although, as mentioned in the Introduction, the planar geometry is expected for a six-coordinate d^6 complex, this chemical behavior is unique among the structurally characterized complexes containing a planar $M–SO_2$ moiety[15] (Table IV). Except for the Os complex, none of the latter demonstrate reversible binding of SO_2, and although the Mn, Rh, and Ni complexes are air sensitive in solution, none of these have been found to give sulfates as end products of the decomposition.

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Registry No. $OsHCl(CO)(PCy_3)_2(SO_2)\cdot 2CHCl_3$, 65150-39-2; $OsCl(CO)(PCy_3)_2(SO_4)$, 65150-33-6; $OsHCl(CO)(PCy_3)_2(SO_2)$, 40583-39-9; O_2, 7782-44-7.

Supplementary Material Available: A listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Structure and Properties of Pseudotetrahedral Dichloro(2-(2-dimethylaminoethyl)pyridine)copper(II)

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The complex dichloro(2-(2-dimethylaminoethyl)pyridine)copper(II), $Cu(C_9H_{14}N_2)Cl_2$ or $Cu(DMAEP)Cl_2$, has been synthesized and its crystal and molecular structure has been determined from three-dimensional counter x-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 7.348$ (3) Å, $b = 8.875$ (4) Å, $c = 9.982$ (4) Å, $\alpha = 74.69$ (2)°, $\beta = 99.06$ (2)°, and $\gamma = 109.65$ (2)°. The observed and calculated densities are 1.59 and 1.603 g cm^{-3}. The structure was refined by full-matrix least-squares methods to an R factor (on F) of 0.031 using 2084 independent intensities. The structure consists of discrete monomeric $Cu(DMAEP)Cl_2$ units with four-coordinate pseudotetrahedral geometry at the copper(II) centers. The copper–ligand bond lengths are normal, but the six-membered chelate ring adopts the half-chair conformation rather than the boat conformation observed in a number of analogues. Electron paramagnetic resonance and electronic spectral data for $Cu(DMAEP)Cl_2$ and its isomorphous bromo analogue afford significant support for spectral–structure correlations; these DMAEP complexes exhibit novel single-line EPR solution spectra at room temperature.

Introduction

Complexes of the type $Cu(AEP)X_2$, where AEP is 2-(2-aminoethyl)pyridine and X is a halogen, were first synthesized by Uhlig and Maaser[1] who suggested that these compounds would be discrete dihalogen bridged dimers with square-pyramidal geometry about the copper ions. However, when X is chlorine[2] or bromine,[3] the compounds are best described as six-coordinate polymers consisting of monohalogen bridged chains connected by dihalogen bridges, the geometry about copper being severely distorted octahedral. Since there are two available pathways for superexchange, the magnetic properties[4] are difficult to account for accurately.

The copper(II) ion has a six-coordinate geometry in polymeric $Cu(py)_2X_2$ compounds.[5-7] When pyridine is replaced by 2-methylpyridine, the methyl groups sterically block coordination at the sixth binding site on copper and $Cu(2\text{-}Me\text{-}py)_2X_2$ compounds are five-coordinate dimers.[8,9] In order to assess the effects of alkyl substitution on AEP in complexes of the general type $CuLX_2$, we examined 2-(2-methylaminoethyl)pyridine (MAEP) compounds. A tightly bound monochloro-bridged chain structure with tetragonal-pyramidal geometry about the copper ion was found[10] for $Cu(MAEP)Cl_2$. When X = Br, the complex is a dibromo-bridged dimer with trigonal-bipyramidal geometry at copper.[11] In both examples coordination was apparently blocked at the sixth site on the copper centers by a proton on C(4) of the six-membered chelate ring rather than by the presence of the methyl group.

Complexes of the types $CuLX_2$ (L = bidentate ligand) and CuA_2X_2 (A = monodentate ligand) adopt a wide variety of structures.[2,3,5-9,12-18] $Cu(MAEP)Cl_2$ is only the second of its type, and $Cu(MAEP)Br_2$ is the first example of a trigonal-bipyramidal, bromine-bridged dimer. In view of the unusual structural and magnetic properties of copper complexes with AEP and substituted AEP ligands and the observation that one methyl substituent does not dominate the stereochemistry of the complexes, we have undertaken a structural and spectroscopic study of the disubstituted complex $Cu(DMAEP)Cl_2$ (DMAEP = 2-(2-dimethylaminoethyl)pyridine.

Experimental Section

Bright green $Cu(DMAEP)Cl_2$ was prepared by addition of 0.361 g (0.002 mol) of copper(II) chloride dihydrate to a solution containing 0.330 g (0.002 mol) of DMAEP in 40 mL of absolute methanol. The resultant green solution was stirred and refrigerated; crystals formed after a few days. Brown $Cu(DMAEP)Br_2$ was prepared similarly using copper(II) bromide. The copper content of the complexes was determined by EDTA titrations.

Weissenberg and precession photography indicated that $Cu(DMAEP)Cl_2$ crystals belonged to the triclinic system, the space group being either C_1^1-$P1$ or C_i^1-$P\bar{1}$. The centrosysmmetric space group was chosen and successful refinement of the structure demonstrated that this choice was correct. Observations were made at 22° using Mo Kα_1 radiation with an assumed wavelength of 0.7093 Å. The cell constants, obtained by least-squares methods, are $a = 7.348$ (3) Å, $b = 8.875$ (4) Å, $c = 9.982$ (4) Å, $\alpha = 74.69$ (2)°, $\beta = 99.06$ (2)°, and $\gamma = 109.65$ (2)°. The observed density of 1.59 g cm^{-3}, obtained by flotation in a mixture of bromoform and benzene, is in good agreement with the calculated density of 1.603 g cm^{-3} assuming two monomeric units in the cell.

The crystal used to collect diffraction data was a thin plate with faces (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (01$\bar{1}$), and (0$\bar{1}$1) and was mounted roughly perpendicular to the (100) face. The separations between opposite pairs of faces were as follows: (100) and ($\bar{1}$00), 0.058 cm; (010) and (0$\bar{1}$0), 0.005 cm; (01$\bar{1}$) and (0$\bar{1}$1), 0.020 cm. Intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator using Mo Kα radiation at a takeoff angle of 1.2°. Data were collected in the θ–2θ scan mode from 0.65° below the calculated Mo Kα_1 position to 0.65° above the calculated Mo Kα_2 position at the rate of 1°/min with 10-s stationary-counter stationary-crystal background counts at both ends of the scan. The pulse height analyzer was set for an approximately 90% window centered on the Mo Kα peak.

An independent set of data ($h,\pm k,\pm l$) was collected with a maximum value for 2θ of 55° (Mo Kα), beyond which there were few intensities greater than background. The three standard reflections which were recorded at intervals of 100 reflections showed no sys-

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