Sulfur Dioxide Adducts of Organophosphinecopper(I) Mercaptide, Phenoxide, and Selenolate Complexes: Coordinated SR^-, OR^-, and SeR^- as Lewis Bases

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Abstract: Organophosphinecopper(I) mercaptide complexes form crystalline 1:1 adducts with sulfur dioxide having the stoichiometry $Cu(PR_3)_n(SR')(SO_2)$, where $n = 1-3$; $PR_3 = PMePh_2, PPh_3, PBz_3, PCy_3$, and tripod (Bz = benzyl, Cy = cyclohexyl, Me = methyl, Ph = phenyl, and tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane); and R′ = Me, Et, Cy, Ph, and C_6F_5. Less stable oxygen and selenium analogues, $Cu(PCy_3)_2(XPh)(SO_2)$, where X = O or Se, have also been prepared, as well as a bis-adduct of a Pt(II) mercaptide, $Pt(PPh_3)_2(SPh)_2(SO_2)_2$. The yellow to orange adducts have SO_2 dissociation pressures in the range 0.5-15 Torr at 25 °C (except for the phenoxide and platinum compounds) and rapidly release SO_2 at ~100 °C to form the mercaptide, phenoxide, or selenolate precursors, $Cu(PR_3)_n(XR')$. The SO_2 complexes have been characterized by their physical properties, including dissociation pressures. An x-ray crystallographic determination of the complex phenylthiotris(methyldiphenylphosphine)(sulfur dioxide)copper(I), $Cu(PPh_2Me)_3(SPh)(SO_2)$, shows that the SO_2 bonds as a Lewis acid to the terminally coordinated mercaptide group. The $S-SO_2$ bond is relatively long, 2.530 Å, accounting for the SO_2 lability.

The Lewis acid character of sulfur dioxide toward a wide variety of main group bases has been recognized for many years,[1-6] and recently transition metal complexes containing "pyramidal," [7-10] or "coplanar" [11-14] $M-SO_2$ moieties have also been reported. However, despite interest in the binding of SO_2 to various substrates, relatively few compounds have been reported in which SO_2 bonds to coordinated ligands. To our knowledge, this type of interaction has been structurally documented only in the compounds $Pt(PPh_3)_2(CH_3)I{\cdot}SO_2$[15] and $[Cu(PPh_2Me)_2I]_2{\cdot}SO_2$,[16] which contain weak $I-SO_2$ interactions (I-S = 3.39 and 3.41 Å).

In this paper we describe the synthesis, properties, and a representative x-ray crystal structure for a series of SO_2 adducts with copper(I) complexes of the type $Cu(PR_3)_n(SR')(SO_2)$. In these compounds, the SO_2 binds directly as a Lewis acid in a quasi-reversible fashion to coordinated XR^- groups. Also, adducts of the oxygen and selenium analogues, $Cu(PCy_3)_2(XPh)(SO_2)$ (X = O, Se), as well as a bis adduct of a Pt(II) mercaptide, $Pt(PPh_3)_2(SPh)_2(SO_2)_2$, are reported.

Experimental Section

Materials, Equipment, and Experimental Methods. Reagent grade chemicals were used without further purification. The sulfur dioxide used was 99.98% pure (Matheson). Phosphines were purchased from the Strem Chemical and Pressure Chemical Companies. The preparations were generally carried out using standard Schlenk techniques[17] under a nitrogen atmosphere to avoid possible ligand oxidation. Instrumental and analytical methods were performed as described elsewhere.[16]

Preparation of $(CuSR)_n$ and $(CuSePh)_n$. Modified versions of the preparations described by Duncan et al.[18] were used to synthesize the polymeric cuprous mercaptides and $(CuSePh)_n$. The ethyl, phenyl, and cyclohexyl derivatives were prepared by mixing, in a 1:2 ratio, an aqueous solution of cupric acetate (0.3 M) with a 0.3 M solution of thiol or selenol in methanol (R = Ph, Cy) or benzene (R = Et). In the case of R = Me, methyl mercaptan gas was bubbled through methanolic cupric acetate solution. In each case a yellow precipitate of the desired product formed immediately and was collected and thoroughly washed with a series of solvents (H_2O, MeOH, and ether, or H_2O, EtOH, benzene, and ether) to eliminate undesired products formed in the reaction. The precipitates were then dried in vacuo overnight, during which process some darkening in color occurred. Yields were greater than 90%.

Preparation of $(CuOPh)_n$. A procedure similar to previously described schemes[19-21] involving reaction of alkoxides with CuCl was used, but instead of CuCl, $[Cu(CH_3CN)_4]PF_6$ in acetonitrile solution was employed as the source of Cu(I). In contrast to the CuCl preparations, this complex easily gives $(CuOPh)_n$ as a solid product upon reaction with ethanolic NaOPh.

Preparation of $Cu(PR_3)_n(SR')(SO_2)$ Complexes. The SO_2 adducts were made in yields of 60-80% by several methods. Details of a typical synthesis are presented below. In several cases, the intermediate $Cu(PR_3)_n(SR')$ compounds were isolated as solids. One complex of this type, $Cu(PPh_3)_2(SPh)$, has been prepared previously by Reichle by another method.[22,23]

To a slurry of 0.58 g (3.3 mmol) of copper thiophenoxide in 25 mL of chloroform was added 2.80 g (10 mmol) of tricyclohexylphosphine. After 1 h of stirring, the colorless solution was filtered to remove traces of insoluble residue and the solvent was removed by rotoevaporation to give a tacky oil. The oil was dissolved in 25 mL of diethyl ether and filtered, and a stream of sulfur dioxide was slowly bubbled through the colorless solution for 1 min. A bright orange color immediately developed and crystals of the product began to deposit. For highly soluble complexes, such as $Cu(PCy_3)_2(SCy)(SO_2)$, it was necessary to add hexane to induce crystallization. The mixture was allowed to stand for ~2 h at room temperature and then cooled overnight at 0 °C. The product was collected on a filter, washed with two 10-mL portions of diethyl ether saturated with SO_2, and dried under a stream of SO_2. Yield, 2.1 g (80%) of $Cu(PCy_3)_2(SPh)(SO_2)$.

Preparation of $Cu(PCy_3)_2(OPh)$. A method for preparation of $Cu(PPh_3)_2(OPh)$ from $Cu(PPh_3)_3Cl$ has been described.[22] However, for the purpose of developing a general synthesis of $Cu(PR_3)_2XR'$ (X = O, S, Se) compounds, the reaction of $(CuOPh)_n$ (prepared as described above and used in situ) with PCy_3 (phosphine/Cu = 3) was utilized. Addition of solid phosphine to a CH_3CN suspension of CuOPh, followed by stirring of the mixture for 0.5 h, yielded a white precipitate which was filtered off and washed with CH_3CN. The crude product was dissolved in hot toluene-heptane, the solution was cooled for several hours at 0 °C, and white microcrystalline $Cu(PCy_3)_2(OPh)$ deposited. Anal. Calcd for $C_{42}H_{71}CuP_2O$: C, 70.3; H, 10.0; P, 8.6; Cu, 8.9. Found: C, 70.5; H, 9.8; P, 8.6; Cu, 8.5.

Reaction of Solid $Cu(PCy_3)_2(OPh)$ with Liquid SO_2. Using a vacuum line, excess liquid SO_2 was distilled onto a solid sample of $Cu(PCy_3)_2(OPh)$ at −63 °C to give a light yellow-green homogeneous solution. Removal of excess SO_2 at this temperature yielded a viscous, foamy, glass-like material possessing a slight (1 Torr) SO_2 dissociation pressure. All SO_2 was easily removed at ambient temperature. The ratio of SO_2 to $Cu(PCy_3)_2(OPh)$ was determined to be 0.89:1.00, thus indicating 1:1 coordination of SO_2 to the phenoxide ligand at −63 °C. The low ratio is probably due to the slight dissociation pressure at the temperature (−63 °C) at which the excess SO_2 was pumped off.

Reaction of Solid $Cu(PBz_3)_2(SPh)$ with Gaseous SO_2. $Cu(PBz_3)_2(SPh)$ can be precipitated as a fluffy white solid by addition of *n*-heptane to a $CHCl_3$ solution containing a 1:3 mole ratio of $(CuSPh)_n$:PBz_3. Anal. Calcd for $C_{48}H_{47}P_2SCu$: C, 73.8; H, 6.1.

Table I. SO_2 Dissociation Pressures (Torr)[a]

Compound	Temp, °C 20	40	50	60	65	70
$Cu(PPh_3)_2(SC_6F_5)(SO_2)$						~30
$Cu(PPh_3)_2(SMe)(SO_2)$	11.3	21.6	29.2	75.0		
$Cu(PPh_3)_2(SEt)(SO_2)\cdot\frac{1}{2}CHCl_3$		18.2[b]	28.0[b]	48.1[b]		
$Cu(PPh_2Me)_3(SPh)(SO_2)$			1.6			7.5
$Cu(PBz_3)_2(SEt)(SO_2)$			4.7	6.9		8.8
$Cu(PBz_3)_2(SPh)(SO_2)$	0.5 (1.8)[c]	2.8 (4.3)	5.4 (5.6)	8.8 (7.6)		(10.7)
$Cu(PCy_3)_2(SCy)(SO_2)$		9.5	12.2	15.8		
$Cu(PCy_3)_2(SPh)(SO_2)$		1.2	2.8	5.4	7.1	9.4
$Cu(PCy_3)_2(SMe)(SO_2)$			3.3	6.3		9.1
$Cu(tripod)(SC_6F_5)(SO_2)$			~30			
$Cu(tripod)(SPh)(SO_2)\cdot CHCl_3$	~3[b]					~33[b]
$Cu(PCy_3)_2(SePh)(SO_2)$	6.5					65.8
$Pt(PPh_3)_2(SPh)_2(SO_2)_2$	>100					

[a] Measured over solid complexes isolated from $CHCl_3$ solutions, after 24 h equilibration. Volatiles were confirmed by mass spectroscopy to be SO_2 or a mixture of SO_2 and $CHCl_3$. [b] These values include dissociation of $CHCl_3$ present in the solid complexes, and thus can be considered only an upper limit for the SO_2 dissociation pressure. [c] Values in parentheses are for the sample prepared by gas-solid reaction, which contained 0.63 mol of SO_2 per mole of substrate.

Found: C, 72.4; H, 5.9. Interaction of this solid with SO_2 gas or SO_2-N_2 mixtures containing SO_2 concentrations as low as 0.1% (V/V) immediately produced an orange coloration. In a quantitative experiment, 0.204 g (0.26 mmol) of $Cu(PBz_3)_2(SPh)$ was treated with excess SO_2 gas (1.24 mmol) at approximately STP conditions. Analysis of the resulting orange adduct showed that it contained 0.77 mol of SO_2 per mole of substrate. After maintaining the solid for 24 h at 50, 60, and 70 °C, the following respective SO_2 dissociation pressures were observed: 14.6, 18.0, and 22.2 Torr. Lowering the temperature back to 50 °C gave a value of 16.5 Torr after 4 days, indicating incomplete reversibility. Removal of this dissociated SO_2 from the system (so that the $SO_2/Cu(PBz_3)_2(SPh)$ ratio was now 0.63:1) greatly improved the reversibility. Equilibration of SO_2 over the solid phase then was complete in a matter of hours and cycling of the temperature gave reproducible dissociation pressures.

Preparation of $Pt(PPh_3)_2(SPh)_2(SO_2)_2$. $Pt(PPh_3)_2(SPh)_2$, prepared by a literature procedure,[24] was dissolved in liquid SO_2 (~0.1 g/mL) in a glass tube to give a bright red-orange solution. The tube was sealed and allowed to stand at ambient temperature for several days, during which time a red-orange precipitate formed. The tube was cooled below −10 °C and opened, and a 4:1 ethanol-toluene mixture was added to facilitate removal of the precipitated adduct. The crystalline complex was filtered off, washed with SO_2-saturated ethanol, and dried in a stream of SO_2 gas. The ratio of SO_2 to metal complex, observed by tensimetry, was 1.72:1.00.

Measurements of SO_2 Dissociation Pressure vs. Temperature. To determine relative stabilities of the various SO_2 adducts, a solid sample was placed in a glass tube which was then attached via an O-ring joint to a grease-free tensimeter[17] or to a small evacuable manifold connected to a Validyne Engineering Corp. AP10 absolute pressure transducer (0-100 Torr). After the system was evacuated at −63 °C, the dissociation pressure was monitored as a function of time at various temperatures. The $SO_2{:}Cu(PR_3)_n(XR')$ ratios were determined by complete decomplexation of SO_2 at 70-120 °C; the SO_2 gas evolved was measured using a calibrated vacuum line. In most cases the composition of the volatiles was checked by mass spectrometry and in each instance shown to be essentially pure SO_2, or a mixture of SO_2 and $CHCl_3$ for those samples containing lattice $CHCl_3$. Dissociation pressures for the complexes are presented in Table I.

Collection and Reduction of the Crystallographic Data and Structure Solution for $Cu(PPh_2Me)_3(SPh)(SO_2)$. Unless otherwise noted, data collection and computations were performed as described in previous publications.[25] Details of the data collection are given in Table II. Optical microscopy and precession photographs of crystals prepared as described above suggested a triclinic lattice. The data crystal was coated with Duco cement to prevent SO_2 dissociation. The intensities of two standard reflections measured after every 50 reflections were found to decrease by approximately 2% due to crystal decomposition. A correction was applied for this decrease in intensity using a polynomial determined by least squares fitting the standard reflection curves.

Table II. X-Ray Data Collection Description

Molecular formula	$CuP_3S_2O_2C_{45}H_{44}$
Formula weight	837.42
Systematic absences	None
Laue symmetry	$\bar{1}$
Space group	$P\bar{1}$
ρ_{obsd} (g/cm^3)	1.32 (by flotation in SO_2-saturated CCl_4/heptane)
ρ_{calcd} (g/cm^3)	1.332
a (Å)	19.159 (8)
b (Å)	11.458 (7)
c (Å)	9.967 (6)
α (deg)	107.18 (3)
β (deg)	90.30 (4)
γ (deg)	93.37 (4)
Temperature, (°C)	22 ± 3
Radiation type	Graphite monochromatized Mo (λ 0.709 39 Å)
Z	2
Scan type	θ-2θ
Base scan width (deg)	2.0
Scan rate (deg/min)	1.0
θ_{min}, θ_{max} (deg)	2, 45
Takeoff angle (deg)	3.0
Transmission coefficients	0.86-0.96
No. reflections collected	5504
No. reflections with $I \geq 3\sigma(I)$	3390
μ (cm^{-1})	9.5
Crystal dimensions (mm)	0.050 × 0.130 × 0.320
Crystal faces	$\{100\}, (01\bar{1}), (0\bar{1}1), (110), (\bar{1}\bar{1}0)$
Cell parameter refinement data	12 reflections with $2\theta \geq 33°$
Diffractometer	Computer Controlled Picker FACS-1
Final R	0.079
Final R_w	0.078

Coordinates for the copper, sulfur, and phosphorus atoms were deduced from an E-map with phases calculated using direct methods. Carbon and oxygen atoms were located using successive difference Fourier syntheses. Phenyl hydrogen atoms were included (but not refined) as an idealized polyhedron (average C-H = 0.95 Å, average C-C-H = 120°, B = 7.0 Å^2) centered on the phenyl groups. A least-squares refinement which included a secondary extinction term[26] and anisotropic thermal motion for all atoms heavier than carbon, resulted in a conventional R factor of 0.085. However, the thermal ellipsoids for the SO_2 group were greatly elongated approximately normal to the S-S bond, and short S-O distances (1.14 and 1.21 Å)

Table III. Final Atomic Parameters[a–c]

A. Positional and Isotropic Thermal Parameters

	x	y	z	B, Å^2		x	y	z	B, Å^2
Cu	0.2443 (6)	−0.1459 (1)	0.1032 (1)	*d*	C19	0.3833 (7)	−0.515 (1)	−0.212 (2)	6.4 (3)
S1	0.2683 (1)	0.0419 (5)	0.2886 (2)	*d*	C20	0.3800 (6)	−0.398 (1)	−0.120 (1)	5.4 (3)
S2	0.1905 (3)	0.2078 (6)	0.4177 (7)	*d*	C21	0.3396 (6)	−0.058 (1)	−0.151 (1)	4.0 (3)
P1	0.1330 (3)	−0.1424 (8)	0.0229 (1)	*d*	C22	0.2769 (6)	−0.032 (1)	−0.204 (1)	4.8 (3)
P2	0.3372 (1)	−0.1604 (3)	−0.0419 (3)	*d*	C23	0.2748 (7)	0.049 (1)	−0.283 (1)	6.2 (3)
P3	0.2463 (1)	−0.2737 (3)	0.2412 (3)	*d*	C24	0.3374 (8)	0.104 (1)	−0.308 (2)	6.7 (3)
O1	0.2112 (8)	0.251 (2)	0.564 (3)	*d*	C25	0.3979 (7)	0.080 (1)	−0.258 (2)	6.5 (3)
O2	0.1198 (8)	0.155 (2)	0.392 (2)	*d*	C26	0.4015 (7)	0.000 (1)	−0.179 (1)	5.6 (3)
C1	0.1106 (6)	0.012 (1)	0.021 (1)	4.2 (3)	C27	0.1964 (6)	−0.217 (1)	0.404 (1)	4.5 (3)
C2	0.1088 (5)	−0.2398 (9)	−0.153 (1)	3.3 (2)	C28	0.2118 (5)	−0.4310 (9)	0.159 (1)	3.5 (2)
C3	0.0494 (7)	−0.222 (1)	−0.226 (2)	6.6 (3)	C29	0.2224 (6)	−0.482 (1)	0.019 (1)	4.7 (3)
C4	0.0341 (7)	−0.304 (1)	−0.363 (2)	6.9 (4)	C30	0.1932 (7)	−0.599 (1)	−0.054 (1)	5.7 (3)
C5	0.0729 (8)	−0.395 (1)	−0.419 (2)	6.8 (4)	C31	0.1532 (7)	−0.658 (1)	0.019 (2)	5.9 (3)
C6	0.1300 (7)	−0.414 (1)	−0.350 (2)	6.3 (3)	C32	0.1418 (7)	−0.611 (1)	0.154 (2)	6.6 (4)
C7	0.1478 (6)	−0.334 (1)	−0.218 (1)	4.5 (3)	C33	0.1717 (7)	0.496 (1)	0.232 (1)	6.0 (3)
C8	0.0655 (5)	−0.190 (1)	0.126 (1)	3.6 (2)	C34	0.3331 (5)	−0.2867 (9)	0.310 (1)	3.3 (2)
C9	0.0491 (6)	−0.313 (1)	0.105 (1)	4.4 (3)	C35	0.3672 (6)	−0.184 (1)	0.399 (1)	4.4 (3)
C10	−0.0001 (7)	−0.354 (1)	0.190 (1)	5.3 (3)	C36	0.4345 (6)	−0.187 (1)	0.447 (1)	4.6 (3)
C11	−0.0312 (7)	−0.266 (2)	0.291 (1)	6.0 (3)	C37	0.4683 (6)	−0.292 (1)	0.410 (1)	5.5 (3)
C12	−0.0170 (7)	−0.148 (1)	0.315 (1)	6.1 (3)	C38	0.4355 (7)	−0.397 (1)	0.324 (2)	6.7 (3)
C13	0.0344 (6)	−0.104 (1)	0.233 (1)	4.9 (3)	C39	0.3663 (6)	−0.394 (1)	0.271 (1)	5.2 (3)
C14	0.4214 (5)	−0.125 (1)	0.058 (1)	4.0 (3)	C40	0.3255 (5)	0.1415 (9)	0.230 (1)	3.5 (2)
C15	0.3501 (5)	−0.3095 (9)	−0.167 (1)	3.4 (2)	C41	0.3938 (6)	0.171 (1)	0.288 (1)	4.8 (3)
C16	0.3260 (6)	−0.341 (1)	−0.303 (1)	5.4 (3)	C42	0.4389 (6)	0.248 (1)	0.234 (1)	5.4 (3)
C17	0.3302 (7)	−0.458 (1)	−0.393 (2)	6.5 (3)	C43	0.4186 (7)	0.293 (1)	0.134 (1)	5.9 (3)
C18	0.3587 (7)	−0.544 (1)	−0.345 (2)	6.1 (3)	C44	0.3514 (7)	0.268 (1)	0.080 (1)	6.0 (3)
					C45	0.3055 (6)	0.193 (1)	0.129 (1)	4.3 (3)

B. Anisotropic Thermal Parameters[e]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00147 (4)	0.0074 (1)	0.0094 (2)	0.0004 (1)	0.0004 (1)	0.0042 (3)	P2	0.00164 (9)	0.0084 (3)	0.0092 (5)	0.0002 (3)	0.0010 (3)	0.0027 (7)
S1	0.0030 (1)	0.0073 (3)	0.0116 (5)	0.0004 (3)	0.0012 (4)	0.0015 (7)	P3	0.0021 (1)	0.0076 (3)	0.0097 (5)	0.0006 (3)	−0.0003 (3)	0.0056 (7)
S2	0.0035 (2)	0.0265 (9)	0.031 (1)	0.0062 (6)	0.0034 (7)	−0.014 (2)	O1	0.0088 (8)	0.039 (3)	0.096 (7)	0.021 (3)	−0.023 (4)	−0.048 (8)
P1	0.00156 (1)	0.0080 (3)	0.0108 (5)	0.0005 (3)	−0.0004 (3)	0.0048 (7)	O2	0.0063 (6)	0.046 (3)	0.056 (5)	0.002 (2)	0.012 (3)	−0.056 (6)

[a] Numbers in parentheses here and elsewhere in the paper refer to the estimated standard deviation in the least significant digit. [b] The SO_2 group was refined as a rigid group of idealized geometry (see Experimental Section). [c] Methyl carbons are C1, C14, and C27, and phenyl carbons are numbered sequentially around the rings. [d] Refined anisotropically. [e] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

and a large O-S-O angle (134°) were obtained. These results are consistent with either severe libration or a twofold disorder of the SO_2 group. We note that the "average" geometry for an SO_2 group disordered by a mirror plane containing the S-S vector and paralleling the O-O vector gives apparent S-O distances of 1.27 Å, an O-S-O angle of 144°, and O-O′ separations between mirror-related oxygens of 1.36 Å assuming an S-O distance of 1.44 Å and an S-S-O angle of 109°, typical for pyramidal X-SO_2 groups.[7-10] However, only two oxygen "peaks" were observed in a difference Fourier synthesis. On the basis of these observations, the SO_2 group was treated as a rigid body of idealized geometry (S-O = 1.440 Å, O-S-O = 114.0°)[9] in subsequent calculations, with the SO_2 group initially positioned in a coplanar S-SO_2 conformation. Refinement with this model produced the final discrepancy factors, $R = 0.079$ and $R_w = 0.078$, and reasonable geometry for a bent SO_2 group (S-S-O = 109.7, 106.3°). In this refinement, the maximum parameter shift was 0.78 esd (y-coordinate for O2). No parameter not associated with the SO_2 group shifted more than 0.25 esd.

A final difference Fourier synthesis revealed residuals such that $|\rho(x)| \leq 0.52$ e Å^{-3} (largest peaks being in the vicinity of methyl carbon C1) and suggested that the disorder model adequately accounts for the scattering density. Final atomic parameters are given in Table III and selected distances and angles are presented in Table IV. Structure factors are available in supplementary tables.

Discussion

Synthesis and Characterization of the Complexes. The $Cu(PR_3)_n(XR')$ complexes were prepared by the schemes shown below. The complexes are all crystalline, yellow to orange solids which in most cases are air-stable for long periods when stored under a partial pressure of SO_2. They can be recrystallized from many organic solvents in the presence of excess SO_2. In some cases, solvent was retained in the crystal lattice of complexes. Generally, the SO_2 adducts were readily obtainable in yields greater than 60% but oil formation was sometimes a problem. Crystalline products were not isolated with bidentate phosphines or with the monophosphines, PEt_3, $P(n\text{-}Bu)_3$, $PPhMe_2$, and $PPhEt_2$. Deliberate attempts to pro-

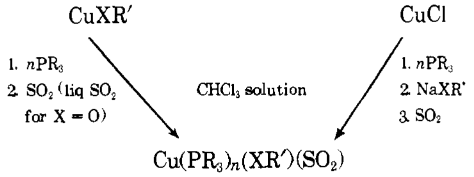

Table IV. Selected Distances (Å) and Angles (deg)[a,b]

Cu-S1	2.404 (2)	P2-C14	1.85 (1)	Cu-S1-S2	132.2 (2)
Cu-P1	2.283 (1)	P2-C15	1.82 (1)	Cu-S1-C40	110.1 (4)
Cu-P2	2.280 (3)	P2-C21	1.82 (1)	S2-S1-C40	94.6 (4)
Cu-P3	2.286 (3)	Cu-P2-C14	111.7 (4)	S1-S2-O1	109.7 (7)
S1-S2	2.530 (5)	Cu-P2-C15	117.6 (4)	S1-S2-O2	106.3 (6)
S1-C40	1.76 (1)	Cu-P2-C21	115.7 (4)	S1-C40-C41	120.1 (9)
P1-C1	1.85 (1)	C14-P2-C15	102.1 (5)	S1-C40-C45	121.9 (8)
P1-C2	1.82 (1)	C14-P2-C21	104.8 (5)	P3-C27	1.85 (1)
P1-C8	1.81 (1)	C15-P2-C21	103.4 (5)	P3-C28	1.83 (1)
Cu-P1-C1	112.9 (3)	P2-C15-C16	122.3 (9)	P3-C34	1.83 (1)
Cu-P1-C2	117.9 (4)	P2-C15-C20	119.4 (9)	Cu-P3-C27	112.2 (4)
Cu-P1-C8	114.5 (3)	P2-C21-C22	118.6 (9)	Cu-P3-C28	115.7 (4)
C1-P1-C2	103.9 (5)	P2-C21-C26	122.7 (9)	Cu-P3-C34	114.2 (4)
C1-P1-C8	104.6 (5)	S1-Cu-P1	106.82 (8)	C27-P3-C28	105.9 (5)
C2-P1-C8	101.3 (5)	S1-Cu-P2	105.3 (1)	C27-P3-C34	102.3 (5)
P1-C2-C3	122.2 (9)	S1-Cu-P3	96.67 (9)	C28-P3-C34	105.4 (5)
P1-C2-C7	126.3 (8)	P1-Cu-P2	121.2 (1)	P3-C28-C29	118.2 (2)
P1-C8-C9	120 (1)	P1-Cu-P3	109.80 (9)	P3-C28-C33	122.0 (1)
P1-C8-C13	120.4 (9)	P2-Cu-P3	113.8 (1)	P3-C34-C35	118.7 (8)
				P3-C34-C39	122.0 (8)

[a] The SO_2 group was refined as a rigid body of idealized geometry (S-O = 1.440 Å, O-S-O = 114.0°). [b] For the phenyl groups, C-C distances were in the range 1.30-1.43 Å (mean 1.38 Å) and the C-C-C angles were in the range 117-124° (mean 119.9°).

voke aerial oxidation of the SO_2 group to sulfate, a reaction observed for many pyramidal M-SO_2 complexes,[9,10] revealed no tendency to undergo this reaction. However, with prolonged oxygenation decomposition reactions did occur, resulting in precipitation of uncharacterized non-sulfato solids.

Satisfactory elemental analyses and SO_2:complex ratios were obtained for the 14 SO_2 adducts studied. These data, together with dissociation temperatures and infrared frequencies for SO_2 vibrations, are presented in Supplementary Table I. These data show that in every case 1:1 adducts are obtained, except for the 1:2 complex $Pt(PPh_3)_2(SPh)_2(SO_2)_2$. The phosphine:copper stoichiometry in the isolated adducts (Table I) appears to be a function of the specific phosphine rather than the initial molar ratio. For example, $Cu(PPh_2Me)_3(SPh)(SO_2)$ was originally crystallized from a solution containing less than $3PR_3$/Cu, but in all other cases complexes with 2:1 ratios crystallized even when the PR_3/Cu ratio was as high as 4:1. For the tridentate phosphine "tripod", a 1:1 ratio of ligand to copper was obtained for the SO_2 adducts, but it is not known whether all three phosphorus atoms are simultaneously coordinated.

The phenoxide complex $Cu(PCy_3)_2(OPh)(SO_2)$ is stable only at low temperatures. A crystalline sample of $Cu(PPh_2Me)_2(SMe)(SO_2)$ spontaneously turned black several weeks after its preparation even though stored at 0 °C, but none of the other adducts underwent this type of decomposition. Also, we were unable to obtain a stable $Cu(PBz_3)_2(SR)$ complex for R = Me, although complexes were easily prepared for R = Et and Ph.

Dissociation of SO_2 from the Complexes. An important property of all these SO_2 adducts is the quasi-reversible binding of SO_2. Removal of SO_2 from the adducts can best be effected by dissolving them in organic solvents and slowly removing solvent in vacuo. In some cases, this is a convenient route to the pure organophosphine copper(I) mercaptides, direct syntheses of which often yield impure oily products. Dissociation pressures of ~0.5-15 Torr are observed at ambient temperature for the SO_2-copper mercaptide complexes, and these values increase to ~7-70 Torr at 70 °C (Table I). Unfortunately, in the tensimetric experiments, true equilibration of SO_2 gas over adducts crystallized from $CHCl_3$ solution was not usually obtained. For most samples, pressure stabilization required a week or more and cycling of the temperature gave irreproducible pressures. Further, the dissociation pressure was sometimes dependent upon the changing composition (SO_2: metal complex ratio) during the experiments. However, the $Cu(PBz_3)_2(SPh)(SO_2)$ adduct formed by solid-gas reaction did exhibit rapid equilibration and good reversibility. A factor that contributes to the above problems is the lability of the phosphines, which dissociate to an extent along with the SO_2 at elevated temperatures. Prolonged high vacuum pumping on $Cu(PPh_2Me)_3(SPh)(SO_2)$ at 70 °C left a residue of approximate stoichiometry $Cu(PPh_2Me)(SPh)$.

Because of the complexity caused (at least in part) by the multiphase, nonequilibrium nature of the tensimetric systems, considerable caution is advisable in interpreting the vapor pressure data. Nevertheless, it is of at least passing interest to note that for most of the adducts, log P vs. $1/T$ plots yield straight lines from which ΔH_{dissoc} values of about 10-15 kcal/mol can be calculated. These crudely measured "heats" indicate influences on the stability of the SO_2 complexes due to the nature of the organic substituents on both the phosphine and mercaptide ligands. It appears that adducts with ligands of high basicity are more stable than those with less basic ligands, which is not surprising since sulfur dioxide is behaving as a Lewis acid toward the XR^- group. The general stability trends appear to be $PPh_2Me > PCy_3 \sim PBz_3 >$ tripod $\sim PPh_3$ and $SR \sim SPh > SC_6F_5 > SePh \gg OPh$, although some reversals of these trends may be found on close examination of Table I. The O-SO_2 and Se-SO_2 interactions are markedly weaker than the S-SO_2 interactions (cf. the series $Cu(PCy_3)_2(XPh)(SO_2)$ (X = O, S, Se)), an effect perhaps due in part to the heterogeneous nature of the bonds to O and Se. Stereochemical factors also may affect the stability of the X-SO_2 bond in these compounds. Our ΔH values may be compared to heats of dissociation measured for SO_2 adducts of the substrates ionic iodide (4-19 kcal/mol)[27,28] thiocyanate (2-4 kcal/mol),[29] thiourea (13 kcal/mol),[28] Cu-I-SO_2 complexes (9-15 kcal/mol),[16] $(PPh_3)_2(CO)ClM$-SO_2 (7-10 kcal/mol),[30] and a variety of alkyl and aryl amines (17-23 kcal/mol).[31] Organic sulfides, ethers, and alcohols form much weaker complexes with SO_2.[32]

The SO_2 stretching vibrations for the adducts (Supplementary Table I) occur over a range of frequencies (ν_{as} 1195-1278 cm^{-1}; ν_s 1051-1093 cm^{-1}) approximately intermediate to those observed for iodide-SO_2 complexes[15,16] (1260-1320; 1090-1135 cm^{-1}) and for metal-SO_2 complexes with "bent" M-SO_2 geometry (~1200; ~1050 cm^{-1}). Fre-

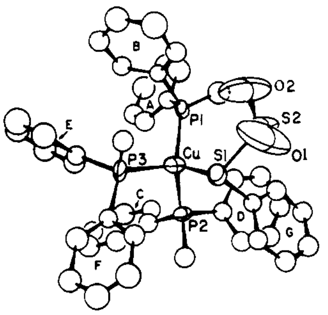

Figure 1. A view of the $Cu(PPh_2Me)_3(SPh)(SO_2)$ coordination unit. The labeled phenyl rings include carbon atoms 2-7(A), 8-13(B), 15-20(C), 21-26(D), 28-32(E), 33-38(F), and 39-45(G). See also footnote, Table III.

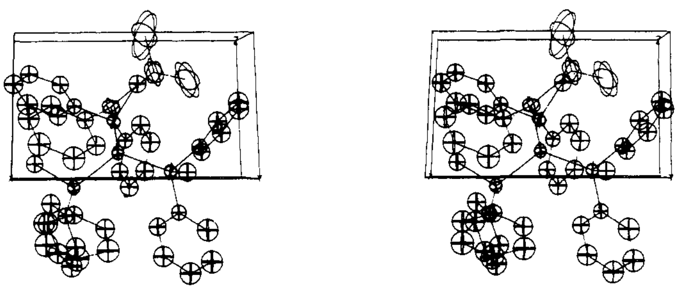

Figure 2. A stereoview of the $Cu(PPH_2Me)_3(SPh)(SO_2)$ molecule.

quently these bands were partially or totally obscured in the infrared by ligand absorptions, but the symmetric S-O stretch was usually the most prominent band in the Raman spectrum.

Interaction of SO_2 with Other Metal Complexes Containing Mercaptide Ligands. Although one might expect a variety of mercaptide complexes to form SO_2 adducts similar to those described above, only limited success has been attained thus far. In part, this may be due to the sparse availability of transition metal complexes containing nonbridging mercaptides, but other factors also seem to be involved. Our preliminary experiments indicate that organophosphine silver(I) mercaptides form SO_2 adducts of stability comparable to the Cu(I) species. At this point in our investigation, the only nongroup 1B metal mercaptide that has been found to form an SO_2 adduct isolable at ambient temperatures is $Pt(PPh_3)_2(SPh)_2$, which yields the red-orange bis complex $Pt(PPh_3)_2(SPh)_2(SO_2)_2$. However, this adduct possesses a much higher SO_2 dissociation pressure than any of the Cu(I) mercaptide compounds (Table I). The complex $(\eta\text{-}C_5H_5)Fe(CO)_2(SPh)$, which is believed to contain a terminally bound mercaptide ligand,[33] does not form a stable SO_2 complex at ambient temperature. This latter result is especially surprising in view of the tendency for $(\eta\text{-}C_5H_5)Fe(CO)_2(SPh)$ solutions to form spontaneously a mercaptide-bridged dimer via displacement of carbonyl by coordinated SPh. The compound $Ir(PPh_3)_2(SPh)(CO)$ readily forms a 1:1 SO_2 adduct, but the infrared spectrum suggests attachment to the metal rather than the mercaptide ligand.[34] A variety of compounds containing bridging mercaptides, such as $[(\eta\text{-}C_5H_5)Fe(CO)(SPh)]_2$, exhibit no interaction with SO_2 even at −63 °C. Mercaptide salts (e.g., NaSPh) reduce SO_2 in solution. Thus, it appears that mercaptides bound to univalent group 1B metals containing phosphine ligands possess just the right combination of Lewis basicity, steric properties, and oxidation/reduction stability to afford isolable SO_2 adducts.

Finally, we anticipate that other Lewis acids will also interact with the mercaptide complexes. Preliminary experiments with BF_3 do indicate complex formation, although we have not studied these reactions in detail.

Description of the Structure of $Cu(PPh_2Me)_3(SPh)(SO_2)$. The crystal structure determination of $Cu(PPh_2Me)_3(SPh)(SO_2)$ shows that the SO_2 molecule has bonded as a Lewis acid to the mercaptide sulfur, which in turn is coordinated to copper (Figures 1 and 2). The S-S distance of 2.530 (5) Å is relatively long, and consistent with the observed SO_2 liability found in these complexes. This S-S distance may be compared to the values 2.040 (3) Å found in an organic disulfide-nickel complex,[35] to 2.06)2) Å found in elemental sulfur,[36] and to 2.39 Å in the $S_2O_4^{2-}$ ion.[37] The S-S distance found in the present case is longer than the sum of the covalent radii (2.06 Å) but much shorter than the sum of the van der Waals radii (4.0 Å).[38]

Although the precision with which the geometry of the SO_2 group is determined in the present structure is impaired by the observed libration or disorder, the geometry of the $S\text{-}SO_2$ group is unambiguously pyramidal. The S-S-O angles are 106.3 (6) and 109.7 (7)°, and the angle between the S-S vector and the SO_2 plane (hereafter referred to as α) is 35°. Other classes of structurally characterized compounds which contain pyramidal $X\text{-}SO_2$ groups also feature long X-S distances and similar α values. In pyramidal $M\text{-}SO_2$ moieties the values of $X\text{-}SO_2$ and α are 2.47–2.49 Å and 21–33°, respectively,[7,8] while in two amine complexes[2] these parameters are 2.06–2.34 Å and 15–22°. In the two structurally determined examples of $M\text{-}I\text{-}SO_2$ moieties,[15,16] these parameters are 21 and 32°, and 3.39 and 3.41 Å. The relative lengthening of $X\text{-}SO_2$ from an expected single bond distance thus appears to decrease in the series $M\text{-}ISO_2 > MSR\text{-}SO_2 > SO_2\text{-}SO_2 > R_3N\text{-}SO_2 \sim M\text{-}SO_2$. This sequence is in general accord with the observed shift of the S-O stretching frequencies and the available SO_2 dissociation pressure data. In these same compounds the average X-S-O angles fall into the ranges 106–110° for the metal complexes and 97–115° for the remainder.

The geometry at copper is pseudotetrahedral with angular distortions which are quite reasonable, considering the three bulky phosphine ligands.[39] The observed S-Cu-P angles (96.67 (9)–106.82 (8)°) are somewhat smaller than the P-Cu-P angles (109.80 (9)–121.2 (1)°), consistent with the greater steric bulk of the phosphine ligands compared to the $SPh\text{-}SO_2$ group. The Cu-P distances, 2.280 (3)–2.286 (3) Å, are normal compared to previously determined pseudotetrahedral copper(I) phosphine compounds.[39] The copper-sulfur distance, 2.404 (2) Å, is definitely at the higher end of the range found in pseudotetrahedral copper(I) complexes containing sulfur donors such as thiourea and phosphine sulfide groups,[40] but in the range found for other transition metal complexes containing bridging mercaptide ligands.[41] In a recently reported organic disulfide structure, Ni-S distances of 2.46–2.47 Å were found.[35]

As expected, geometry at the mercaptide sulfur is pyramidal with Cu-S-C = 110.1 (4)°, Cu-S-S = 132.2 (2)°, and C-S-S = 94.6 (4)°. The S-C bond length, 1.76 (1) Å, is slightly shorter than corresponding values, 1.79–1.83 Å, found in complexed organic disulfides.[35] Internal geometries for the phosphine and thiophenoxide ligands show no unusual features.[39]

Several interesting conformational features are evident in Figure 2. The phosphines are arranged so that the methyl and phenyl groups form a pinwheel arrangement when viewed down the Cu-S vector, in a manner similar to that observed in $Cu(PPh_2Me)_3Cl$.[39] Also, the SO_2 group has bent away from the mercaptide phenyl group. The orientation of the SO_2 group appears to be dictated by steric repulsion factors. The mercaptide phenyl and a phosphine phenyl group are approximately centered over, and parallel to, each other. These phenyl rings form an angle of 15.3° and the distance between their centers is 4.1 Å, similar to the expected van der Waals separation for phenyl groups.[38] Intermolecular, "graphitic" phenyl ring stacking of this type has been observed in several other phosphine complexes,[39] but no striking intermolecular packing features were observed for this structure.

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Supplementary Material Available: Supplementary Table I (characterization data for SO_2 adducts) and a listing of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. Z. Lecher and W. B. Hardy, *J. Am. Chem. Soc.*, **70**, 3789 (1948).
(2) J. D. Childs, D. van der Helm, and S. D. Christian, *Inorg. Chem.*, **14**, 1386 (1975).
(3) A. P. Zipp, *J. Inorg. Nucl. Chem.*, **36**, 1399 (1974).
(4) N. F. Albertson and W. C. Fernelius, *J. Am. Chem. Soc.*, **65**, 1687 (1943).
(5) S. I. A. El Shiekh, B. C. Smith, and M. E. Sobeir, *Angew. Chem. Int. Ed. Engl.*, **9**, 308 (1970).
(6) E. J. Woodhouse and T. H. Norris, *Inorg. Chem.*, **10**, 614 (1971).
(7) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **8**, 1921 (1969).
(8) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).
(9) P. G. Eller, R. R. Ryan, and D. W. Moody, *Inorg. Chem.*, **15**, 2442 (1976).
(10) D. W. Moody and R. R. Ryan, *Inorg. Chem.*, **15**, 1823 (1976).
(11) C. Barbeau and R. J. Dubey, *Can. J. Chem.*, **51**, 3684 (1973).
(12) L. H. Vogt, Jr., J. J. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).
(13) R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, **15**, 797 (1976).
(14) R. R. Ryan and P. G. Eller, *Inorg. Chem.*, **15**, 494 (1976).
(15) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 224 (1973).
(16) P. G. Eller, G. J. Kubas, and R. R. Ryan, *Inorg. Chem.*, in press.
(17) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(18) W. E. Duncan, E. Ott, and E. E. Reid, *Ind. Eng. Chem.*, **23**, 381 (1931).
(19) T. Kawaki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **45**, 1499 (1972).
(20) G. M. Whitesides, J. S. Sadowski, and J. Lilburn, *J. Am. Chem. Soc.*, **96**, 2829 (1974).
(21) T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Am. Chem. Soc.*, **94**, 658 (1972).
(22) W. T. Reichle, *Inorg. Chim. Acta*, **5**, 325 (1971).
(23) Reichle (ref 22) prepared $Cu(PPh_3)_2(XPh)$ (X = O, S) by reacting $Cu(PPh_3)_3Cl$ with NaXPh in refluxing THF/toluene. We find that in certain cases, this type of synthesis will work at ambient temperature using chloroform as solvent. However, in several instances the chloride ligand was not displaced by XPh^- (X = O, S, Se), even at chloroform reflux temperatures.
(24) R. Zanella, R. Ros, and M. Graziani, *Inorg. Chem.*, **12**, 2736 (1973).
(25) R. R. Ryan and B. I. Swanson, *Inorg. Chem.*, **13**, 1681 (1974).
(26) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); A. C. Larson, *ibid.*, 664 (1967).
(27) S. Wasif and S. B. Salama, *J. Chem. Soc., Dalton Trans.*, 2148 (1973).
(28) P. G. Eller, and G. J. Kubas, to be submitted for publication.
(29) A. Salama, S. B. Salama, M. Sobeir, and S. Wasif, *J. Chem. Soc. A*, 1112 (1971).
(30) C. T. Mortimer and S. J. Ashcroft, *Inorg. Chem.*, **10**, 1326 (1971).
(31) W. E. Byrd, *Inorg. Chem.*, **1**, 762 (1962).
(32) P. A. D. deMaine, *J. Chem. Phys.*, **26**, 1042 (1957).
(33) M. Ahmad, R. Bruce, and G. R. Knox, *J. Organomet. Chem.*, **6**, 1 (1966).
(34) G. J. Kubas, unpublished results.
(35) L. G. Warner, M. M. Kadooka, and K. Seff, *Inorg. Chem.*, **14**, 1773 (1975).
(36) D. E. Sands, *J. Am. Chem. Soc.*, **87**, 1395 (1965).
(37) J. D. Dunitz, *Acta Crystallogr.*, **9**, 579 (1956).
(38) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., (1966).
(39) J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, **15**, 1155 (1976).
(40) See, for example, E. A. Vizzini, I. F. Taylor, and E. L. Amma, *Inorg. Chem.*, 7, 1351 (1968), and references cited therein.
(41) P. J. Vergamini and G. J. Kubas, *Prog. Inorg. Chem.*, **21**, 261 (1976).

A Theoretical Model for the Effects of Solvent and Protein Dielectric on the Redox Potentials of Iron–Sulfur Clusters

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Abstract: A theoretical model for the effects of solvent and protein dielectric on the redox potentials of iron–sulfur clusters is formulated to account for observed differences between the potentials of synthetic analogues and proteins. Each of the redox processes is considered to be accompanied by a change in the charge on the iron–sulfur cluster such that the free energy change will in part be dependent on the difference in charging energies associated with the interaction of a cluster with its environment. The model also considers that the electrostatic interactions within a cluster are dependent on the macroscopic dielectric of its environment and thus affect the free energy change for a redox process. The results of calculations based on the difference in the electrostatic free energy changes associated with a redox process are consistent with observed differences in the redox properties of the analogues and the proteins.

Most recent research[1-4] on iron–sulfur proteins has been directed toward describing the detailed structure of the iron-coordination centers. Chemical,[5] spectroscopic,[1-4] and x-ray structural analyses[6-11] have indicated that these proteins are characterized by three types of coordination centers consisting of one, two, and four iron atoms coordinated to inorganic sulfide and/or the thiolate groups of cysteine residues. The description of these centers has been augmented by the elegant syntheses[12-16] of iron–sulfur cluster complexes which are close structural representations of the three redox centers in the proteins. It is anticipated that all such research will provide an understanding of the redox properties of the proteins and the relationship of protein structure to the intrinsic properties of the iron–sulfur coordination centers. Each of the iron–sulfur centers in proteins is characterized by two redox states coupled by a single electron transfer reaction. Redox potentials of −0.057 V[17] (rubredoxin), −0.42 V[18,19] (plant ferredoxin), and −0.40 V[19] (bacterial ferredoxin) correspond to iron–sulfur proteins with one, two, and four iron atoms centers, respectively. Redox potentials of the synthetic complexes in nonaqueous solutions exhibiting corresponding reactions are up to 0.85 V[14] more negative than the proteins and synthetic