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Reactions of $\text{Ph}_3\text{Sb}=\text{S}$ with Copper(I) Complexes Supported by N-Donor Ligands: Formation of Stable Adducts and S-Transfer Reactivity

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Abstract

In the exploration of sulfur-delivery reagents useful for synthesizing models of the tetracopper-sulfide cluster of nitrous oxide reductase, reactions of $\text{Ph}_3\text{Sb}=\text{S}$ with Cu(I) complexes of *N,N,N',N'*-tetramethyl-2*R*,3*R*-cyclohexanediamine (TMCHD) and 1,4,7-trialkyltriazacyclononanes (R_3tacn ; R = Me, Et, iPr) were studied. Treatment of $[(\text{R}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$ (R = Me, Et, or iPr) with one equivalent of $\text{S}=\text{SbPh}_3$ in CH_2Cl_2 yielded adducts $[(\text{R}_3\text{tacn})\text{Cu}(\text{S}=\text{SbPh}_3)]\text{SbF}_6$ (**1–3**), which were fully characterized, including by X-ray crystallography. The adducts slowly decayed to $[(\text{R}_3\text{tacn})_2\text{Cu}_2(\mu\text{-}\eta^2\text{-S}_2)]^{2+}$ species (**4–6**) and SbPh_3 , or more quickly in the presence of additional $[(\text{R}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$ to **4–6** and $[(\text{R}_3\text{tacn})\text{Cu}(\text{SbPh}_3)]\text{SbF}_6$ (**7–9**). The results of mechanistic studies of the latter process were consistent with rapid intermolecular exchange of $\text{S}=\text{SbPh}_3$ between **1–3** and added $[(\text{R}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$, followed by conversion to product via a dicopper intermediate formed in a rapid pre-equilibrium step. Key evidence supporting this step came from the observation of saturation behavior in a plot of the initial rate of loss of **1** versus the initial concentration of $[(\text{Me}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$. Also, treatment of $[(\text{TMCHD})\text{Cu}(\text{CH}_3\text{CN})]\text{PF}_6$ with $\text{S}=\text{SbPh}_3$ led to the known tricopper cluster $[(\text{TMCHD})_3\text{Cu}_3(\mu_3\text{-S})_2](\text{PF}_6)_3$ in good yield (79%), a synthetic procedure superior to that previously reported (Brown, E. C.; York, J. T.; Antholine, W. E.; Ruiz, E.; Alvarez, S.; Tolman, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 13752–13753).

Introduction

The environmentally important reduction of N_2O to N_2 is catalyzed enzymatically by nitrous oxide reductase,¹ which has been shown on the basis of X-ray crystallography² and other spectroscopic techniques³ to contain a unique tetracopper-sulfide cluster supported by multiple histidine residues in its active site. The novel structure of this cluster and hypotheses for the mechanism of N_2O coordination and reduction at its copper centers⁴ has stimulated extensive efforts to create copper-sulfur model complexes supported by N-donor ligands.^{5–6} These efforts have focused on the use of relatively few types of sulfur-containing reagents (e.g., S_8 and Na_2S_2) in reactions with Cu(I) and Cu(II) species. Studies of the copper-sulfur compounds characterized so far have raised interesting bonding questions,^{7–8} and, in one instance, have led to the discovery of reactivity with N_2O .⁶ Nonetheless, only a

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Supporting Information Available. Illustrative experimental procedures, spectra, and kinetics results, and representations of the X-ray crystal structures of complexes **2** and **3** (PDF); X-ray structural data (CIFs). This material is available free of charge via the Internet at <http://pubs.acs.org>.

limited array of N-donor ligated copper-sulfur motifs have been characterized and an accurate model of the nitrous oxide active site has yet to be constructed.

In seeking to broaden the scope of available copper-sulfur complexes as a means to address mechanistic and electronic structural issues relevant to the enzyme active site, we are exploring reactions of copper precursors with an expanded array of sulfur-containing reagents. Several studies have shown that triphenyl antimony sulfide ($\text{Ph}_3\text{Sb}=\text{S}$) is useful for sulfur transfer reactions,⁹ including for the preparation of transition metal sulfide complexes.¹⁰⁻¹¹ The utility of Ph_3SbS likely stems from the thermodynamic instability of the Sb-S bond, which is weaker than the related bonds in $\text{R}_3\text{E}=\text{S}$ ($\text{E} = \text{P}$ or As) congeners.¹² Herein, we report the results of an investigation of the reactivity of $\text{Ph}_3\text{Sb}=\text{S}$ with selected Cu(I) complexes of *N,N,N',N'*-tetramethyl-2*R*,3*R*-cyclohexanediamine (TMCHD) and 1,4,7-trialkyltriazacyclononanes (R_3tacn ; $\text{R} = \text{Me}, \text{Et}, \text{iPr}$). Key findings include the isolation and structural characterization of novel $\text{LCu(I)-S}=\text{SbPh}_3$ ($\text{L} = \text{R}_3\text{tacn}$; $\text{R} = \text{Me}, \text{Et}, \text{iPr}$) adducts, which are the first examples of transition metal complexes bound to $\text{Ph}_3\text{Sb}=\text{S}$ to be structurally characterized by X-ray crystallography.¹³ These complexes subsequently decay cleanly to $[\text{Cu}_2(\mu-\eta^2:\eta^2-\text{S}_2)]^{2+}$ species, particularly when treated with additional $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$, and mechanistic insights for this process were obtained through kinetics studies. In addition, by using $\text{Ph}_3\text{Sb}=\text{S}$ an improved synthetic route to the $[\text{Cu}_3\text{S}_2]^{3+}$ core⁸ was discovered.

Experimental Section

General Considerations

All solvents and reagents were obtained from commercial sources and used as received unless otherwise noted. The solvents CH_2Cl_2 , pentane, and Et_2O were dried over CaH_2 and distilled under vacuum or passed through solvent purification columns (Glass Contour, Laguna, CA). The complexes $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$ ($\text{R} = \text{Me}$,¹⁴ Et ,¹⁵ iPr ¹⁶), $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{BPh}_4$ ($\text{R} = \text{Et}$ ¹⁵ or iPr ¹⁷), $[(\text{Me}_3\text{tacn})_2\text{Cu}_2(\text{S}_2)](\text{SbF}_6)_2$ ¹⁴ and $[(\text{TMCHD})\text{Cu}(\text{CH}_3\text{CN})]\text{PF}_6$ ¹⁸ were prepared according to published procedures. All metal complexes were prepared and stored in a glovebox under a dry N_2 atmosphere. Triphenylantimony sulfide ($\text{Ph}_3\text{Sb}=\text{S}$) and 2,3-dimethylbutadiene were purchased from Strem and Aldrich, respectively, and were used without purification. NMR spectra were recorded on either Varian VI-300 or VXR-300 spectrometers at $\sim 20^\circ\text{C}$. Chemical shifts (δ) were referenced to residual solvent signal and integrated intensities compared to 1,3,5-trimethoxybenzene added as an internal standard. UV-vis spectra were recorded on an HP8453 (190–1100 nm) diode-array spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratory (Ledgewood, NJ). Electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker BioTOF II instrument. IR spectra were obtained using a ThermoNicolet Avatar 370 FT-IR.

$[(\text{R}_3\text{tacn})\text{Cu}(\text{S}=\text{SbPh}_3)]\text{SbF}_6$ ($\text{R} = \text{Me}$ (**1**), Et (**2**), or iPr (**3**))

All three complexes were prepared according to this illustrative procedure: In an inert atmosphere, to a solution of the $\text{S}=\text{SbPh}_3$ (32 mg, 0.083 mmol) in CH_2Cl_2 (4 mL) was added $[(\text{Me}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$ (43 mg, 0.083 mmol) in CH_2Cl_2 (1 mL). After stirring for 1 h, the mixture was filtered and the volume of the filtrate was reduced to ~ 1 mL, and Et_2O (15 mL) was added, resulting in formation of a yellow precipitate. The supernatant was decanted and the yellow powder was washed with Et_2O (3×6 mL). The product was isolated in crystalline form by layering Et_2O into a concentrated THF solution at -20°C (65 mg, 92%). Analogous procedures were used to isolate **2** and **3** as yellow crystals in 41% and 32% yields, respectively. **1**: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.77\text{--}7.61$ (m, 15H), 2.59–2.53 Hz (m, 12H), 2.38 (s, 9H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, CD_2Cl_2): $\delta = 134.37, 133.44$,

130.97, 55.03, 49.02 ppm. UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in CH_2Cl_2]: 356 (2100). Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{CuF}_6\text{N}_3\text{SSb}_2$: C, 37.90; H, 4.24; N, 4.91. Found: C, 37.77; H, 4.24; N, 4.99. ESI-MS: $[\text{Cu}(\text{Me}_3\text{tacn})(\text{S}=\text{SbPh}_3)]^+$ calc. m/z 620.0, found 620.3. FT-IR: 2859.2, 1480.5, 1460.1, 1437.5, 1363.4, 1300.0, 1152.8, 1130.2, 1089.4, 1065.5, 1017.0, 966.3, 984.1, 889.5, 773.5, 751.3, 735.4, 692.4, 656.4 cm^{-1} . **2**: ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.74-7.60 (m, 15H), 2.60-2.53 Hz (m, 18H), 1.10 (t, J = 6.0 Hz, 9H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ = 134.6, 133.4, 130.9, 55.3, 53.3, 13.0 ppm. UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in CH_2Cl_2]: 356 (2300). Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{CuF}_6\text{N}_3\text{SSb}_2$: C, 40.13; H, 4.72; N, 4.68. Found: C, 39.76; H, 4.70; N, 4.65. ESI-MS: $[\text{Cu}(\text{Et}_3\text{tacn})(\text{S}=\text{SbPh}_3)]^+$ calc. m/z 662.0, found 662.2. FT-IR: 2972.4, 1479.3, 1437.6, 1378.9, 1347.9, 1315.0, 1136.6, 1124.9, 1067.4, 1041.1, 1031.4, 995.7, 928.8, 897.9, 876.2, 860.3, 851.7, 827.1, 812.7, 796.8, 751.0, 739.1 cm^{-1} . **3**: ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.73-7.59 (m, 15H), 2.66-2.61 Hz (m, 9H), 2.47-2.44 Hz (m, 6H), 1.13 (d, J = 6.0 Hz, 18H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ = 138.75, 134.69, 133.38, 130.91, 58.29, 50.83, 19.70 ppm. UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in CH_2Cl_2]: 356 (2300). Anal. Calcd for $\text{C}_{33}\text{H}_{48}\text{CuF}_6\text{N}_3\text{SSb}_2$: C, 42.17; H, 5.15; N, 4.47. Found: C, 42.11; H, 5.23; N, 4.46. ESI-MS: $[\text{Cu}(\text{iPr}_3\text{tacn})(\text{S}=\text{SbPh}_3)]^+$ calc. m/z 704.1, found 704.3. FT-IR: 2965.7, 1491.5, 1478.4, 1437.0, 1386.8, 1368.5, 1351.5, 1299.1, 1265.1, 1167.0, 1129.4, 1067.2, 1020.3, 995.7, 968.1, 856.7, 841.0, 750.3, 737.9, 721.3, 692.6, 656.5 cm^{-1} .

$[(\text{Et}_3\text{tacn})_2\text{Cu}_2(\mu\text{-S}_2)](\text{BPh}_4)_2$ (5**)**

Elemental sulfur (1.8 mg, 0.007 mmol) was added to a solution of $[(\text{Et}_3\text{tacn})\text{Cu}(\text{NCCCH}_3)]\text{BPh}_4$ (36 mg, 0.056 mmol) in CH_2Cl_2 (4 mL). After stirring for 2 h, solvent was removed under reduced pressure to yield a brown solid. The brown solid was washed with Et_2O (2×6 mL), extracted with DMF (2 mL), and then filtered. Slow diffusion of Et_2O into the dark brown filtrate at room temperature afforded the product as deep green crystals (16 mg, 46%). ^1H NMR (300 MHz, d_7 -DMF): δ = 7.32 (s, 16H), 6.96 (t, 16H), 6.81 (t, 8H), 3.16-3.09 Hz (m, 36H), 1.36 (t, J = 6.0 Hz, 18H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, d_7 -DMF): δ = 137.11, 135.71, 126.33, 122.62, 93.84, 56.04, 54.64 and 12.39 ppm. UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in DMF]: 410 (7400), 378 (7600). Anal. Calcd for $\text{C}_{72}\text{H}_{94}\text{B}_2\text{Cu}_2\text{N}_6\text{S}_2$: C, 68.83; H, 7.54; N, 6.69. Found: C, 68.45; H, 7.42; N, 6.70. FT-IR: 3052.7, 2978.9, 1579.6, 1478.5, 1465.9, 1386.9, 1270.4, 1258.5, 1144.8, 1122.9, 1069.9, 1033.3, 1018.3, 999.5, 921.0, 862.4, 842.3, 821.8, 792.9, 771.5, 742.3, 732.0, 710.1, 700.6, 668.2 cm^{-1} .

$[(\text{iPr}_3\text{tacn})_2\text{Cu}_2(\mu\text{-S}_2)](\text{BPh}_4)_2$ (6**)**

A similar procedure to that used for the preparation of **5** was followed, except THF was used as the reaction solvent and the product was isolated as dark red crystals from CH_2Cl_2 at -20 °C (37% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.33 (s, 15H), 7.04 (t, J = 6.0 Hz, 14H), 6.89 (t, J = 6.0 Hz, 11H), 3.15-3.06 Hz (m, 5H), 2.95-2.74 (m, 4H), 2.65-2.46 (m, 11H), 2.33-2.20 (m, 10H), 1.26-1.08 (d, J = 6.0 Hz, 36H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ = 136.44, 126.22, 122.42, 60.47, 51.75, 45.10, 19.79 and 18.46 ppm. UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in CH_2Cl_2]: 476 (7200), 380 (11000). Anal. Calcd for $\text{C}_{78}\text{H}_{106}\text{B}_2\text{Cu}_2\text{N}_6\text{S}_2$: C, 69.88; H, 7.97; N, 6.27. Found: C, 69.91; H, 7.78; N, 6.24. FT-IR: 3053.5, 2978.0, 1579.8, 1480.7, 1467.0, 1451.0, 1426.7, 1390.1, 1369.2, 1347.1, 1291.9, 1268.7, 1166.3, 1141.9, 1129.4, 1067.3, 1046.6, 1033.5, 962.4, 943.1, 841.7, 761.0, 749.3, 734.1, 705.6, 680.6, 668.1 cm^{-1} .

$[(\text{R}_3\text{tacn})\text{Cu}(\text{SbPh}_3)]\text{SbF}_6$ (7**, $\text{R} = \text{Me}$; **8**, $\text{R} = \text{Et}$; **9**, $\text{R} = \text{iPr}$)**

These complexes were prepared similarly, according to the following representative procedure for **7**. In an inert atmosphere, to a solution of SbPh_3 (40.0 mg, 0.113 mmol) in CH_2Cl_2 (4 mL) was added $[(\text{Me}_3\text{tacn})\text{Cu}(\text{NCCCH}_3)]\text{SbF}_6$ (58.0 mg, 0.113 mmol) in CH_2Cl_2

(1 mL). The mixture was stirred 3 h, filtered, and the volume of the filtrate was reduced to ~1 mL under reduced pressure. A portion of Et₂O (15 mL) was added to yield a white precipitate. The supernatant solution was decanted and the white powder was washed three times with Et₂O (3 × mL). The white product was recrystallized by diffusion of Et₂O into a concentrated CH₂Cl₂ solution at room temperature to generate the product as colorless crystals (71 mg, 76 %). **7**: ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.48–7.43 (m, 15H), 2.90 Hz (s, 12H), 2.73 (s, 9H) ppm; ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 135.87, 130.89, 130.27, 55.98, 50.69 ppm. Anal. Calcd for C₂₇H₃₆CuF₆N₃Sb₂: C, 39.37; H, 4.41; N, 5.10. Found: C, 38.87; H, 4.61; N, 4.86. ESI-MS: [Cu(Me₃tacn)(SbPh₃)]⁺ calc. m/z 588.0, found 588.1. FT-IR: 1463.1, 1434.1, 1363.8, 1299.2, 1153.8, 1127.8, 1085.8, 1069.8, 1057.1, 1015.0, 1000.3, 985.9, 768.3, 737.6, 697.7 cm⁻¹. **8** (68% yield): ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.48–7.41 (m, 15H), 2.90–2.85 Hz (m, 18H), 1.15 (t, J = 6.0 Hz, 9H) ppm; ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 135.85, 130.88, 130.26, 56.87, 54.68, 14.46 ppm. Anal. Calcd for C₃₀H₄₂CuF₆N₃Sb₂: C, 41.62; H, 4.89; N, 4.85. Found: C, 41.50; H, 5.20; N, 4.92. ESI-MS: [Cu(Et₃tacn)(S=SbPh₃)]⁺ calc. m/z 662.0, found 662.2. FT-IR: 1434.2, 1375.8, 1338.5, 1121.2, 1067.2, 1037.6, 999.7, 931.38, 768.2, 737.3, 699.67 cm⁻¹. **9** (70 % yield): ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.49–7.41 (m, 15H), 3.15–3.11 (m, 3H), 2.93–2.89 Hz (m, 6H), 2.80–2.75 Hz (m, 6H), 1.13 (d, J = 6.0 Hz, 18H) ppm; ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 135.9, 130.85, 130.25, 59.69, 51.77, 20.13 ppm. Anal. Calcd for C₃₃H₄₈CuF₆N₃Sb₂: C, 43.66; H, 5.33; N, 4.63. Found: C, 43.30; H, 5.72; N, 4.62. ESI-MS: [Cu(iPr₃tacn)(SbPh₃)]⁺ calc. m/z 672.1, found 672.2. FT-IR: 1434.4, 1389.4, 1367.0, 1347.1, 1161.7, 1123.2, 1066.5, 997.3, 964.31, 756.2, 739.2, 720.6, 699.6 cm⁻¹.

[(TMCHD)₃Cu₃(S)₂](PF₆)₃ (**12**)

In an inert atmosphere, to a solution of the [(TMCHD)Cu(NCCH₃)]PF₆ (31 mg, 0.073 mmol) in CH₂Cl₂ (3 mL) was added S=SbPh₃ (29 mg, 0.049 mmol) in CH₂Cl₂ (1 mL). After the mixture was stirred for 2 h, it was filtered and the solvent was removed from the filtrate under vacuum to yield a deep green solid, which was washed with Et₂O (3 × 6 mL). The deep green powder obtained was crystallized from CH₂Cl₂ at –20 °C to form dark amber crystals of the product (28 mg, 79%). The product was identified by its X-ray crystal structure and the similarity of its UV-vis spectrum to previously reported data.^{8a}

General Procedures for NMR Kinetics

In a glovebox, appropriate volumes of starting materials in CD₂Cl₂ were mixed in a vial and the volumes were quickly adjusted to 1 mL so that the concentrations of adducts **1–3** and [(R₃tacn)Cu(CH₃CN)]SbF₆ were 4.7 mM and 47 mM, respectively. The solution was then quickly transferred to a J. Young NMR tube that was removed from glovebox and placed in the spectrometer probe. The progress of the reaction was monitored by ¹H NMR spectroscopy at room temperature with 1,3,5-trimethoxybenzene as an internal standard. The initial rates were determined in experiments in which the first 5–10% of the reaction was followed; the rate constants were obtained by linear fitting of the initial rate change. In the experiments with 2,3-dimethylbutadiene, identical procedures were used except 20 equivalents of 2,3-dimethylbutadiene was added to the mixture. Data analysis and graphical representations were performed using the program Kaleidagraph.

Results and Discussion

Synthesis and Characterization of LCu(I)-S=SbPh₃ Adducts and [L₂Cu₂(S₂)]²⁺ Decay Products

Reaction of [(R₃tacn)Cu(NCCH₃)]SbF₆ (R = Me, Et, or iPr) with one equivalent of S=SbPh₃ in CH₂Cl₂ yielded adducts **1–3**, respectively, as yellow crystalline solids (Scheme 1). The complexes are stable in the solid state when stored under nitrogen, but in solution they

decompose slowly (see below). The formulations of **1–3** are based on NMR, UV-vis, and FT-IR spectroscopy, CHN analysis, ESI-MS, and X-ray crystallography. Notable identifying features include (a) ^1H NMR spectra with sharp peaks in the diamagnetic region and multiplets for the $\text{Ph}_3\text{Sb}=\text{S}$ hydrogen atoms shifted $\sim 0.2\text{--}0.3$ ppm downfield from uncomplexed $\text{Ph}_3\text{Sb}=\text{S}$ (Figure S1), (b) a shoulder in UV-vis spectra with λ_{max} at ~ 350 nm ($\epsilon = \sim 2100\text{--}2300\text{ M}^{-1}\text{cm}^{-1}$), and (c) parent ions $[(\text{R}_3\text{tacn})\text{Cu}(\text{SSbPh}_3)]^+$ with appropriate isotope patterns in ESI mass spectra (Figure S2).

The X-ray crystal structures of complexes **1–3** are shown in Figures 1 (**1**) and S3 (**2** and **3**), with selected bond distances and angles listed in Table 1. To our knowledge, they represent the first such structures with $\text{Ph}_3\text{Sb}=\text{S}$ coordinated to a metal center.¹⁹ They contain similar four-coordinate Cu(I) centers with highly distorted tetrahedral geometries characterized by τ_4 values: 0.640 (**1**), 0.657 (**2**), and 0.634 (**3**).²⁰ Essentially, the distortion involves perturbation of the Cu-S bonds from the idealized trigonal axis towards coplanarity with two of the N-donor atoms on the supporting ligand (N2 and N3 for **1**; Figure 1), presumably as a result of steric interactions between the N-donor ligand substituents and the phenyl rings of the coordinated $\text{Ph}_3\text{Sb}=\text{S}$ moiety. These steric effects also appear to influence the $\text{Cu}\cdots\text{Sb}$ distance, which increases as the size of the R group of the ligand increases from 3.411 Å (**1**), 3.490 Å (**2**), to 3.547 Å (**3**). The Cu-S-Sb moiety adopts a ‘bent’ conformation with Cu-S-Sb bond angles between $100.1\text{--}104.6^\circ$. The average Cu-N bond lengths range between 2.06–2.17 Å, comparable to those in other copper(I) complexes of R_3tacn ligands.^{17,21} The Cu-S distances of complexes **1–3** (2.167–2.203 Å) are shorter than typical copper(I)-thioether sulfur interactions (~ 2.30 Å),²² and longer than copper(I)-thiolate interactions (2.13–2.18 Å),²³ but comparable to known Cu(I)-S=PPh₃ complexes (2.21–2.27 Å).²⁴ Complexation of $\text{Ph}_3\text{Sb}=\text{S}$ to the copper center induces little if any change in the S-Sb bonding, as the S-Sb distances in **1–3** (2.281–2.283 Å) are only slightly longer than that in free $\text{S}=\text{SbPh}_3$ (2.244(1) Å).²⁵

By monitoring solutions of **1** in CD_2Cl_2 by ^1H NMR spectroscopy with an internal standard (Figure S4) at 20 °C the slow decay ($t_{1/2} \sim 12\text{h}$) of **1** to SbPh_3 and the disulfido-dicopper(II) species $[(\text{Me}_3\text{tacn})_2\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)](\text{SbF}_6)_2$ (**4**) was observed in accordance with the stoichiometry shown in Scheme 1. A similar decay reaction of **2** occurred to yield the respective disulfido-dicopper(II) complex (**5**, with SbF_6^- counterion), but at a significantly slower rate ($t_{1/2} \sim 2\text{d}$). Complex **3** decayed at a similar rate as **2**, but the nature of the product(s) in this case was not clear. The disulfido-dicopper(II) complexes **4–6** formed much more rapidly and with higher yields/conversions upon addition of $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$ to solutions of **1–3**, but in these reactions the adducts $[(\text{R}_3\text{tacn})\text{Cu}(\text{SbPh}_3)]\text{SbF}_6$ (**7**, R = Me; **8**, R = Et; **9**, R = iPr) formed instead of free SbPh_3 (Scheme 1).

The disulfido-dicopper(II) complexes **4–6** were identified by comparison of ^1H NMR spectra with data reported previously (**4**)¹⁴ or obtained from independently prepared samples of the variants **5** and **6**. These latter complexes were isolated as BPh_4^- salts by treating $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{BPh}_4$ with S_8 and were fully characterized by CHN analysis and NMR, FTIR, and UV-vis spectroscopy. Complexes **4–6** share similarly sharp ^1H NMR features in the diamagnetic region, consistent with singlet ground states arising from disulfide-mediated antiferromagnetic coupling between the Cu(II) ions. They also share diagnostic $\text{S}_2^{2-} \rightarrow \text{Cu(II)}$ LMCT transitions in UV-vis spectra at λ_{max} 380–400 nm ($\epsilon \sim 8000\text{--}14,000$).^{26,7b} In addition, the X-ray structure of **5** was solved (Figure 2). The X-ray structures of **5** is similar to that previously reported for **4**:¹⁴ as illustrated by analogous S-S (4: 2.165(4) Å; 5: 2.150(1) Å) and Cu-Cu (4: 3.84 Å; 5: 3.88 Å) distances and square pyramidal coordination geometries ($\tau_5 = 0.03$ for **4** and 0.01 for **5**).²⁸

The adducts [(R₃tacn)Cu(SbPh₃)]SbF₆ (**7**, R = Me; **8**, R = Et; **9**, R = iPr) formed in the reactions of **1–3** with [(R₃tacn)Cu(CH₃CN)]SbF₆ also were identified by comparison of ¹H NMR spectra with data obtained from independently prepared samples. These samples were synthesized in good yield (~70%) from the reaction of SbPh₃ with [(R₃tacn)Cu(CH₃CN)]SbF₆. They were isolated as colorless crystalline solids and were fully characterized by CHN analysis, NMR and FTIR spectroscopy, and ESI-MS. Notably, the mass spectrum for each complex exhibits a parent ion with the appropriate isotope pattern for [(R₃tacn)Cu(SbPh₃)]⁺ (illustrated for R = Me in Figure S5).

Mechanistic Studies

A series of experiments were performed in order to gain insight into the reactions of the adducts **1–3** with [(R₃tacn)Cu(CH₃CN)]SbF₆ to yield the disulfido-dicopper(II) complexes **4–6** and the SbPh₃ adducts **7–9** (Figure S6). First, the reactions of the complexes with identical supporting ligands under pseudo-first-order conditions (i.e., **1** + 10 equiv. [(Me₃tacn)Cu(CH₃CN)]SbF₆, **2** + 10 equiv. [(Et₃tacn)Cu(CH₃CN)]SbF₆, and **3** + 10 equiv. [(iPr₃tacn)Cu(CH₃CN)]SbF₆) in CD₂Cl₂ were monitored as a function of time by ¹H NMR spectroscopy. At initial concentrations [1–3]₀ = 4.7 mM at 20 °C, the consumption of **1–3** followed first-order kinetics (Figures S6 and S7). The rates measured for the reactions of **2** and **3** are similar, with both being >~10 times slower than that of **1**, as reflected by the measured *k*_{obs} values (averages from 3 replicate runs) of 6.6(5) × 10^{−4} s^{−1} (**1**), 8.4(1) × 10^{−5} s^{−1} (**2**), and 6.0(4) × 10^{−5} s^{−1} (**3**). The results are roughly consistent with the relative steric profiles of the reactant pairs (**1** < **2** ~ < **3**) and support a mechanism wherein steric interactions among the reactant pairs influence the rate (e.g., involving interaction of the Cu(I)-S=SbPh₃ adduct with the added Cu(I) reactant).

To further test this hypothesis, reactions of [(Me₃tacn)Cu(CH₃CN)]SbF₆ with **1** were examined by measuring initial reaction rates of disappearance of **1** as a function of [(Me₃tacn)Cu(CH₃CN)]SbF₆₀ (Figure 3). The initial rate saturates as the initial concentration of the added Cu(I) reagent increases. This finding is consistent with a mechanism (Scheme 2) involving an initial rapid pre-equilibrium (*K*_{eq}) involving formation of a dicopper intermediate (**A**) followed by a rate-determining product formation step (*k*₂). The fit of the data to the corresponding eq. 1 is shown in Figure 3 (solid line), yielding *K*_{eq} = 200 M^{−1} and *k*₂ = 1.2 × 10^{−4} s^{−1}. The proposed structure for **A** is speculative, as it was not observed directly. While the product formation process from **A** (*k*₂) must involve multiple steps, including a step in which a second sulfur atom is added, the decay of **1** is first order in [**1**] (see above) which implies that a unimolecular reaction of **A** is rate-controlling (e.g., cleavage of the S-Sb bond).

$$rate = \frac{k_2[1][Cu(I)]}{K_{eq}^{-1} + [Cu(I)]} \quad \text{eq. (1)}$$

We also considered the possibility that the reactions of **1–3** to form the disulfido-dicopper(II) complexes **4–6** might involve decomposition of S=SbPh₃ to S₂.^{9a} This decomposition was reported to occur in CS₂ via a second-order process with a rate constant of 0.014(2) M^{−1}s^{−1} at 35 °C, with the release of S₂ suggested by the formation of cyclic sulfides **10** and **11** when 2,3-dimethylbutadiene was used as a trapping reagent (Scheme 3). We found that mixtures of S=SbPh₃ (4.7 mM) and 2,3-dimethylbutadiene (20 equiv.) in CD₂Cl₂ at 20 °C were unchanged after ~3 d, with no evidence for formation of **10** or **11**. In a second experiment, ¹H NMR spectroscopic monitoring of a mixture of **1** and 2,3-dimethylbutadiene (20 equiv.) revealed slow generation of **10** and loss of **1** via a first-order process with a rate constant equal to 1.4(4) × 10^{−5} s^{−1} (*t*_{1/2} = ~14 h). There was no evidence

for the presence of the disulfido-dicopper(II) complex **4** during this process. Interestingly, under identical conditions **4** also decayed in the presence of 2,3-dimethylbutadiene to yield **10**. This reaction of **4** is characterized by a first-order rate constant of $1.7(3) \times 10^{-4} \text{ s}^{-1}$, corresponding to a rate approximately 10 times faster than that of the reaction of **1** to yield **10**. The rate of decay of **1** to yield **10** in the presence of 2,3-dimethylbutadiene is similar to that observed for the decay of **1** to **4** in its absence, suggesting that S_2 formation cannot be ruled out in the pathways of both reactions. However, these reactions are significantly slower than that for the reaction of **1** with $[(\text{Me}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$ to give **4** and **7**. On this basis and in view of the kinetic data described above, it appears unlikely that S_2 formation is important in the reaction of **1** with $[(\text{Me}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$.

This latter reaction is further complicated by exchange of the $\text{S}=\text{SbPh}_3$ unit between the Cu(I) centers. This exchange was identified by ^1H NMR spectroscopy and ESI-MS analysis of the reaction of **1** with $[(\text{R}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$ ($\text{R} = \text{Et}$ or $i\text{Pr}$). Shortly after mixing, the ^1H NMR spectrum showed peaks due to all four species in the equilibrium shown in Scheme 4. From the relative integrations after equilibrium was reached (~ 10 min), K'_{eq} values of 0.41 ($\text{R} = \text{Et}$) or 0.054 ($\text{R} = i\text{Pr}$) were measured. These results were corroborated by ESI-MS (Figure S8), where parent ion peak envelopes for the cationic portions of **1** and **2** ($\text{R} = \text{Et}$, $\sim 1:1$ ratio) or **1** and **3** ($\text{R} = i\text{Pr}$, $\sim 6:1$ ratio) were observed immediately after mixing of the respective reagents. The trend in K'_{eq} values correlates inversely with the degree of steric interactions between the ligand substituents and the bound $\text{S}=\text{SbPh}_3$ moiety (K'_{eq} decreases as the steric interactions increase, $\text{R} = \text{Et} < i\text{Pr}$). Importantly, equilibration is rapid relative to the decay to the disulfido-dicopper(II) complexes, and thus occurs prior to the suggested pathway for the decay reaction shown in Scheme 2.

Reaction of $\text{S}=\text{SbPh}_3$ with $[(\text{TMCHD})\text{Cu}(\text{NCCH}_3)]\text{PF}_6$

In contrast to the reactions with the Cu(I) complexes of R_3tacn ligands that led to isolable Cu(I)- $\text{S}=\text{SbPh}_3$ adducts, no such adducts were identified when the Cu(I) complex of the bidentate diamine TMCHD was treated with $\text{S}=\text{SbPh}_3$. Instead, the known tricopper cluster $[(\text{TMCHD})_3\text{Cu}_3(\text{S})_2](\text{PF}_6)_3$ (**12**) was isolated cleanly in good yield (79%). This procedure for the synthesis of **12** is superior to that previously reported involving use of $\text{S}_{8,8a}$ facilitating advanced spectroscopic studies of the cluster aimed at addressing contentious bonding and oxidation state issues.⁸ Presumably, an initial Cu(I)- $\text{S}=\text{SbPh}_3$ adduct forms in the reaction, but due to its lower coordination number is more prone to oligomerization than the analogs supported by the tridentate R_3tacn ligands.

Summary and Conclusions

In explorations ultimately aimed at preparing copper-sulfur complexes to model the active site of nitrous oxide reductase, we have found that $\text{Ph}_3\text{Sb}=\text{S}$ forms stable adducts $[(\text{R}_3\text{tacn})\text{Cu}(\text{S}=\text{SbPh}_3)]\text{SbF}_6$ (**1–3**), the first examples of which have been structurally characterized by X-ray crystallography. These adducts undergo slow decay in solution to form $[(\text{R}_3\text{tacn})_2\text{Cu}_2(\mu-\eta^2:\eta^2-\text{S}_2)]^{2+}$ species (**4–6**) and SbPh_3 . Conversion to **4–6** is accelerated by addition of $[(\text{R}_3\text{tacn})\text{Cu}(\text{NCCH}_3)]\text{SbF}_6$ to **1–3**, and yield $[(\text{R}_3\text{tacn})\text{Cu}(\text{SbPh}_3)]\text{SbF}_6$ (**7–9**) as coproduct instead of free SbPh_3 . Mechanistic studies of this reaction revealed rapid exchange of $\text{Ph}_3\text{Sb}=\text{S}$ between the Cu(I) sites and pre-equilibrium formation of a dicopper intermediate. We speculate that the dicopper intermediate contains a bridging $\text{Ph}_3\text{Sb}=\text{S}$ moiety and that the rate-controlling step in the reaction involves loss of Ph_3Sb from that intermediate. Subsequent more rapid events that ultimately result in $[\text{Cu}_2(\mu-\eta^2:\eta^2-\text{S}_2)]^{2+}$ core formation remain unclear. Reaction of $[(\text{TMCHD})\text{Cu}(\text{CH}_3\text{CN})]\text{PF}_6$ with $\text{S}=\text{SbPh}_3$ did not lead to an observable adduct, and instead led to the known tricopper cluster $[(\text{TMCHD})_3\text{Cu}_3(\mu_3-\text{S})_2](\text{PF}_6)_3$ in good yield. Overall, the results demonstrate the utility of $\text{Ph}_3\text{Sb}=\text{S}$ for delivering sulfur to Cu(I) centers supported by

N-donor ligands, cleanly yielding thermodynamically stable $[\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)]^{2+}$ and $[\text{Cu}_3\text{S}_2]^{3+}$ cores.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Representation of the X-ray crystal structure of **1**, showing the cationic portion with all non-hydrogen atoms as 50% thermal ellipsoids (H atoms omitted for clarity, only heteroatoms labeled).

Figure 2. Representation of the X-ray structure of **5** (BPh_4^- salt), showing the dicationic portion with all non-hydrogen atoms as 50% thermal ellipsoids (H atoms omitted for clarity, only heteroatoms labeled). Selected bond distances ($\text{\AA}$) and angles (deg) are as follows: Cu1-N1, 2.202(3); Cu1-N2, 2.017(2); Cu1-N3, 2.003(2); Cu1-S1, 2.2152(8); S1-S1', 2.1501(14); Cu1 $\cdots$ Cu1', 3.876; N1-Cu1-N2, 86.17(10); N1-Cu1-N3, 86.13(10); N2-Cu1-N3, 88.50(10); N1-Cu1-S1, 108.49(7); N2-Cu1-S1, 160.58(7); N3-Cu1-S1, 104.76(8); S1-Cu1-S1', 58.03(3).

Figure 3.

Plot of the initial rate of decay (¹H NMR) of **1** vs. [[(Me₃tacn)Cu(CH₃CN)]SbF₆]₀ for the reaction of **1** with [(Me₃tacn)Cu(CH₃CN)]SbF₆ to yield **4** and **7** in CD₂Cl₂ at 20 °C. Each data point is an average of data for 3 replicate runs. Error bars span the range of values for the replicate runs. The line is a fit of the data to eq. 1 (*R* = 0.95).

Scheme 1.
Reactions of Cu(I)-S=SbPh₃ adducts.

Scheme 2.

Proposed mechanism for the formation of **4** from the reaction of **1** with $[(\text{Me}_3\text{tacn})\text{Cu}(\text{CH}_3\text{CN})]\text{SbF}_6$.

Scheme 3. Decay of S=SbPh_3 to S_2 as determined by trapping with 2,3-dimethylbutadiene.

Scheme 4. Equilibration of Cu(I)-S=SbPh₃ and Cu(I)-NCCH₃ complexes.

Table 1Selected Bond Distances (Å) and Angles (deg) for the X-ray structures of **1–3**.^a

	1	2	3
Cu1-N1	2.160(2)	2.006(6)	2.178(2)
Cu1-N2	2.107(2)	2.030(8)	2.161(2)
Cu1-N3	2.199(2)	2.157(4)	2.166(2)
Cu1-S1	2.1671(8)	2.1813(10)	2.2027(7)
S1-Sb1	2.2832(7)	2.2735(9)	2.2812(7)
Cu1...Sb1	3.411	3.490	3.547
N1-Cu1-N2	84.96(9)	91.3(3)	84.52(8)
N1-Cu1-N3	83.41(8)	71.1(2)	84.08(8)
N2-Cu1-N3	83.96(9)	82.2(3)	84.39(8)
N1-Cu1-S1	114.17(6)	115.8(2)	127.05(6)
N2-Cu1-S1	148.91(7)	150.2(2)	143.48(6)
N3-Cu1-S1	120.92(6)	117.09(10)	113.59(6)
Cu1-S1-Sb1	100.06(3)	103.14(4)	104.55(3)

^aEstimated standard deviations indicated in parentheses.