Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Nitrosonium Reactivity of (NHC)Copper(I) Sulfide Complexes

Abraham J. Jordan,[†] Rebecca K. Walde,[†] Kelly M. Schultz,[‡] John Bacsa,^{†,§} and Joseph P. Sadighi^{*,†©}

[†]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

[‡]Murdock Hall, Department of Chemistry, Linfield College, McMinnville, Oregon 97128, United States

[§]X-ray Crystallography Center, Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322, United States

Supporting Information

ABSTRACT: This study examines the reactivity of a series of copper(I) sulfide complexes stabilized by the expanded-ring N-heterocyclic carbene (NHC) 1,3-bis-(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2ylidene (7Dipp) toward the nitrosonium ion (NO⁺). 7Dipp is shown to support neutral sulfide- and disulfidebridged dicopper(I) complexes, as well as mononuclear copper(I) hydrosulfide. The addition of NO⁺ to each of these results in the formation of NHC-supported copper(I) cations and elemental sulfur. Reduction of copper(I) to copper(0) is observed upon reaction of NO⁺ with dicopper(I) sulfide or disulfide, whereas ammonium ion formation is observed upon reaction of copper(I)hydrosulfide with NO⁺. Ammonium ion formation is likewise observed upon reaction of NO⁺ with (7Dipp)copper(I) hydride.

N itric oxide (NO $^{\bullet}$) and dihydrogen sulfide (H₂S) are important biological signaling molecules whose chemistries are often linked through the proposed "cross-talk" products^{1,2} thionitrous acid (HSNO or SNO⁻), nitroxyl (HNO), and perthionitrite (SSNO⁻).^{3–5} Many recent studies have shed light on the properties and reactivity of these transient species, but much still remains unknown.⁴⁻⁶ Of particular interest is their interaction with transition metals, but there are few studies relating well-defined transition-metal complexes and "cross-talk" products. The addition of HS⁻ to iron nitrosyl complexes (sodium nitroprusside or iron porphyrin) initially forms an iron-bound HSNO complex, observable by mass spectrometry in the case of the iron porphyrin system, before HSNO decomposition products are observed (Scheme 1a).^{7–9} A "masked" terminal nickel sulfide reacts with NO[•] to yield a nickel nitrosyl and the SNO⁻ anion, which reacts with further NO[•] to yield the SSNO⁻ anion (Scheme 1b).¹⁰ An ethylenediaminetetraacetate (EDTA)supported diruthenium disulfide reacts with NO[•] to yield the Ru-SNO complex, observed by mass spectrometry (Scheme 1c).¹¹ Last, SSNO⁻ and SNO⁻ anions have been isolated as bis(triphenylphosphine)iminium salts.¹² Few studies have examined the reactivity of "cross-talk" products with copper.

Copper sulfide clusters have garnered much attention because of their prevalence in biological systems, particularly in the active sites of nitrous oxide reductase¹³ and molybdenum/copper carbon monoxide dehydrogenase.¹⁴





Copper sulfides tend to form higher-order complexes, featuring three or more copper centers; $^{15-25}$ copper/sulfur clusters with two metal centers are rare²⁶ but include a number of dicopper(II) disulfide complexes $^{27-40}$ and a single dicopper(I) sulfide complex.^{26,41} We envisioned that similar low-nuclearity sulfur-bound copper(I) complexes could shed light on the reactivity of various "cross-talk" products. Considering the sulfur atom(s) to be S^{2-} (or SS^{2-}), the addition of nitrosonium (NO⁺) would formally lead to HSNO, SNO⁻, SSNO⁻, and HNO products.

Warren and co-workers have shown that a copper(II) thiolate reacts reversibly with NO[•] at low temperature to yield a bound alkyl thionitrite.⁴² They have also shown that Nheterocyclic carbene (NHC)-supported copper(I) thiolates react with NO⁺ to cleanly generate a thiolate-bridged dicopper(I) cation and free organic thionitrites (Scheme

Received: June 5, 2019

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1d,e).⁴³ In this study, we have examined the reactivity of NHC-supported copper(I) sulfide, disulfide, and hydrosulfide complexes with NO^+ .

We initially set out to determine whether sterically encumbering expanded-ring NHCs stabilize a dicopper(I) sulfide core. We have previously shown that the expanded-ring NHC 1,3-bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene (7Dipp)^{44,45} supports a stable copper(I) hydride dimer.⁴⁶ Gratifyingly, (7DippCu)₂S (1) could be generated in good yield from the reaction of 7DippCuCl with excess Na₂S following an analogous procedure from Hillhouse and co-workers (Scheme 2).²⁶ The 7Dipp-supported copper-





(I) hydrosulfide (2) was readily synthesized from 7DippCuCl and potassium hydrosulfide. Another route to sulfide-bridged dicopper(I) shown by Hillhouse and co-workers, deprotonation of a hydrosulfide complex by copper(I) alkoxide, also proved viable with the 7Dipp ligand. Interestingly, deprotonation of 2 by sodium *tert*-butoxide resulted in the formation of 1 as the major species, with a presumed loss of Na₂S, offering another avenue to the bridging sulfide. Rapid conversion of 2 by either deprotonation route was evident from the bright-yellow color of 1 and confirmed by ¹H NMR spectroscopy.

While there are numerous examples of dicopper(II) disulfides (vide supra), we have found no examples of dicopper(I) disulfides. Initial attempts to synthesize a 7Dipp-supported dicopper(I) disulfide by the addition of elemental sulfur to **1** resulted in the formation of numerous products, regardless of stoichiometry, suggesting a tendency to form mixtures of higher-order copper oligosulfides. As an alternative, **3** reacts with bis(phenylacetyl) disulfide to give the 7Dipp-supported dicopper(I) disulfide (**4**), isolated as an orange-yellow solid (Scheme 3). The addition of PPh₃ to a solution of **4** in C₆D₆ resulted in conversion to **1** by sulfur abstraction with concomitant formation of Ph₃P=S, as confirmed by ¹H and ³¹P NMR.

Recrystallization of 1 from CH₃CN (-35 °C) resulted in crystals suitable for X-ray diffraction. The structure (Figure 1a) is similar to that of the dicopper(I) sulfide reported by Hillhouse and co-workers.²⁶ Only one molecule of four in the asymmetric unit is shown. The Cu···Cu distances range from 3.475(2) to 3.677(2) Å and the Cu–S–Cu angles from 110.66(6) to 120.68°. Crystals of 4 suitable for X-ray diffraction resulted after recrystallization from Et₂O (-35 °C). The structure of 4 (Figure 1b) reveals end-on binding of the disulfide unit to the copper(I) centers, analogous to that

Scheme 3. Synthesis of a Disulfide-Bridged Dicopper Complex

Communication

(a)



Figure 1. Thermal ellipsoid depiction (50% probability) of 1 (a) and 4 (b). Selected interatomic distances (Å) and angles (deg) for 1 (one molecule shown of four in the asymmetric unit): C1_10-Cu3 1.909(3), Cu3-S2 2.117(1), C1_11-Cu4 1.892(3), Cu4-S2 2.108(2), Cu3-Cu4 3.475(2); C1_10-Cu3-S2 163.94(9), C1_11-Cu4-S2 168.60(9), Cu3-S2-Cu4 110.66(6). Selected interatomic distances (Å) and angles (deg) for 4: Cu1-C1 1.906(3), Cu1-S1 2.132(1), S1-S1 2.113(2); C1-Cu1-S1 178.02(9), Cu1-S1-S1 99.80(7).

reported by Karlin and co-workers for a dicopper(II) disulfide.²⁹ Many side-on dicopper(II) disulfides have also been reported.^{27–30,33,34,36,37,39,40} Complex 4 features a Cu–S distance of 2.132(1) Å, an S–S distance of 2.113(2) Å, and a Cu–S–S angle of 99.80(7)°.

The addition of NO⁺ to a solution of **2** in CD₃CN results in the formation of 7DippCu⁺ as its acetonitrile adduct (**5**; Scheme 4a). Ammonium ion (NH_4^+) formation was evident by the appearance of a 1:1:1 triplet resonance, due to ${}^{1}H^{-14}N$ coupling, at 5.91 ppm in the ${}^{1}H$ NMR spectrum (Scheme 4a and Figure S15). Notably, NH₃ is observed from the decomposition of an iron-bound HSNO complex in a buffered aqueous solution,⁷ whereas ammonium ion formation, shown herein, occurred in a dried, deuterated solvent. The sample after the addition of NO⁺ appeared cloudy, suggesting precipitation of elemental sulfur. The subsequent addition of PPh₃ generated a clear solution, and formation of Ph₃P==S was confirmed by ${}^{31}P$ NMR. We thus suggest the formation of HSNO (copper-bound or free), which releases elemental sulfur, generating HNO. Subsequent decomposition of HNO

Scheme 4. Nitrosylation of Copper(I) Hydrosulfide



would form NH_4^+ and should generate N_2O . An analysis of the reaction headspace by gas chromatography-mass spectrometry shows a peak at m/z 44, corresponding to N_2O (Supporting Information p S20). To balance these observed products, we thus infer the formation of NO_3^- (Scheme 4). On the basis of this hypothesis, the reaction of NO^+ with copper(I) hydride should generate HNO, with the Cu-H acting as a source of H⁻, and likewise lead to NH_4^+ formation. The ¹H NMR spectrum following dissolution of (7DippCuH)₂ and NO⁺ in CD₃CN reveals the formation of [7DippCu-NCCD₃]⁺, with a 1:1:1 triplet resonance corresponding to NH_4^+ (Scheme 4b).

Last, we investigated whether NO⁺ would act as a Lewis acid or an oxidant toward 1 and 4. Furthermore, we wondered whether oxidation would occur at the copper centers or the sulfur atom(s). Calculations by Hillhouse and co-workers show the highest occupied molecular orbital consisting mainly of a nonbonding S p orbital but with some copper character (see the Supporting Information of ref 26). Furthermore, oxidation of the dicopper(I) sulfide complex by CO_2 or N_2O to dicopper(I) sulfate was recently reported.⁴¹ Interestingly, dicopper(I) sulfide and disulfide react similarly with NO⁺ (1 equiv). Reactions in CD₃CN result in decomposition to copper(0), while the ¹H NMR spectra show the presence of 5 (Scheme 5). We have been unable to determine the amount of copper(0) formed, but the mass balance suggests about 50% conversion of 1 to 5. On the basis of these findings, we inferred the formation of elemental sulfur, which was confirmed by the resonance for Ph₃P=S in the ³¹P NMR spectra after the addition of Ph₃P. We thus conclude that an NHC-coordinated Cu-SNO (or Cu-SSNO) complex is unstable if formed, decomposing to form copper(0), elemental sulfur, and NO[•]. Knowing that organic thiols react with t-BuONO to yield organic thionitrites,⁴⁷ we added *t*-BuONO to 2 but saw no appreciable reaction after 24 h. After heating at 50 °C, significant decomposition was evident. We also cannot rule out the possibility of outer-sphere electron transfer from 1, or 4, to NO⁺ with subsequent decomposition. Although the reaction between 1 and [thianthrene]^{•+} gave a complex mixture, oxidation of sulfide to elemental sulfur was confirmed by the resonance for Ph₃P=S in the ³¹P NMR spectrum after the addition of Ph₃P.

The reaction of 1 with NO⁺ in weakly coordinating fluorobenzene at -35 °C, with subsequent warming to room temperature, also resulted in decomposition to copper(0) and a single set of resonances in the ¹H NMR spectrum (CD₂Cl₂). The ¹⁹F NMR spectrum revealed a very broadened and upfield-shifted BF₄⁻ resonance. Following the addition of Ph₃P



to the NMR sample, the ¹H and ³¹P NMR spectra were consistent with the formation of $[7DippCu-PPh_3]^+$. The ³¹P NMR spectrum also showed the resonance for $Ph_3P=S$, confirming that elemental sulfur had been formed. Furthermore, the ¹⁹F NMR spectrum following Ph₃P showed a sharp BF_4^- resonance, no longer shifted upfield from that of the free ion. This finding suggests that weakly coordinating BF₄⁻ can interact with the copper(I) center. Labile BF_4^- complexes of (NHC)gold(I) cations have likewise been reported.⁴⁸ The reaction of 7DippCuCl and AgBF₄ in a fluorobenzene solution resulted in identical ¹H NMR shifts in addition to a broadened, upfield shift of the BF₄⁻ resonance. ¹H NMR spectra taken of mixtures kept at or below -35 °C showed 7DippCu⁺ fragments as the major or the only detectable species. Additionally, we saw no evidence for the formation of Nheterocyclic thiourea [(7Dipp)=S] or for nitrosylation of the 7Dipp ligand.

We have outlined the nitrosonium reactivity of a series of NHC-supported copper(I) sulfide complexes. The syntheses and structures of new neutral sulfide- and disulfide-bridged dicopper(I) complexes, in addition to their related hydrosulfide complex, show the expanded-ring NHC 7Dipp to be a capable supporting ligand. The reaction with NO⁺ results in oxidation at the sulfur atom(s) to elemental sulfur and the formation of (NHC)copper(I) cations. Despite the high oxidation potential of NO^{+} (0.87 V vs Fc in CH_3CN),⁴⁹ this oxidation leads to a net reduction of a copper(I) center. The reaction of 7Dipp-supported copper(I) hydrosulfide leads to elemental sulfur, (NHC)copper(I) cation, N₂O, and NH₄⁺, possibly via decomposition of HSNO. Furthermore, the 7Dipp-supported copper(I) hydride dimer reacts with NO⁺ to yield an ammonium ion, suggesting the formation and decomposition of HNO. These reactions model possible pathways in the generation and subsequent reactivity of molecules related to H_2S and NO^{\bullet} signaling, specifically HSNO, from copper(I) sulfide complexes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01676.

Experimental procedures and spectral and crystallographic data (PDF)

Accession Codes

CCDC 1920859 and 1920862 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: joseph.sadighi@chemistry.gatech.edu.

ORCID [©]

Joseph P. Sadighi: 0000-0003-1304-1170

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Georgia Institute of Technology School of Chemistry and Biochemistry, and College of Sciences, for generous support of this research. We thank the U.S. National Science Foundation (Grant CHEM REU-1560335) for support of K.M.S.

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