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ARTICLE TYPE

A Cu(II) mediated new desulfurization pathway involving elimination of ethylene sulfide[†]

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Reaction of thiodiacetate anion (tda) with [Cu(TMEDA)(NO₃)₂] (TMEDA = N,N,N',N'-tetramethyl ethylene-diamine) in stoichiometric ratio afforded the complex $\{[Cu(TMEDA)(tda)] \cdot (H_2TMEDA)(NO_3)_2 \cdot H_2O\}$ (1). When [Cu(TMEDA)(NO₃)₂] was added in excess, it yielded a μ -oxalato complex $\{[Cu_2(TMEDA)_2(\mu-ox)(H_2O)_2](NO_3)_2 \cdot 2CH_3CN\}$ (2). The reaction involves a facile room temperature desulfurization of thiodiacetate moiety via elimination of ethylene sulfide (thiirane).

Introduction

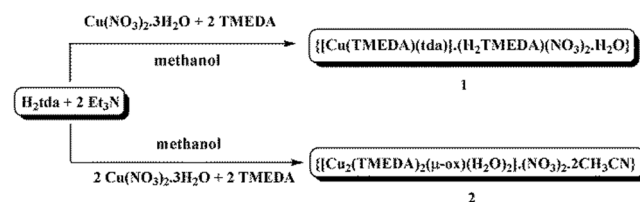
Copper complexes are redox active and are notable for their preference for distorted coordination geometries. Owing to the widespread occurrence of Cu centers in the active site of biomolecules and metalloenzymes,¹ there has been a continuing interest in nitrogen/sulfur and nitrogen/oxygen coordination to this metal.² We started the present work with an aim to synthesize and structurally characterize co-ordination complexes of Cu(II) with N, O and S donor ligands. The rationale behind our strategy is based on the chemical features of 2,2'-thiodiacetic acid (H₂tda) ligand which is a versatile flexible multidentate ligand, possessing both soft, S (thioether) and hard, O (carboxylate) donor atoms. It is able to adopt various coordination modes in transition metal complexes³ as well as transition metal and lanthanide coordination polymers.⁴ It was also aimed to examine the interaction of the coordinated ligand with Cu²⁺ ions which led to an unusual desulfurization of the ligand accompanied by elimination of ethylene sulfide (thiirane).

A continual problem in using fossil fuels is the difficulty in removal of sulfur. The currently applied methods of removing sulfur industrially are hydrodesulfurization, oxidative desulfurization and biodesulfurization.⁵ Hydrodesulfurization is the most widely used process in the petroleum industry which requires high temperature (320-440 °C) and high hydrogen pressure (150-2250 psi).⁶ In addition, failure of the catalytic process in certain cases⁷ underlines the need for alternative technologies. Notably, all these chemical reactions of desulfurization involve scissoring of C-S bond(s) and a process involving removal of an organosulfur compound obtained by breaking of one or more C-C bonds is yet to be established. Importance of such a process though unrevealed yet, should be

viewed in light of synthesis and isolation of organosulfur molecules (and their further use) instead of H₂S.

Results and Discussion

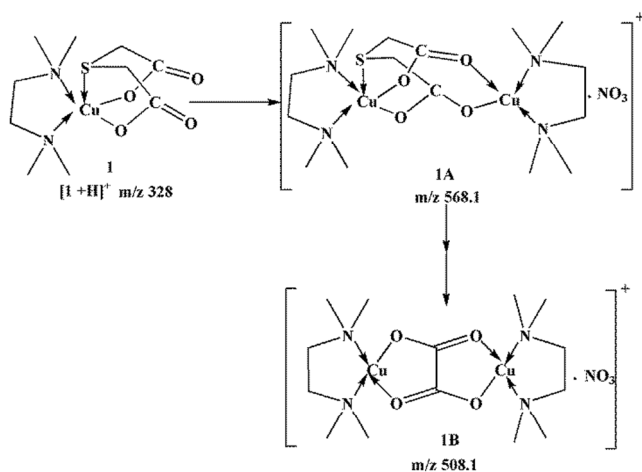
When Cu(NO₃)₂, TMEDA, H₂tda and triethylamine were taken respectively in 1:2:1:2 stoichiometric ratio, a ternary complex **1** was formed in which the tda ligand exhibited a tridentate mode of bonding. However, when the ratio of the reactants was changed to 2:2:1:2 respectively, an oxalate complex, $[Cu_2(TMEDA)_2(\mu-ox)(H_2O)_2]^{2+}$ (**2**) was formed (Scheme 1). Alternatively, **2** could also be generated when **1** was treated with Cu(NO₃)₂ and TMEDA in stoichiometric proportions.



Scheme 1

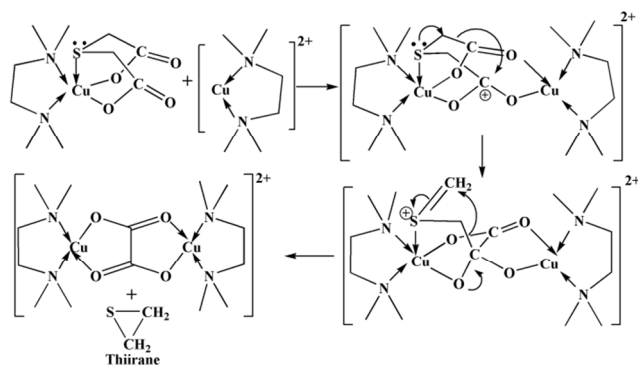
The formation of complex **2** involves complete desulfurization of H₂tda. During recent years a number of studies have been carried out to explore and understand Cu(II) catalysed decarboxylation,⁸ however, desulfurization process though industrially important has not risen to the fore. Desulfurization of mercaptoacetate with Cu(II)-bipy system giving the ternary oxalate complex $[Cu(bipy)(ox)] \cdot 2H_2O$, has been reported.⁹ Initial step in this process is believed to be the formation of a transient ternary complex of the type $[Cu(bipy)(SCH_2CO_2)]$, followed by its oxidation at the thiolate carbon. Recently, we have reported desulfurization of ternary Cu(II) thiocarboxylate complexes under ambient conditions by a facile hydrolysis of the thiocarboxylate group giving the corresponding carboxylate complexes.¹⁰ However, in the present case, none of these pathways are being followed. Possibly, the reaction is initiated by the coordination of a Cu²⁺ ion by the free oxygen atom of a carboxylate group of complex **1** and desulfurization step involves the elimination of a thiirane molecule from thiodiacetate moiety. The reaction was followed by ESI-MS over a period of 2 hours (see Supporting Information). At t=0, the spectrum shows two signals at m/z 328 and m/z 568.1 which correspond to (1+ H)⁺ and one of the

intermediates, **1A** respectively (**Scheme 2**). After 2 hours, a new signal at $m/z = 508.1$ for **1B** is detected which clearly indicates formation of **2** via removal of thiirane.



Scheme 2

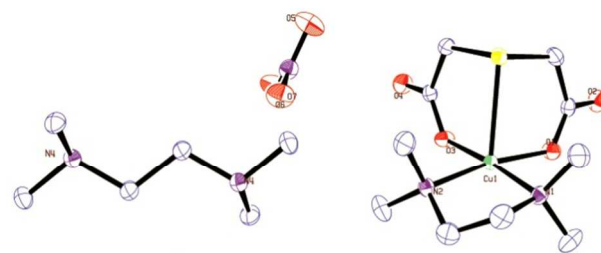
5 In order to identify the products unequivocally, the reaction was monitored by LC-MS as well as GC-MS. The LC-MS of the reaction mixture at intervals of 10, 60, 120, 720 minutes showed that the signals obtained after 120 and 720 min. are identical. So, it was assumed that the reaction practically reaches to completion
10 within 2 hours. For GC-MS, the reaction was stopped after 90 min. and complex **2** was precipitated out from the reaction mixture by adding excess of diethyl ether. The organic fraction remaining in solution after this work up was subjected to GC-MS analysis (see Supporting Information). The identity and yield of
15 thiirane was determined by GCMS by comparison with standard solution of thiirane. GCMS: Retention time: 4.07 mins, m/z 58, yield: 71%. The peak at m/z 58 corresponds to $C_2H_2S^+$ radical cations which are produced by dissociated ionization of
20 thiirane.¹¹ On the basis of these findings, the following mechanism is proposed (**Scheme 3**). It may be pointed out that C-C bonds are more stable thermodynamically and quite resistant to cleavage by metal complexes. Recently, Sattler and Parkin have reported insertion of a metal atom (tungsten) leading to cleavage
25 of a C-C bond of quinoxaline.¹² This reaction is being viewed as a potential process of denitrogenation of fossil fuels.¹³ To the best of our knowledge, the occurrence of such a desulfurization reaction has no precedent in the chemistry of sulfur compounds.



Scheme 3

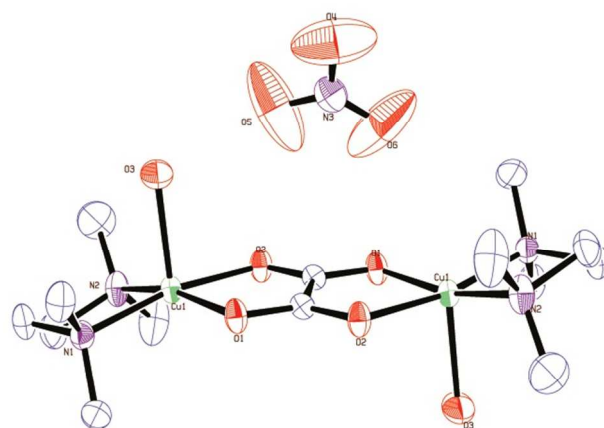
The complexes **1** and **2** have been characterized by spectroscopic methods the details of which are given in supporting information.

The structures of the complexes were determined by single crystal X-ray diffraction analyses.

Neha Sareen, Suryabhan Singh, Subrato Bhattacharya
Figure 1

35

A protonated TMEDA molecule along with NO_3^- ion co-crystallized with complex **1**. In this complex, Cu(II) atom resides in a N_2O_2S distorted square pyramidal environment (**Figure 1**).
40 Thiodiacetate serves as a tridentate ligand and is coordinated to the metal atom in a facial O₂O+S apical conformation. The *fac* O₂O + S apical mode of bonding is quite common in metal-tda compounds.^{3,14} The basal plane is defined by two N donors of TMEDA and two carboxylate oxygens whereas the apical
45 position is occupied by S (thioether). N donors preferentially occupy trans position relative to the O (carboxylate) donor atoms, such a preference being a direct consequence of the bidentate nature of the auxiliary ligand (TMEDA) and the facial O₂+S apical conformation adopted by tda. The Cu1-S1 (thioether) bond
50 length is comparable to those in previously documented tda and N-N donor mixed ligand complexes of Cu(II).¹⁴ The mean planes of the two five membered sharing the Cu-S bond subtend an interplanar angle of 88.29°. The [Cu(TMEDA)(tda)] units linked together via water molecules through hydrogen bonding between
55 the free carboxylate oxygen of tda and hydrogen atom of water (O-H...O = 2.125 Å) to form a linear chain.

Neha Sareen, Suryabhan Singh, Subrato Bhattacharya
Figure 2

The molecular structure of complex **2** is shown in **Figure 2**. The structure consists of a centrosymmetric binuclear oxalate-
60 bridged [Cu₂(TMEDA)₂(OH₂)₂(μ-C₂O₄)₂]²⁺ unit and two nitrate ions. A molecule of acetonitrile crystallizes with it. The

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coordination geometry at the copper centers can be described as slightly distorted square pyramidal with a single oxalate ion bridging the two metal centers; metal-metal distance being 5.187 Å. O1 and O2 atoms of oxalate and the two N atoms of TMEDA occupy the corners of approximate square planar base around Cu1 while the apical position is occupied by the oxygen atom of a water molecule. The geometry at the Cu(1)-ox-Cu(2) unit is evocative of the other Cu(II)-oxalate complexes reported earlier.¹⁵ The oxalate group is planar (maximum atomic deviation = 0.002 Å) while copper atoms are displaced 0.218 Å out of the basal plane constituted by N1, N2, O1 and O2. The nitrate ions are linked to water molecules through H-bonds (O-H...O = 1.778 Å). Apart from the hydrogen bonding, there is weak interaction between oxygen atom of nitrate and methylene hydrogen with a distance of 2.668 Å. A linear chain is formed in the lattice in which the complex and the nitrate ions alternate each other.

Conclusions

It has been observed that thiodiacetate ligand forms stable complex with (TMEDA)Cu(II), however, excess of Cu(II) leads to the decomposition of the ligand. This provided a new route of desulfurization along with elimination of thiirane. Though the reported reaction is non-catalytic further studies on other sulfur containing ligands will prove fruitful to reach to a generalization regarding desulfurization reaction and a catalytic process may be developed in due course.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of experimental methods, spectral data, crystallographic data in CIF format. CCDC reference numbers: 951794 and 951795. See DOI: 10.1039/b000000x/

‡ The X-ray data were collected on Xcalibur Eos Oxford Diffractometer equipped with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data collections of all complexes were carried out at room temperature (20 °C). Absorption corrections were made using multi-scan method. Data integration and reductions were processed with CRYSLIS PRO software.¹⁶ Structures were solved by direct methods and refined by full matrix F^2 refinement (SHELX-97)¹⁷ using the WINGX program package.¹⁸ Since crystals of **2** were efflorescent, a crystal in the crystallization vessel was picked, coated with epoxy resin and immediately used for X-Ray data collection.

Crystal data of complex **1** C₁₃H₃₁CuN₄O₈S. M= 467.02, Monoclinic, a= 8.6003(4), b= 31.6173(18), c= 7.5682(3) Å, β (°) = 99.671(4), V= 2028.69(17) Å³, space group= P2₁/c, Z= 4, μ = 1.226 mm⁻¹, 17618 reflections collected, 4849 reflections unique, R_{int} =0.0322, R1 = 0.0424, wR2(all data) = 0.0854

Crystal data of complex **2** C₁₈H₄₂Cu₂N₈O₁₂. M= 689.70, Monoclinic, a= 7.9935(7), b= 20.8314(15), c= 9.5650(8) Å, β (°) = 99.958(7), V=

1557.0(2) Å³, space group= P2₁/c, Z= 2, μ = 1.431mm⁻¹, 12243 reflections collected, 3681 reflections unique, R_{int} =0.1544, R1 = 0.0728, wR2(all data) = 0.1855

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CAPTIONS TO FIGURES

Scheme 1 Synthesis of complexes **1** and **2**

Scheme 2 Plausible mechanism of desulfurization

Figure 1 ORTEP drawing of complex **1**. The hydrogen atoms are omitted for clarity. Selected metric data- Bond lengths (Å): Cu(1)-O(3) 1.9470(17), Cu(1)-O(1) 1.9680(17), Cu(1)-N(2) 2.027(2), Cu(1)-N(1) 2.055(2), Cu(1)-S(1) 2.6655(7); Bond angles (°): O(3)-Cu(1)-O(1) 90.46(8), O(3)-Cu(1)-N(2) 91.85(8), O(1)-Cu(1)-N(2) 170.50(8), O(3)-Cu(1)-N(1) 174.80(8), O(1)-Cu(1)-N(1) 91.01(8), N(2)-Cu(1)-N(1) 85.90(9), O(3)-Cu(1)-S(1) 80.90(5), O(1)-Cu(1)-S(1) 82.24(5), N(2)-Cu(1)-S(1) 107.22(6), N(1)-Cu(1)-S(1) 104.24(6).

Figure 2 ORTEP drawing of complex **2**. The hydrogen atoms are omitted for clarity. Selected metric data-Bond lengths(Å): Cu(1)-O(1) 1.983(4), Cu(1)-O(2) 1.988(4), Cu(1)-N(2) 2.010(5), Cu(1)-N(1) 2.015(5), Cu(1)-O(3) 2.235(5); Bond angles (°): O(1)-Cu(1)-O(2) 83.82(14), O(1)-Cu(1)-N(2) 165.6(2), O(2)-Cu(1)-N(2) 94.17(17), O(1)-Cu(1)-N(1) 91.98(16), O(2)-Cu(1)-N(1) 169.03(17), N(2)-Cu(1)-N(1) 87.4(2), O(1)-Cu(1)-O(3) 94.78(19), O(2)-Cu(1)-O(3) 90.39(18), N(2)-Cu(1)-O(3) 99.5(2), N(1)-Cu(1)-O(3) 100.1(2)

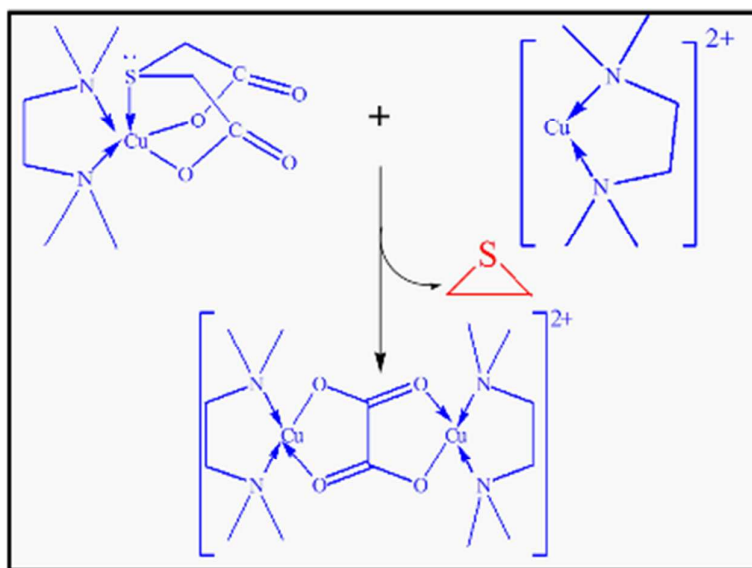
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A facile and unusual route of desulfurization of thiodiacetate moiety accompanied by elimination of thiirane.