

## Many facets of reactions of thiocyanate anions with bare and complexed copper(II) ions

Supriti Paul<sup>1</sup> and Debashis Ray<sup>2</sup>

<sup>1</sup>Bethune College, Kolkata-700 006 and <sup>2</sup>Indian Institute of Technology, Kharagpur-721302

**Abstract:** Solution phase reactions of transition metal ions with small anions in the presence and absence of supporting anionic or neutral ligand system give variety of products. Such reactions using  $\text{SCN}^-$  with bare copper(II) ions and ligand anion bound copper(II) ions provided  $\text{CuSCN}$ ,  $\{[\text{Cu}^{\text{II}}_2(\mu\text{-L})(\mu\text{-H}_2\text{O})\cdot\text{H}_2\text{O}][\text{Cu}^{\text{I}}(1,3\text{-NCS})_2]\}_n$  and  $\{[\text{Cu}^{\text{II}}_2(\text{L}^1)_2][\text{Cu}^{\text{I}}_4(1,3\text{-SCN})_4(1,1,3\text{-SCN})_2]\}_n$  respectively. When preformed precursor complex is used, the terminal and bridging ligand substitution as well as the extrusion of anion bound copper ions took place in a concerted manner. Physical characterization and X-ray structure analysis established the controlling factors that influence the identity of the resulting products. In one case, the competitive coordination behavior was observed, when both the ligand anion and the inorganic anion is available in the reaction medium.

**Introduction:** In organic solvent medium, the thiocyanate ( $\text{SCN}^-$ ) anion can coordinate to the available metal ions in different coordination modes, endowing the solid surfaces of the products with different structures, electronic and catalytic properties. Thiocyanate anion ( $\text{SCN}^-$ ) is a well-known inorganic species and is widely used in solid-state chemistry. As nitrogen atom in  $\text{SCN}^-$  anion is harder than sulfur atom, one may intuitively think that the preference of coordination modes of  $\text{SCN}^-$  anion can be explained and predicted by HSAB theory.  $\text{SCN}^-$  anion is special in that it can coordinate to the metal ion center through N or S atom. Since the electrons of S lie higher in energy than those of N due to the smaller electro negativity of S, S has a stronger preference to coordinate to the metal ion to maximize the covalent bonding interaction energy in terms of frontier molecular orbital interactions. However, S bearing with smaller negative charge than N thus has a smaller tendency to form electrostatic interaction with metal ion in terms of electrostatic interaction. Therefore, it is expected that sulfur prefers the metal ion that has low-lying LUMO to maximize the covalent bonding interaction term, while N favors metal bearing with a high positive charge to maximize the electrostatic interaction.

Copper(II) thiocyanate is a coordination polymer (CP) with formula  $\text{Cu}(\text{SCN})_2$ .<sup>1</sup> It is a black solid which slowly decomposes in moist air. (Figure 1)<sup>2</sup> It was first described in 1838 by Carl Ernst Claus and its structure is determined in 2018.<sup>3</sup>

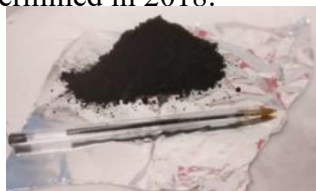


Figure1. Black powder of  $\text{Cu}(\text{SCN})_2$

The structure of  $\text{Cu}(\text{SCN})_2$  was determined *via* powder X-ray diffraction and consists of chains of  $\text{Cu}(\text{NCS})_2$  linked together by weak  $\text{Cu-S-Cu}$  bonds into two-dimensional layers. Jahn-Teller distortion is present within the structure and, each copper(II) center is octahedral and coordinated by four sulfur and two nitrogen atoms. The sulfur end of the  $\text{SCN}^-$  ligand is doubly bridging. (Figure 2)

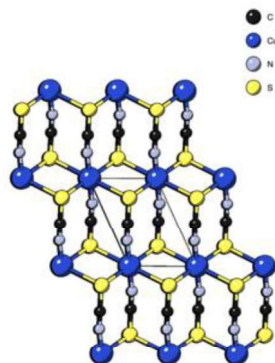
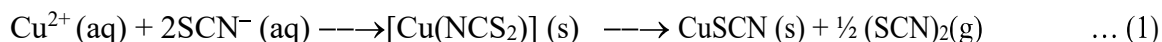


Figure 2. Crystal structure of copper(II) thiocyanate

Copper(II) thiocyanate, like copper(II) bromide and copper(II) chloride, is a quasi-low-dimensional antiferromagnet and it orders at 12K into a conventional Néel ground state. Pure copper(II) thiocyanate can be obtained as a black or dark-brown solid from the reaction of concentrated solutions of copper(II) and a soluble ammonium or potassium thiocyanate salt in water. With rapid drying, pure  $\text{Cu}(\text{NCS})_2$  can be isolated. Reaction at lower concentrations and for longer periods of time generates instead copper(I) thiocyanate.  $\text{Cu}(\text{NCS})_2$  is unstable and decomposes quickly to  $\text{CuSCN}$  according to reaction of following eq. 1.



On standing, the precipitate decomposes to a white cuprous salt and the reduction process is accelerated by heating the solution. When the reaction mixture is heated in a bath of boiling water, the black precipitate immediately transformed to white  $\text{CuSCN}$  with vigorous gas evolution. The product isolated from the above reaction 1 is not only temperature but also concentration dependent. When 0.25 M solutions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{KSCN}$  are mixed, no  $\text{Cu}(\text{SCN})_2$  forms, instead white  $\text{CuSCN}$  is precipitated after a few minutes at room temperature.

Solution reactivity of  $\text{SCN}^-$  anions in low concentration with complexed copper(II) ions can take a completely different course of action. The situation is further interesting when the reaction in non-aqueous medium is carried out with binuclear thiocyanate free copper(II) complex.<sup>4,5</sup>

Over a decade ago, we showed that it is possible to synthesize a hetero valence copper(II) plus copper(I) based metal-organic framework structure  $\{[\text{Cu}^{\text{II}}_2(\mu\text{-L})(\mu\text{-H}_2\text{O}) \cdot \text{H}_2\text{O}][\text{Cu}^{\text{I}}(1,3\text{-NCS})_2]\}_n$  (2) from the precursor aqua-bridged  $[\text{Cu}_2]$  complex  $[\text{Cu}^{\text{II}}_2(\mu\text{-L})(\mu\text{-H}_2\text{O})]\text{ClO}_4 \cdot 1.5\text{H}_2\text{O}$  (1) of heptadentate  $(\text{N}_4\text{O}_3)$ imidazolidinylphenolate Schiff base ligand,  $\text{H}_3\text{L}$ .<sup>6</sup> (Figure 3) Thiocyanate coordination induced aqua bridge cleavage and reductive

extrusion of copper(I) ions lead to the formation of  $\text{Cu}^{\text{I}}(\text{NCS})_2^-$  anions as a molecular building block and generation of 1D anionic chains as an extended coordination framework host for **2** and quantitatively replace all the  $\text{ClO}_4^-$  ions from **1** *via* anion metathesis. Once formed these chains trap the original cationic  $[\text{Cu}_2]$  complex part in a layer arrangement. The copper atoms of **2** stay in a distorted square-pyramidal environments of  $\text{Cu}^{\text{II}}\cdots\text{Cu}^{\text{II}}$  separation of 3.29 Å. (Figure 4) Within the anionic layer part, the presence of two symmetric end-to-end thiocyanate bridges with  $\text{Cu}^{\text{I}}\text{-SCN}$  and  $\text{Cu}^{\text{I}}\text{-NCS}$  distances of 2.61 Å (av.) and 1.924 Å (av.), respectively, results in a  $\text{Cu}^{\text{I}}\cdots\text{Cu}^{\text{I}}$  separation of 5.51 Å (av.) within the linear chain structure. The investigation specifies that the presence of  $\text{Cu}_2$  based macro-cations play a critical role, like alkyl amine in zeolite synthesis, as template in the process of assembling **2**. Moreover, the structure of the polyanionic chains has great influences on the ultimate layering of the cationic  $\text{Cu}^{\text{II}}_2$  units.

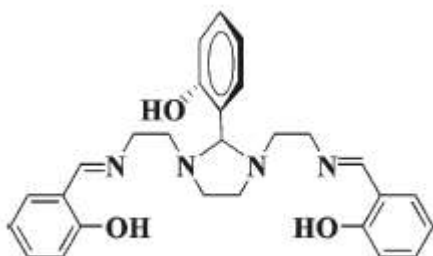


Figure 3. Ligand  $\text{H}_3\text{L}$

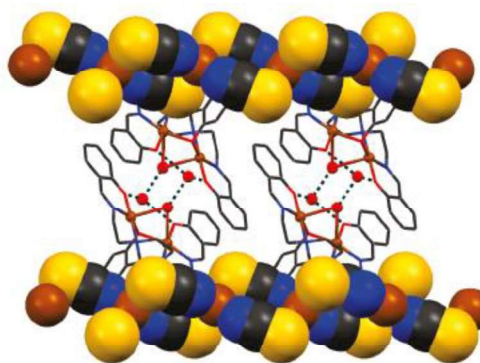


Figure 4. The 1D anionic chains in a spacefill model showing the coordination framework host

In 2013 Mitra et al.<sup>7</sup> showed that the reaction of reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{HL}^1$  in presence of  $\text{NaSCN}$  led to the formation of  $\{[\text{Cu}^{\text{II}}_2(\text{L}^1)_2][\text{Cu}^{\text{I}}_4(1,3\text{-SCN})_4(1,1,3\text{-SCN})_2]\}_n$  (**3**), through partial  $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$  reduction. (Figure 5) In **3**, the arrays of cationic  $[\text{Cu}^{\text{II}}_2(\text{L}^1)_2]^{2+}$  units are inserted in between 2D layers of  $\{[\text{Cu}^{\text{I}}_4(\text{SCN})_6]^{2-}\}_n$  and connected *via*  $\mu$ -1,1,3- $\text{SCN}^-$  links giving a 3D network structure. In another attempt, reaction of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  with  $\text{HL}^2$  in the presence of  $\text{NaSCN}$  provided a mixed-valence pentanuclear cluster  $\{[\text{Cu}^{\text{II}}_2(\text{L}^2)_2(\text{NCS})]_2[\text{Cu}^{\text{I}}(\text{SCN})(1,1\text{-SCN})(1,3\text{-SCN})]\}$  (**4**). In **4**, two cationic  $[\text{Cu}^{\text{II}}_2(\text{L}^2)_2(\text{NCS})]^+$  units are bridged by the anionic  $[\text{Cu}^{\text{I}}(\text{SCN})_3]_2^-$  unit through long  $\text{Cu}\text{-SCN}$  links. (Figure 6)

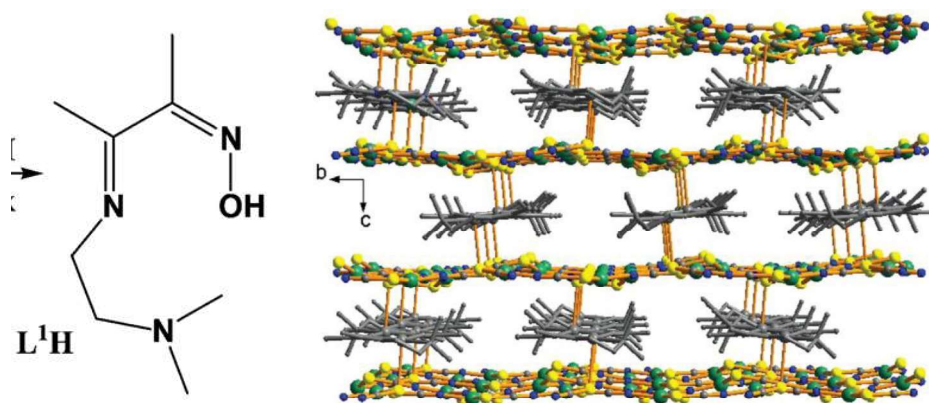


Figure 5. Ligand  $HL^1$  and the sandwiched crystal packing of  $Cu^{II}_2(L^1)_2$  within  $Cu^4(1,3-SCN)_4(1,1,3-SCN)_2$

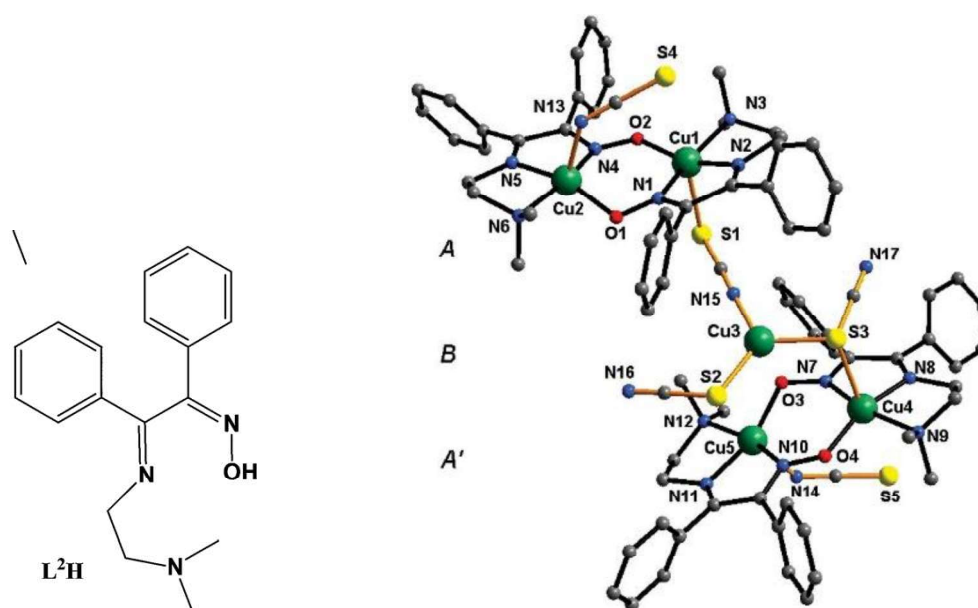


Figure 6. Ligand  $HL^2$  and the sandwiched crystal packing of  $[Cu^{II}_2(L^2)_2(NCS)]_2$  connected to  $Cu^I(SCN)(1,1-SCN)(1,3-SCN)$

### Summary and Future Scope

This micro review thus clearly highlights the several aspects of reactions of  $SCN^-$  anions with bare copper(II) ions and copper(II) ions already connected to three different ligand systems. In case of **2** the selective coordination of  $SCN^-$  anion to one  $Cu^{II}$  removes the bridged water molecule. Wherein the coordination of three  $SCN^-$  ions to  $Cu^{II}$  ion is not permitted to provide anionic complex species like  $[Cu(NCS)_3(OH_2)]^-$ . Instead, partial reduction of metal ion centers following metathesis is observed for anionic coordination chain formation. Direct replacement of  $ClO_4^-$  anions by  $SCN^-$  anions is not observed due to the greater affinity of the copper(II) ions for  $SCN^-$  anions. The review work in this segment of experimental coordination chemistry thus clearly established the role of chelating organic ligand anions in stabilizing the copper(II) or copper(I) centers. Phenolate or oximate based donors try to stabilize the bivalent state without showing any kind of reduction reaction. When thiocyanate

anions are consumed for reduction reactions the reduced copper(I) states like to prefer the coordination with other available  $\text{SCN}^-$  anions in 1,1-, 1,3- and 1,1,3- coordination modes and many types of coordination chains. Thus the future endeavor in this direction could be directed for new ligand system incorporating N, O, S and P donor atoms. Getting synthetically feasible and electronically favorable ligand system would definitely be a challenge to any synthetic and structural chemist. Many such complexes of copper(I) thiocyanate-bridged systems with phosphine donor ligands can also function as luminescent material for optoelectronic components and devices.<sup>8</sup>

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