Metal derivatives of heterocyclic-2-thiones: Variable donor ability, C–S rupture and new structural motifs

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Abstract. The chemistry of thio-ligands based on heterocyclic-2-thiones, namely, pyridine-2-thione (SNC_5H_5) , imidazolidine-2-thione $(SN_2C_3H_6)$, imidazoline-2-thione $(SN_2C_3H_4)$, 1-methyl-imidazoline-2thione $(SN_2C_4H_6)$ and thiazolidine-2-thione $(S_2NC_3H_5)$ with coinage and some other metals are described. The synthesis, solvent effect, isolation of new products after C-S rupture and crystal structure are also discussed. For example, copper(I) bromide with 1-methyl-imidazoline-2-thione ($SN_2C_4H_6$) in acetonitrile formed Cu^{1} trinuclear complex, { $Cu_{3}(\kappa^{1}-Br)_{3}(\mu-SN_{2}C_{4}H_{6})_{3}$ }·CH₃CN. This reaction in the presence of chloroform involved C-S bond rupture, oxidation of sulphur to sulphate and bromination of ring and formed a tetranuclear cluster, $Cu_4(\kappa^1-N-(N_2C_4H_5Br)_4(\mu_4-O)(\mu-Br)_6]$ (N₂C₄H₅Br = 2-bromo-1-methyl-imidazole). The reaction of copper(I) chloride with 1-methyl-imidazoline-2-thione ($SN_2C_4H_6$) in acetonitrile also involved C-S rup ture and formed a chloro-bridged dinuclear complex [Cu₂{ κ^2 -N,N-(N₂C₄H₅)₂S}₂(μ -Cl)₂Cl₂] {(N₂C₄H₅)₂S = 1, 1'-dimethyl-2,2'-di-imidazolyl sulphide}. Significantly copper(I) bonded to more polarisable iodide ion (Cu-I) does not involve C–S rupture and in this case it formed Cu^I polynuclear complex, $\{Cu_2(\mu-I)_2$ $SN_2C_4H_6)_2$. Both copper(I) chloride and copper(I) bromide with 1-methyl-imidazoline-2-thione in dimethyl sulphoxide involved C-S rupture and oxidation of sulphur to sulphate and formed a sulphate chelated Cu^{II} complex, $[Cu^{II} \{\kappa^2-N, N-(N_2C_4H_5)_2S\}(\eta^2-O, OSO_2)(\kappa^1-OH_2)]$. Imidazolidine-2-thione $(SN_2C_3H_6)$ with copper(I) chloride/bromide in dimethyl sulphoxide gave a sulphate bridged polynuclear complex, $[Cu^{II}] \kappa^2$ -N,N- $(N_2C_3H_5)_2S$ $(\mu$ -O,OSO₂) $(\kappa^1$ -OH₂)]_n { $(N_2C_3H_5)_2S = 2,2'$ -thio-di-2-imidazoline}. Other metals such as silver, zinc, cadmium and mercury formed monomers or dimers.

Keywords. Heterocyclic-2-thiones; pyridine-2-thione; copper; silver; polynuclear; C–S rupture.

1. Introduction

Heterocyclic-2-thiones are an important class of N, Sdonor ligands owing to the relevance of their metal complexes in the biological systems.¹ Metal derivatives of heterocyclic-2-thiones have shown a variety of biochemical applications: as antidandruff, antifungal, antibacterial, antimicrobial, antibiotic and in shampoos, hair creams, plant diseases, hepatitis, DNA cleavage, etc.² The chemical interest in these organic compounds is due to their multifunctional donor ability, usually through heterocyclic nitrogen and exocyclic sulphur donor atoms. Consequently, a wide variety of coordination compounds, ranging from mono- to poly-nuclear have been reported.^{3–15} The oxidation of sulphur by the metal ions and C-S bond cleavage reactions mimic the metabolism of organic sulphur in mammals.¹⁶ Transformation of organic sulphur to inorganic sulphate is a possible approach to a solution of the problem of pollution of organic sulphur complexes.¹⁷ In this paper, the chemistry of some metals, particularly copper(I) with thio-ligands as listed in chart 1, is briefly discussed. The reaction conditions involve different solvents, stirring or keeping reaction mixture undisturbed, use of different metal salts and variation in metal to ligand ratio. The work is detailed as follows.

2. Copper

2.1 Mono-, di-, and poly-nuclear complexes

Reaction of pyridine-2-thione (SNC₅H₅) with copper(II) chloride in ethanol formed a yellow insoluble compound, [CuCl(SNC₅H₅)]¹⁸ which on further reaction with two moles of PPh₃ in CHCl₃ yielded a tetrahedral complex, [CuCl(κ^1 -SNC₅H₅)(PPh₃)₂] **1**.¹⁹ Direct reaction of SNC₅H₅ with copper(I) chloride in acetonitrile also yielded yellow insoluble compound, [CuCl(SNC₅H₅)] which on reaction with one mole of PPh₃ did not form a dinuclear complex, rather same complex **1** was formed.²⁰ Likewise, copper(I) bromide with SNC₅H₅ in the presence of one or two moles of PPh₃ has formed mononuclear [CuBr(κ^1 -SNC₅H₅)(PPh₃)₂] **2** and dinuclear [Cu₂Br₂(μ -SNC₅H₅)₂(PPh₃)₂] **3** complexes.²¹ There are no similar complexes with copper(I) iodide.

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Chart 1. Heterocyclic thiones.

Among diphosphane ligands, 1, 2-*bis*(diphenyl-phosphino) ethane with copper(I) bromide has formed a P,P'bridged dimer, $[Cu_2Br_2(\mu-P,P-dppe)_2(\kappa^1-SNC_5H_5)_2]$ 4 (dppe = Ph₂P-CH₂-CH₂-PPh₂).^{22,23}

In an effort to prepare a complex similar to 4, copper(I) iodide was reacted with SNC₅H₅ in acetonitrile followed by the addition of dppe in CHCl₃ (1:1:1 molar ratio), which however yielded a complex of composition, $Cu_3I_3(dppe)_3(\kappa^1-SNC_5H_5)$ 5 (figure 1).²⁴ The single crystal X-ray study has shown that it is a trinuclear complex. In the moiety $Cu_3I_{3}(dppe)_3$, the two copper(I) centres are bridged by the iodide ligands forming $Cu(\mu-I)_2Cu$ core, while the third copper(I) centre is terminally bonded to another iodide ligand. It is first triangular cluster of Cu^I with a heterocyclic thioamide. The reactions of copper(I) iodide with SNC₅H₅ in the presence of a series of diphosphane ligands, Ph₂P-X-Ph₂P $\{X = -(CH_2)_m, m = 1 (dppm), 3 (dppp), 4 (dppb); \}$ -CH=CH- (dppen)} in CH₃CN-CHCl₃ mixture (1:1:1 molar ratio) did not yield any compound similar to 5, but in each case an iodo-bridged hexanuclear Cu^Ilinear polymer, { $Cu_6(\mu_3-SNC_5H_5)_4(\mu-SNC_5H_5)_2(I_4)$ - $(\mu-I)_2$ - $_n$ ·2nCH₃CN 6 was obtained (figure 2).²⁴ In the formation of this chain polymer, three Cu(I) iodide and three SNC₅H₅ ligands, appear to have combined via bridging S donor atoms to form boat-shaped trinuclear Cu₃S₃I₃ core, and two such cores combined in an inverse manner via four S-donor atoms (μ_3 -S), to form centrosymmetric hexanuclear repeat unit, $Cu_6S_6I_4(\mu$ -I)₂-, which finally formed the iodo-bridged infinite linear chain polymer. Linear chains are separated by the non-bonded acetonitrile molecules. This polymer is the first such example of a linear chain formed with a hexanuclear Cu₆S₆I₆ core in copper chemistry as well as in metal-heterocyclic thioamide chemistry. In addition, it has the first μ_3 -S mode of neutral pyridine-2-thione, ever reported.^{3,4} Reaction of copper(I) iodide with SNC₅H₅ in acetonitrile followed by stirring with one or two moles of PPh₃ did not yield a compound similar to 2 or 3; rather polymer 6 was again the preferred product.

The ¹H NMR spectrum of **5** in CDCl₃ (poorly soluble) showed peaks due to $-CH_2$ - protons of alkane moiety of dppe at δ 2.62 ppm. The pyridyl and phenyl



Figure 1. Molecular structure of complex $[Cu_3I_3(dppe)_3(\kappa^1-SNC_5H_5)]$ **5**.



Figure 2. Molecular structure of $\{Cu_6(\mu_3-SNC_5H_5)_4(\mu-SNC_5H_5)_2(I_4)-(\mu-I)_2-\}_n \cdot 2nCH_3CN 6.$



Figure 3. Molecular structure of $\{Cu_6(\mu_3-SN_2C_3H_6)_2(\mu_2-SN_2C_3H_6)_4Br_2(\mu-Br)_4\}_n$ 7.

protons showed multiplets in the region, δ 6.62 to 7.62 ppm; NH proton signal was too broad to be detected. The proton NMR spectrum of the partially soluble compound **6** in CDCl₃ showed NH proton signal at 13.20 ppm versus free ligand signal at 13.40. Pyridyl H(3), H(4) and H(5) protons shifted to high field, and were broad peaks due to two types of SNC₅H₅ ligands in the compound **6**. Interestingly, H(6) protons did not merge, and two broad singlets at 7.56 and 7.47 ppm were clearly visible.

Reaction of copper(I) bromide with imidazolidine-2-thione (SN₂C₃H₆) in 1:2 molar ratio in acetonitrile– chloroform mixture yielded an unusual Cu^I linear chain polymer, {Cu₆(μ_3 -SN₂C₃H₆)₂(μ_2 -SN₂C₃H₆)₄Br₂(μ -Br)₄}_n 7 (figure 3).²⁵ Copper(I) iodide also formed similar polymer, {Cu₆(μ_3 -SN₂C₃H₆)₂(μ_2 -SN₂C₃H₆)₄I₂(μ -I)₄}_n **8**. These reactions in 1:1 molar ratio in acetonitrile alone gave insoluble products, so 1:2 molar ratio was used. The polymers **7** and **8** are isostructural and formation of these polymers is believed to take place, via 6-membered trinuclear Cu₃S₃X₃ cores of Cu₃X₃(μ_2 -SN₂C₃H₆)₃ species having three bridging S atoms and three terminal X atoms. Two units of this species interacted via two S and two X groups in side-on fashion unlike inverse fashion as in **6**, forming the repeat unit Cu₆(μ_3 -SN₂C₃H₆)₂(μ_2 -SN₂C₃H₆)₄X₂(μ_2 -X)₄. Two halide ligands of repeat unit interact with other repeat units forming the infinite polymers. From the filtrate of reaction of copper(I) bromide with imidazolidine-2-thione (SN₂C₃H₆), sulphur-bridged dimer [Cu₂Br₂(μ -SN₂C₃H₆)₂(κ ¹-SN₂C₃H₆)₂] **9**¹⁰ and that of copper(I) iodide reaction, another polymer {Cu₆(μ_3 -SN₂C₃H₆)₄(μ -SN₂C₃H₆)₂(μ -I)₂I₄}_n **10** similar to **8** but involving polymerisation through sulphur were obtained.¹⁰

The proton NMR spectrum of compound **7** in CDCl₃ and of **8** in CD₃CN showed the bands due to CH₂ and NH protons at low field vis-à-vis free ligand.²⁵ The sulphur-bridged polymer **10** showed a very weak peak due to CH₂ protons at δ , 3.79 ppm, which is low-field relative to the free ligand CH₂ peak at δ , 3.59 ppm; its NH protons could not be identified probably due to low solubility of complex (cf Ligand NH proton signal at δ , 6.40 ppm).

Copper(I) chloride with imidazolidine-2-thione $(SN_2C_3H_6)$ merely formed an unsymmetrical dimer, $[Cu_2(\mu-SN_2C_3H_6)(\kappa^1-SN_2C_3H_6)_3Cl_2]$ 11, in which one copper is three coordinate and another is four coordinate.¹⁰ Copper(I) thiocyanate with imidazolidine-2-thione in 1:1 or 1:2 molar ratios formed the same polymer { $Cu(\mu-S,N-SCN)(\mu-SN_2C_3H_6)_n$ 12. The polymer 12 has shown peaks at δ , 6.66 (NH) and 3.65 (CH₂) ppm in CD₃CN. When a mixture of copper(I) chloride and imidazolidine-2-thione in 1:2 molar ratio in acetonitrile was left undisturbed at room temperature, two polymers of composition, $\{Cu_6(\mu_3-SN_2C_3H_6)_2(\mu-SN_2C_3H_6)_4Cl_2(\mu-Cl)_4\}_n$ 13 and $\{Cu_8(\mu_3-SN_2C_3H_6)_4(\mu-SN_2C_3H_6)_4(\kappa^1-Cl)_8\}_n$ 14 were isolated. The same reaction in 1:1 molar ratio yielded only polymer 14. Polymer 13 is similar to 7, but 14 has different structure (figure 4).⁹ The chemistry of imidazoline-2-thione $(SN_2C_3H_4)$ with copper(I) halides in 2:1 molar ratio did not yield polymers similar to that formed by imidazolidine-2-thione $(SN_2C_3H_6)$. There was a change in colour from colourless to green (probably due to Cu^{II}) when solution was left



Figure 4. Molecular structure of $\{Cu_8(\mu_3-SN_2C_3H_6)_4(\mu-SN_2C_3H_6)_4(\kappa^1-Cl)_8\}_n$ 14.

in open for several days and no crystalline product could be isolated. The addition of triphenylphosphine (Ph₃P) yielded crystalline products. Thus, the reaction with copper(I) chloride in 1:1:2 (M:L:PPh₃) molar ratio yielded a compound of unusual composition, [Cu₂(SN₂C₃H₄)(PPh₃)₄Cl₂]·CH₃OH **15**, whose X-ray crystallography showed that its crystals consist of four-coordinated [CuCl(SN₂C₃H₄)(PPh₃)₂] **15a** and three-coordinated [Cu(PPh₃)₂Cl] **15b** independent molecules in the same unit cell. In contrast, crystals of complexes of copper(I) bromide/iodide with imidazolidine-2-thione are formed by single molecules of [CuBr(SN₂C₃H₄)(PPh₃)₂]·H₂O **16** and [CuI(SN₂C₃H₄)(PPh₃)₂] **17** respectively.²⁶

The ¹H NMR of ligand imidazoline-2-thione $(SN_2C_3H_4)$ in dimethyl sulphoxide shows a singlet at 6.65 ppm due to equivalent ring (C^4H , C^5H) protons. When this ligand coordinates to the metal via its S electrons in 15-17, ring protons become magnetically inequivalent and thus two expected doublets due to C⁴H, C⁵H protons merge into an unresolved triplet. Each of complexes 15-17 showed a triplet at a low field (7.23, 15; 6.74, 16; 6.79 ppm, 17). Interestingly, NMR spectrum of com- $[CuCl(SN_2C_3H_4)(PPh_3)_2] \cdot [CuCl(PPh_3)_2]$ plex 15 showed two sets of PPh₃ signals which revealed formation of $[CuCl(SN_2C_3H_4)(PPh_3)_2]$ the 15a (7.25-7.27 ppm) and $[Cu(PPh_3)_2Cl]$ **15b** (7.46-7.67 ppm, PPh_3) in the solution state. Similarly, complexes $[CuBr(SN_2C_3H_4)(PPh_3)_2] \cdot H_2O$ 16 and $[CuI(SN_2C_3H_4)(PPh_3)_2]$ **17** showed one set of PPh₃ signals in the regions 7.27-7.41 and 7.27-7.47 ppm, respectively and another set of weak PPh₃ signals in the regions, 7.47–7.68 ppm showed the formation of compounds, namely, Cu(PPh₃)₂Br and Cu(PPh₃)₂I similar to 15b. The NH proton signals could not be identified in complexes 15 and 17 due to broadening. The ³¹P NMR spectra of compounds 15–17 showed signals at -3.42(15a), -4.30 (16) and -5.10 (17) with coordination shifts ($\Delta\delta$) of 1.28, 0.40 and -0.40 ppm, respectively. The signal due to $[CuCl(PPh_3)_2]$ **15b** has been identified at 30.74 ppm.

Copper(I) iodide with imidazoline-2-thione $(SN_2C_3H_4)$ and Ph_3P in 1:1:1 molar ratio has formed a sulphur-bridged dinuclear complex $[Cu_2I_2(\mu-SN_2C_3H_4)_2(PPh_3)_2]$ **18**. The central $Cu(\mu-S)_2Cu$ core forms a parallelogram with unequal Cu–S bond distances. Copper(I) chloride and bromide did not form crystalline products. Copper(I) halides (Cl, Br, I) with 1-methyl-imidazoline-2-thione $(SN_2C_4H_6)$ in 1:2 molar ratio yielded sulphur-bridged dinuclear $[Cu_2X_2(\mu-SN_2C_4H_6)_2]$ complexes (19-21, X = Cl to I).²⁷ The ¹H NMR spectrum of compound **21** showed

a signal for imino hydrogen, -NH- at 11.95 ppm, which is at low field vis-à-vis that of the free ligand (11.31 ppm). This signal could not be identified in complexes 19 and 20 even in dimethyl sulphoxide- d_6 and this is attributed to broadening of -NH signals due to quadrupolar relaxation (^{14}N , I = 1). The C⁴H and C⁵H protons of complexes **19–21** in the range of 6.64– 7.51 ppm showed a slight up-field shift ($SN_2C_4H_6$, 6.68–6.67 ppm). The methyl hydrogen appeared in the range of 3.33–3.67 ppm, and remained almost unchanged in these complexes (free ligand, 3.62 ppm). The C^4H and C^5H protons of complex 18 appeared at 7.25 ppm and are at low field vis-à-vis that of the free ligand (6.64 ppm). The signals of phenyl hydrogens of Ph₃P molecule in this complex lie in range of 7.26–7.71. The ³¹P NMR spectrum of **18** showed a signal at -78.35 ppm with a coordination shift, $\Delta \delta =$ $\{\delta_{\text{complex}} - \delta_{\text{ligand}}\}$, 34.81 ppm indicating a coordinated Ph_3P in this complex.²⁶

Copper(I) halides with 1-methyl-imidazoline-2thione $(SN_2C_4H_6)$ in acetonitrile have yielded a trinuclear complex, $\{Cu_3(\kappa^1-Br)_3(\mu-SN_2C_4H_6)_3\}\cdot CH_3CN$ 22 (figure 5), and 1D polymer, $\{Cu_2(\mu-I)_$ $SN_2C_4H_6)_2$ [n 23 (figure 6).²⁸ Polymer 23 has alternating Cu₂I₂ and Cu₂S₂ cores involving sulphur/iodine bridging in a twisted ribbon type arrangement. The ¹H NMR spectra of compounds 22 and 23 in dimethyl sulphoxide have shown weak signals. Trinuclear complex 22 has shown a broad NH peak at δ 12.40 ppm, which is at low-field relative to the free ligand $(SC_4H_6N_2, 11.31 \text{ ppm})$, but similar signal in 23 could not be identified, probably due to the anticipated broadening of the signals due to quadrupolar nucleus (^{14}N) . The C^4H , C^5H and methyl protons of complexes 22 and 23 have shown shifts to low-field vis-à-vis the free ligand. Further, in their electronic absorption studies, each



Figure 5. Molecular structure of trinuclear complex, $\{Cu_3(\kappa^1-Br)_3(\mu-SN_2C_4H_6)_3\}\cdot CH_3CN$ 22.



Figure 6. Molecular structure of $\{Cu_2(\mu-I)_2(\mu-SN_2C_4H_6)_2\}_n$ 23.

of complexes in their 10^{-4} M solutions showed one intense band at 267 (22) and 268 (23) nm, respectively. However, 10^{-3} M solutions of complexes showed very intense absorption in 260–300 nm region along with weak bands at 771 and 806 nm, respectively (22 and 23). The fluorescence studies in 10^{-5} – 10^{-6} M solutions have shown intense fluorescent bands at $\lambda_{em} =$ 319 (22) and 322 nm (23) corresponding to excitation wavelengths of 258 and 272 nm, respectively (figure 7).

2.2 *C*–*S* rupture in copper-heterocyclic-2-thione reactions

The reaction of copper(I) chloride with imidazolidine-2-thione (SN₂C₃H₆) in acetonitrile yielded a copper(I) polymer, {Cu^I₈(μ_3 -SN₂C₃H₆)₄(μ -SN₂C₃H₆)₄(κ^1 -Cl)₈}_n **14**, ⁹ which when kept in dimethyl sulphoxide changed into a sulphate bridged polymer, [Cu^{II}{ κ^2 -N,N-(N₂C₃H₅)₂S}(μ -O,OSO₂)(κ^1 -OH₂)]_n **24** (figure 8) containing chelating 2,2'-thio-di-2-imidazoline thioether {(N₂C₃H₅)₂S}.²⁹ It is first example of *in situ* generation of 2,2'-thio-di-2-imidazoline {(N₂C₃H₅)₂S}³⁰ from imidazolidine-2-thione (SN₂C₃H₆) and its coordination to Cu^{II}. The electronic absorption spectrum of complex **24** in dmso showed very intense absorption in 266 nm



Figure 7. Fluorescence spectra of complexes 22 and 23.

region along with a weak band at 676 nm. The former band is assigned as a charge transfer band $(O \rightarrow Cu)$, while second band as a d-d transition. Reaction of copper(I) bromide with 1-methyl-imidazoline-2thione in acetonitrile formed trinuclear Cu^I complex $[Cu_3Br_3(SN_2C_4H_6)]$ 22,²⁸ but in dimethyl sulphoxide it has formed a sulphate chelated mononuclear Cu^{II} complex, $[Cu^{II} {\kappa^2 - N, N - (N_2C_4H_5)_2S}(\kappa^2 - O, OSO_2)(\kappa^1 - C_2C_4H_5)_2S}$ OH₂)] 25 (figure 9).²⁹ Here, copper(I) chloride with 1-methyl-imidazoline-2-thione in dimethyl sulphoxide has formed a chloro-bridged dimer, $[Cu_2 \{\kappa^2 - \kappa^2\}]$ $N,N-(N_2C_4H_5)_2S_2(\mu-Cl)_2Cl_2$ = 1, 1'-dimethyl-2,2'-di-imidazolylsulphide} along with free $CuSO_4 \cdot 5H_2O$ (figure 10).³¹ It may be added here that the reaction of 1-methyl-imidazoline-2-thione with copper(I) chloride in acetonitrile or acetonitrilechlorform mixture also formed same products. This



Figure 8. Structure of $[Cu^{II} {\kappa^2-N, N-(N_2C_3H_5)_2S}(\mu-O,OSO_2)(\kappa^1-OH_2)]_n$ 24.



Figure 9. Structure of complex $[Cu^{II}{\kappa^2-N,N-(N_2C_4H_5)_2S}(\kappa^2-O,OSO_2)(\kappa^1-OH_2)]$ 25.



Figure 10. Structure of complex $[Cu_2\{\kappa^2-N,N-(N_2C_4H_5)_2S\}_2(\mu-Cl)_2Cl_2]$ 26.

thio-ligand when added to copper(II) chloride, initially reduced Cu^{II} to Cu^I as solution becomes colourless, which again starts colour change and same products were formed. This reaction in methanol is known to yield **26**.^{3,8} Mechanism of formation of **24** is shown in scheme 1 and is similar for **25** and **26**.

Reaction of copper(I) bromide with 1-methylimidazoline-2-thione in acetonitrile formed a trinuclear Cu^I complex [Cu₃Br₃(SN₂C₄H₆)] **22**.²⁸ However, the addition of chloroform to acetonitrile has formed a Cu^{II} tetranuclear cluster, [Cu₄(κ^1 -N-(N₂C₄H₅Br)₄(μ_4 -O) (μ -Br)₆] **27** (figure 11) (N₂C₄H₅Br = 2-bromo-1methyl-imidazole) along with free CuSO₄·H₂O.³² The formation of complex **27** is shown in scheme 2. The complex **27** is weakly fluorescent at $\lambda_{em} = 329$ nm corresponding to excitation wavelength of 270 nm (figure 12). The ESI-mass spectrum of complex **27** did not show molecular ion peak but it has shown peaks which support various components of this complex. The important peak at m/z value 163.4 corresponds to



Scheme 1. Mechanism of formation of 24.



Figure 11. Molecular structure of complex $[Cu_4(\kappa^1-N-(N_2C_4H_5Br)_4(\mu_4-O)(\mu-Br)_6]$ **27**.

2-bromo-1-methyl-imidazole ($N_2C_4H_5Br^{81}$). Another important peak at m/z value 268.3 corresponds to Cu^{63}_4O species. This reaction is an example where 1-methyl-imidazoline-2-thione has been converted into 2-bromo-1-methyl-imidazole under ambient conditions with copper(I) bromide as a brominating agent (Sandmeyer type bromination). Finally, thiazolidine-2-thione also showed C–S rupture along with the C–N bond formation.³¹

3. Other metals

The thio-ligands, namely, imidazolidine-2-thione, 1-methyl-imidazoline-2-thione, thiazolidine-2-thione,



Scheme 2. Mechanism of formation of 27.



Figure 12. Fluorescence spectrum of complex 27.

pyridine-2-thione with silver(I), zinc(II), cadmium(II) and mercury(II) have formed monomeric or dimeric complexes either in the presence or absence of triphenyl phosphine.^{33–35} The structure around a metal centre can be regarded as distorted tetrahedral.

4. Conclusion

The use of lower metal to ligand ratio prevented C– S rupture and kept Cu^I oxidation state stable. When a metal salt was stirred with a thione ligand there was general tendency to form precipitate and prevent crystal formation. However, keeping a mixture of a metal salt and a thione ligand undisturbed yielded crystalline products. The presence of triphenylphosphine assisted crystal formation and coordinated to the metal centre in several cases. The C–S rupture occurred when anions were Cl⁻, Br⁻, BF⁻₄ and NO⁻₃. The greater solvent polarity assisted Cu–X bond rupture by forming Cu–X···solvent interactions. Likewise, dimethyl sulfoxide and dimethyl formamide coordinated to metal centre in Cu–X but electronegative O donor atom of dimethyl sulphoxide did not stabilize Cu^I state. More readily Cu^I formed, the greater was tendency to induce C–S rupture.³¹

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