Metal Derivatives of Heterocyclic Thioamides: Synthesis and Crystal Structures of Copper Complexes with 1-Methyl-1,3-imidazoline-2-thione and 1,3-Imidazoline-2-thione

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Abstract. Reactions of copper(I) halides (Cl, Br, I) with 1-methyl-1, 3-imidazoline-2-thione (mimzSH) in 1 : 2 molar ratio yielded sulfur-bridged dinuclear $[Cu_2X_2(\mu-S-mimzSH)_2(\eta^1-S-mimzSH)_2]$ (X = I, 1, Br, 2; Cl, 3) complexes. Copper(I) iodide with 1,3-imidazoline-2-thione (imzSH₂) and Ph₃P in 1 : 1 : 1 molar ratio has also formed a sulfur-bridged dinuclear $[Cu_2I_2(\mu-S-imzSH_2)_2(PPh_3)_2]$ (4) complex. The central $Cu(\mu-S)_2Cu$ cores form parallelograms with unequal Cu-S bond distances {2.324(2), 2.454(3) Å} (1); {2.3118(6), 2.5098(6) Å} (2); {2.3075(4), 2.5218(4) Å} (3); {2.3711(8), 2.4473(8) Å} (4). The Cu···Cu separations, 2.759–2.877 Å in complexes 1-3 are much shorter than 3.3446 Å in complex 4. The weak intermolecular interactions {H₂CH···S[#] (2); CH···Cl[#] (3); NH···I[#] (4)} between dimeric units in complexes 2-4 lead to the formation of linear 1D polymers.

Keywords: Copper; 1,3-Imidazoline-2-thione; 1-Methyl-1,3-imidazoline-2-thione

Introduction

Heterocyclic thioamides bearing the functional groups such as $-N(H)-C(=S)- \leftrightarrow -N=C(-SH)-$ or -N(H)-C(= $S = N(H) - \leftrightarrow -N = C(-SH) - N(H)$, have shown diverse bonding properties both in the neutral and in anion forms (after losing -NH hydrogen). These ligands have formed monomers, dimers, oligomers and polymers [1-12a]. The five membered ring ligand, namely, 1-methyl-I) has 1,3-imidazoline-2-thione (mimzSH, formed monomeric and dimeric complexes with Cu^I, viz. $[CuBr(mimzSH)(Ph_3P)_2]$ [12b], $[CuI(mimzSH)(Ph_3P)_2]$ [12c], [Cu₂(mimzSH)₅]SO₄ [13], [Cu(mimzSH)₃](NO₃) [14], [Cu₂(mimzSH)₆] · 2BF₄ [15], [Cu₂(mimzSH)₄(CN)₂] [16] and [Cu₂(mimzSH)₄(SCN)₂] [17]. As regards 1, 3-imidazoline-2-thione (imzSH₂, II), only a few mononuclear copper(I) complexes have been reported from this laboratory [18]. Chart 1 displays various bonding modes of 1, 3-imidazoline-2-thione and its derivatives : (i) η^{1} -S- terminal (mode A) [12c], (ii) μ-S- bridging (mode B) [16], (iii) μ-N, S- bridging (mode C) [12d], and (iv) N, S- chelating (mode D) [12e].

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Chart 1

As noted above there are only a few copper(I) halide 1-methyl-1,3-imidazoline-2-thione complexes with (mimzSH, I), namely, mononuclear, [Cu(mimzSH)-Br(Ph₃P)₂] [12b] and [Cu(mimzSH)I(Ph₃P)₂] [12c], and a dinuclear, [Cu₂Cl₂(mimzSH)₄] [19]. Also there is no dimeric complex of imzSH₂ ligand with any coinage metal. In continuation of our interest in the metal coordination chemistry of heterocyclic thioamides [7, 8, 12], we are reporting in this paper a series of dinuclear complexes of copper(I) 1-methyl-1,3-imidazoline-2-thione halides with and 1,3-imidazoline-2-thione.

Experimental Section

Materials and Techniques

The ligands, 1-methyl- 1, 3-imidazoline-2-thione, 1, 3-imidazoline-2-thione, and triphenyl phosphine were procured from Aldrich Sigma Ltd. Copper(I) halides were prepared by reducing an aque-



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	1	2	3	4
Empirical formula	C ₈ H ₁₂ CuIN ₄ S ₂	C ₈ H ₁₂ BrCuN ₄ S ₂	C ₈ H ₁₂ ClCuN ₄ S ₂	$C_{42}H_{38}Cu_2I_2N_4P_2S_2$
Formula weight	418.78	371.79	327.33	1105.70
T/K	293(2)	103(2)	103(2)	103(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	ΡĪ
a/Å	10.7928(10)	8.3490(9)	8.3348(7)	9.218(2)
b/Å	8.1112(7)	14.962(2)	14.6699(12)	9.415(2)
c/Å	15.7687(12)	10.3160(10)	10.2426(8)	13.455(2)
α/°	90	90	90	90.690(2)
β/°	105.775	98.811(5)	100.4310(10)	105.194(2)
γ/°	90	90	90	111.309(2)
V /Å ³	1328.4(2)	1273.59(2)	1231.67(17)	1042.5(3)
Z	4	4	4	1
$D_{color}/mg m^{-3}$	2.094	1.939	1.765	1.761
u /mm ⁻¹	4.261	5.158	2.306	2.714
Reflections collected	14011	8216	13720	9351
Unique reflections, R(int)	3155, 0.0374	3154, 0.0459	3444, 0.0216	3915, 0.0211
Final R indices $[I > 2\sigma(I)]$,	,	· · · · ·	
R1	0.0692	0.0269	0.0235	0.0270
wR2	0.1847	0.0604	0.0586	0.0765

Table 1Crystal data for complexes 1-4

ous solution of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of NaX (X = Cl, Br, I) in water [20]. Elemental analysis for C, H and N were carried out using a thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. The I.R spectra of the ligands and the complexes were recorded in the range, 4000-200 cm⁻¹ (using KBr pellets) on the FTIR-SHIMADZU 8400 Fourier Transform Spectrophotometer and on Pye–Unicam SP-3-300 spectrophotometer. ¹H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in CDCl₃ with TMS as the internal reference. ³¹P NMR spectra were recorded at 121.5 MHz with (CH₃O)₃P as the external reference taken as zero position.

Synthesis of complexes

$[Cu_2I_2(\mu-S-mimzSH)_2(\eta^1-S-mimzSH)_2] (1)$

To a solution of 1-methyl-1, 3-imidazoline-2-thione (0.025 g, 0.22 mmol) in dry acetonitrile (10 mL) was added a solution of copper(I) iodide (0.020 g, 0.11 mmol) in dry acetonitrile (10 mL). The reaction was stirred for 30 minutes at room temperature. To this reaction mixture was added chloroform (5 mL) and the contents were stirred for a further period of 2 h. Light green crystals were formed on slow evaporation at room temperature. Yield, 64 %, m.p. 170-175 °C. Anal. calcd for $C_8H_{12}CuIN_4S_2$ (%): C, 22.91; H, 2.86; N, 13.36. Found:C, 23.18; H, 3.07; N, 13.66.

IR (KBr, cm⁻¹): v(N-H), 3221-3114(m-s); $v(C-H)_{Me}$, 3028(m), 3018(m); $v(C-H)_{ring}$, 2939(m), 2910(w); $v(C-N) + \delta(C-H)$, 1570(sh), 1468(s); v(C=S), 915(m); $\delta(N-CH_3)$, 787(s). ¹H NMR data (δ ; CDCl₃): 11.95 (s, 1H,N³H), 7.51 (m, 1H, C⁴H), 6.82 (m, 1H, C⁵H), 3.65 (3H, CH₃).

Compounds 2 and 3 were prepared similarly.

$[Cu_2Br_2(\mu-S-mimzSH)_2(\eta^1-S-mimzSH)_2] (2)$

Yield, 75 %, m.p. 180-185 °C. Anal. calcd for C₈H₁₂CuBrN₄S₂ (%): C, 25.84; H, 3.23; N, 15.07. Found: C, 26.38; H, 3.45; N, 15.12.

IR (KBr, cm⁻¹): v(N-H), 3138-3115(m-s); $v(C-H)_{Me}$ 3020(m); $v(C-H)_{ring}$ 2940(m); $v(C-N) + \delta(C-H)$, 1570(s), 1462(s); v(C=S), 910(m); $\delta(N-CH_3)$, 779(s). ¹H NMR data (δ ; CDCl₃: 7.34 (1H, C⁴H), 6.79 (1H, C⁵H), 3.64 (3H, CH₃).

$[Cu_2Cl_2(\mu-S-mimzSH)_2(\eta^1-S-mimzSH)_2] (3)$

Yield, 0.028 g, 80 %, m.p. 140-142 °C. Anal. calcd for $C_8H_{12}CuClN_4S_2$ (%): C, 29.36; H, 3.67; N, 17.12. Found: C, 29.43; H, 3.59; N, 16.52.

IR (KBr, cm⁻¹): v(N–H), 3219-3115(m-s); v(C–H)_{Mc} 3016(m); v(C–H)_{ring}, 2939(m); v(C–N) + δ (C-H), 1570(s), 1468(s); v(C=S), 916(m); δ (N–CH₃), 789(s). ¹H NMR data (δ , CDCl₃): 7.42 (1H, C⁴H), 6.82 (1H, C⁵H), 3.67 (3H, CH₃).

$[Cu_2I_2(\mu-S-imzSH_2)_2(PPh_3)_2]$ (4)

To a solution of 1, 3-imidazoline-2-thione (0.025 g, 0.25 mmol) in dry acetonitrile (12 mL) was added a solution of copper(I) iodide (0.047 g, 0.25 mmol) in dry acetonitrile (12 mL), and after stirring for 1 h, white precipitates were formed. To these precipitates, PPh₃ (0.065 g, 0.25 mmol) was added and a clear solution was obtained. White crystals are formed on slow evaporation at room temperature. Yield, 82 %, m.p. 205-212 °C. Anal. calcd. for $C_{21}H_{19}Cu-IN_2P_2S$ (%): C, 45.57; H, 3.44; N, 5.06. Found: C, 45.04; H, 3.59; N, 4.94.

IR (KBr, cm⁻¹): v(N–H), 3070(w); v(C–H)_{ring}, 2950(s), 2897(s); v(C–N), 1577(s), 1468(s); v(P–C_{Ph}), 1093(s); v(C=S), 920(m). ¹H NMR data (δ , CDCl₃: 7.25 (2H, C^{4,5}H), 7.44-7.71(15H, PPh₃). ³¹P NMR (CDCl₃), δ = -78.35, $\Delta\delta$ = 34.81.

X-ray crystallography

Prismatic crystals of complexes 1-4 were mounted on an automatic Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator, and Mo-K_{α} radiation ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 293 K for 1 and 103 K for 2–4. The structures were solved by the direct methods and refined by full matrix least square based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using XCAD-49 (data reduction), and SHELXL (absorption correction, structure solution refinement and molecular graphics) [21]. The crystallographic data are given in Table 1.



Scheme 1

Results and Discussion

Syntheses

Scheme 1 depicts formation of complexes 1-4. The reactions of copper(I) iodide, bromide and chloride with 1- methyl-1, 3 imidazoline-2-thione (mimzSH) in 1 : 2 (M:L) molar ratio in CH₃CN formed compounds of composition $[Cu_2X_2(mimzSH)_4]$ (X = I, 1; Br, 2; Cl, 3), which were crystallized from CH₃CN/CHCl₃ mixture. Complex [Cu₂Cl₂(mimzSH)₄] is reported in literature also [19]. The ligand imzSH₂ did not yield complexes similar to 1-3, and Ph₃P was necessary to obtain a stable and crystalline complex. Thus reaction of copper(I) iodide with imzSH₂ and Ph₃P in 1 : 1 : 1 (M : L : PPh₃) molar ratio formed a compound of composition [Cu₂I₂(imzSH₂)₂(Ph₃P)₂] (4). Other copper(I) halides (Br, Cl) with imzSH₂ and Ph₃P did not yield similar crystalline products. Compounds 1-4 are soluble in chloroform, dichloromethane and acetonitrile and are stable to air and moisture.

Complexes 1-3 showed v(N-H) bands in the range, $3114-3221 \text{ cm}^{-1}$, whereas complex 4 showed this peak 3070 cm^{-1} at (mimzSH, 3125-3157, imzSH₂, $3116-3150 \text{ cm}^{-1}$). This showed that the ligands are coordinating as neutral ones. The diagnostic v(C=S) band appeared in the low energy region, 910–916 cm⁻¹ vis-a-vis the free ligands (mimzSH, 930; imzSH₂, 930 cm⁻¹). This shift is attributed to the weakening of C=S bond due to coordination to the metal center via thione sulfur. A characteristic v(P-C_{Pb}) band at 1093 cm⁻¹ showed the presence of Ph₃P in complex 4 [13]. The single crystal x-ray crystallography has been used to establish the crystal and molecular structures of complexes.

Crystal structures of complexes

Dimeric complexes 1-3 crystallized in monoclinic system with space groups P2₁/c (1), P2₁/n (2 and 3) and compound 4 crystallized in triclinic system with space group $P\overline{1}$. The atomic numbering schemes of compounds 1 and 4 are shown in Figures 1 and 2 respectively (see supporting information for 2 and 3). Dimer 1 consists of two terminally bonded iodides and mimzSH ligands along with two sulfurbridged mimzSH ligands. The central Cu(μ -S)₂Cu core is a



Figure 1 Structure of complex (1) with numbering scheme



Figure 2 Packing diagram of complex $[Cu_2I_2(\mu$ -S-mimzSH)₂(η^1 -S-mimzSH)₂] (1)

parallelogram with unequal Cu–S bond distances $\{2.324(2), 2.454(3) \text{ Å}\}$ (1), which are longer than the terminal Cu–S bond distance $\{2.301(3) \text{ Å}\}$. The core Cu–S distances are close to 2.358 and 2.459 Å observed in $[Cu_2(\mu-S-mimzSH)_2(\eta^1-S-mimzSH)_4](BF_4)_2$ 6 [15], or in other similar heterocyclic thioamide complexes [16–18]. The Cu–I bond distance, 2.6456(14) Å (1), is much shorter than the sum of ionic radii of Cu⁺ and I⁻, 2.97 Å [22], and is close to 2.6729(11) Å observed in a tetrahedral complex $[Cu(\eta^{1}-imzSH_2)(PPh_3)_2I]$ [18]. Bond parameters of **2** and **3** are similar. The C-S bond distances of bridging {1.722(9) Å (1), 1.710(2) Å (2), 1.7153(14) Å (3)} as well terminal mimzSH ligands {1.701(9) (1), 1.699(2) (2), 1.7002(14) (3)} are longer than 1.684(2) Å in free mimzSH [23] indicating partial double bond character of C=S in complexes. It is pointed out here that the bond parameters of the dimer **3** are similar to previously reported parameters [18].

Dinuclear complex $[Cu_2I_2(\mu-S-imzSH_2)_2(Ph_3P)_2]$ (4) consists of two terminally bonded iodides, two sulfur-bridged imzSH2 and two terminal Ph3P ligands with central Cu(µ-S)₂Cu core. The central Cu(μ -S)₂Cu core is a parallelogram unequal Cu-S bond with distances {2.3711(8). 2.4473(8) Å} and Ph₃P ligands are in trans positions. The bridging Cu-S bond distances are similar to that of complex 1. The Cu-I bond distance, 2.6211(5) Å is close to 2.6729(11) Å in the mononuclear complex, [CuI($imzSH_2$)(Ph₃P)]₂ [18]. The Cu-P distances are close to the literature values [18, 24, 25]. The bridging C-S distance of 1.694(3) Å in 4 is longer as expected than 1.643(10) Å in $[CuI(\eta^{1}-S-imzSH_{2})(Ph_{3}P)]_{2}$ [18].

The bond angles at each copper lie in the ranges, $99.02-119.70^{\circ}$ (1), $101.461-115.574^{\circ}$ (2), $106.298-115.057^{\circ}$ (3) and $92.10-116.15^{\circ}$ (4), and reveal that copper has distorted tetrahedral geometry.



Figure 3 Structure of complex 4 with atomic numbering scheme

Table 2 shows bond parameters of some dinuclear complexes of mimzSH and pyridine-2-thione (py2SH) or imzSH₂ with tertiary phosphines as co-ligands. The central cores in these complexes adopt shape of a parallelogram. In complexes [CuX₂L₄] (X = I, 1, Br, 2, Cl, 3, SCN, 5), the Cu...Cu separations are less than or close to twice the sum of van der Waals radius of Cu atom (2.80 Å) [22]. However, the complex [Cu₂L₆]²⁺ (6) with all the sulfur ligands



Figure 4 Packing diagram of complex $[Cu_2I_2(\mu-S-imzSH_2)_2(PPh_3)_2]$ (4)

bonded, the distance marginally increases to 3.003 Å due to the difference in electronegativity of halide / pseudohalide groups [15]. The mixed-ligand complexes $[CuX_2L_2(PPh_3)_2]$ (4, 7 and 8) have longest Cu···Cu separations (3.3446-3.250 Å). Further the angles at bridging sulfur and copper atom vary in complementary fashion.

Table 2 Important bond lengths/Å and bond angles/° in $Cu(\mu{-}S)_2Cu$ cores

Complex	Cu-S	C-S	M-S-M	s-m-s	Cu…Cu
[Cu ₂ I ₂ (mimzSH) ₄] (this work) 1	2.324(2), 2.454(3)	1.722(9)	73.141(19)	109.51(8)	2.759(2)
[Cu ₂ Br ₂ (mimzSH) ₄] (this work) 2	2.3118(6), 2.5098(6)	1.710(2)	70.49(8)	106.85(2)	2.877(6)
[Cu ₂ Cl ₂ (mimzSH) ₄] (this work) 3	2.3075(4), 2.5218(4)	1.715(2)	72.42(13)	107.57(1)	2.858(4)
[Cu ₂ I ₂ (imzSH) ₂ (PPh ₃) ₂] (this work) 4	2.371(8), 2.44(8)	1.694(3)	87.90(2)	92.10(2)	3.3446
[Cu ₂ (SCN) ₂ (mimzSH) ₄] 5 [17]	2.377, 2.457	-	72.6	95.9	2.861
[Cu ₂ (mimzSH) ₆](BF ₄) ₂ 6 [15]	2.358, 2.459	1.705	77.2	102.8	3.003
[Cu ₂ I ₂ (py2S) ₂ (p-tol ₃ P) ₂] 7 [24]	2.39(4), 2.42(4)	1.69(1)	85.25(1)	94.75(1)	3.263(4)
[Cu ₂ Br ₂ (py2S) ₂ (p-tol ₃ P) ₂] 8 [12]	2.389(2), 2.415(2)	1.717(4)	85.14(6)	94.86(6)	3.250(2)

H-bonding

The important H-bonding parameters of complexes 1-4 are given in Table 3. The NH- hydrogens of both the terminal and bridging mimzSH ligands have only formed intra-molecular H-bonds, {N¹H_(br.)...X, N¹H_(ter)...X} with iodine, and there is no inter-dimer interaction in complex 1. The intra-molecular H-bonding in complexes 2 and 3 is similar to that of 1. In complex 2, the two dimeric units are interconnected via long intermolecular H-bonds (CH...S) and (CH...X) to form a tetramer along a-axis (see sup-

plementary). Two such tetrameric units are interconnected by a dimeric unit via weak interaction between methyl hydrogen and sulfur (H₂CH···S) along b-axis. In complex **3**, the two dimeric units are interconnected by weak intermolecular H-bonding, between CH of terminal mimzSH and the chlorine atom, (CH···Cl), which is repeated along b-axis to form a linear polymer (see supporting information).

 Table 3
 Hydrogen bonds/Å for Complexes 1–4

Complex No.	D-H···A	d(D-H)	$d(H \cdots A)$	d(D…A)	<(DHA)
1	N(1A)-H(1AA)…I	0.86	2.95	3.753(8)	155.6
	N(1B)-H(1BA)…I	0.86	2.91	3.706(8)	155.6
2	N(1A)-H(1AA)····Br	0.88	2.41	3.270(2)	164.8
	N(1B)-H(1BA)-Br	0.88	2.60	3.433(2)	158.5
3	N(1A)-H(1A)Cl	0.83(2)	2.33(2)	3.1441(13)	169(2)
	N(1B)-H(1B)····Cl	0.87(2)	2.50(2)	3.3272(13)	160.0(2)
4	N(1)-H(1A)…I ^{#2}	0.88	2.91	3.705(2)	150.3
	N(2)-H(2B)…I	0.88	2.84	3.678(2)	160.4

1, ^{#1} -x+1,-y,-z; 2, ^{#1} -x+2,-y,-z+2; 3, ^{#1} -x+1,-y+1,-z+1; 4, ^{#1} -x+2,-y+1,-z ^{#2} x+1,y,z

The H-bonding pattern is different in complex 4 due to the presence of two NH moieties in imzSH₂. One of the imino hydrogens forms intra-molecular H-bond with the iodine (NH…I) and second imino hydrogen is engaged in intermolecular H-bonding (NH…I) and this leads to the formation of a linear chain polymer.

Solution Phase Behavior

Proton NMR spectrum of compound 1 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 even in dmso-d₆ and this is attributed to broadening of -NH signals due to quadrupolar relaxation (¹⁴N, I = 1). The C⁴H and C⁵H protons of complexes 1-3 in the range, 6.64-7.51 ppm showed a slight upfield shift (mimzSH, 6.68-6.67 ppm). The methyl hydrogen appeared in the range, 3.33-3.67 ppm, and remained almost unchanged in these complexes (free ligand, 3.62 ppm). The $C^{4}H$ and $C^{5}H$ protons of complex 4 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, 7.26-7.71. The ³¹P NMR spectrum of 4 showed a signal at -78.35 ppm with a coordination shift, $\Delta \delta = \{\delta_{complex} - \delta_{ligand}\}$, 34.81 ppm indicating a coordinated Ph₃P in this complex [25].

Conclusion

It may be interesting to compare the coordination chemistry of the title ligands with that of 1, 3- imidazolidine-2thione (imzdSH₂). For instance, while reactions of copper(I) halides (I, Br) with imzdSH₂ in CH₃CN- CHCl₃ mixture in 1 : 2 molar ratio resulted in the formation of polymeric materials [7, 8], the similar reactions with 1-methyl-1,3imidazoline-2-thione have formed rather dinuclear $[Cu_2X_2(mimzSH)_4]$ complexes. However, the 1,3-imidazoline-2-thione formed neither polymers nor dinuclear complexes, and the dimer $[Cu_2I_2(imzSH_2)_2(Ph_3P)_2]$ **4** was obtained only in the presence of Ph₃P using a different reaction ratio (1 : 1 : 1).

Supplementary material: Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC: for 1-4 is 676823-676826. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336-033; email: deposit@ccdc.cam.ac.uk; or http:// www.ccdc.cam.ac.uk).

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