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Note

Convenient synthesis of copper (I) thiolates and related compounds

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Abstract

Copper (I) salts of various anions including thiolates, diethyl dithiocarbamate, diethyl dithiophosphate, trithiocyanurate, 1-cyano-3-methylisothiourea, 2-aminothiazole, and tetrakis(1-imidazolyl)borate are conveniently synthesized by reducing copper (II) sulfate in aqueous ammonia. The addition of phosphine ligands to several of the products is demonstrated, and the crystal structure of $[Cu_2(MBT)_2(DPPE)_3]\cdot Et_2O$ (MBT = 2-mercaptobenzothiazolate, DPPE = 1,2-bis(diphenylphosphino)ethane) is reported.

Keywords: Copper (I); Thiolates; Phosphines; Dithiocarbamates; Dithiophosphates; Tetrakis(1-imidazolyl)borate

1. Introduction

Sulfur- and aromatic nitrogen-based anions form relatively stable compounds with copper (I). This is due to the favorable soft acid-soft base interaction. Recently, Cu(I) thiolates and similar species have been attracting considerable attention owing to their interesting photochemical properties [1]. Copper (I) thiolates, which are widely regarded as being polymeric, have been prepared by direct addition of an excess of thiol to aqueous solutions of copper (II) salts [2,3] or by electrochemical reduction of Cu(II) in the presence of thiol [4]. Dithiocarbamate salts of copper (I) have been prepared from dithiuram disulfides or by conproportionation of the copper (II) dithiocarbamate with copper metal [5]. Dithiophosphate salts of copper (I) can be made by reacting dithiophosphates with copper (I) salts (such as CuCl) dissolved in aqueous ammonia [6]. However, the foregoing solutions are fairly unstable, readily developing a blue color indicative of copper (II). Dithioanion salts of copper (I) are typically oligomeric, e.g. $[Cu(S_2CNEt_2)]_4$ [7] and $[Cu(S_2P(O^iPr)_2)]_n$ (n = 4, 6) [8].

A general strategy for the preparation of copper (I) salts of sulfur and nitrogen anions was suggested by a report of copper (I) acetylide synthesis from aqueous solution [9]. The two-step procedure involves reduction of copper (II) sulfate with hydroxylamine in the presence of ammonia to form the stable Cu(I) ammine complex, and reaction with the acid or alkali form of the desired anion, Eqs. (1) and (2) [10]. In this note, we demonstrate the generality of this procedure for preparing a variety of Cu(I) thiolates and related compounds, including the diethyldithiocarbamate ($S_2CNEt_2^-$), diethyldithiophosphate ($S_2P(OEt)_2^-$), 1-cyano-3-methylisothioureate ($CMIT^-$), tetrakis(1-imidazolyl)borate (BIm_4^-), 2-aminothiazolate, and trithiocyanurate ($TTC^-, C_3N_3S_3^-$).

$$2CuSO_4 + 4NH_3 + 2NH_2OH + 2OH^- \rightarrow 2[Cu(NH_3)_2]^+ + 2SO_4^{2-} + N_2\uparrow + 4H_2O. \quad (1a)$$

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$$4CuSO_4 + 8NH_3 + 2NH_2OH + 4OH^- \rightarrow 4[Cu(NH_3)_2]^+ + 4SO_4^{2-} + N_2O\uparrow + 5H_2O. \quad (1b)$$

$$[Cu(NH_3)_2]^+ + OH^- + HSR \rightarrow CuSR\downarrow + 2NH_3 + H_2O. \quad (2)$$

2. Experimental

2.1. General

All compounds were reagent grade and were used as received. All copper-containing products were analyzed for copper content by atomic absorption, as previously described [11].

2.2. Preparation of CuSPh

To an ice-cold mixture of 25 mL conc. aq. NH_3 and 100 mL H_2O was added $CuSO_4\cdot5H_2O$ (6.26 g, 25.1 mmol) forming a royal blue-colored solution. Over a period of 45 min., solid $NH_2OH\cdot HCl$ (3.89 g, 56.0 mmol) was added. Stirring overnight at 25 °C under N_2 purge produced a colorless solution of $[Cu(NH_3)_2]^+$. Using a syringe, a solution of PhSH (2.84 g, 25.8 mmol) in 125 mL EtOH was added. A pale yellow solid formed immediately. The solid product was collected via filtration and was washed with H_2O, EtOH, and ether in succession and vacuum-dried (3.89 g, 22.5 mmol, 89.6%). Other Cu(I) thiolates and the 2-aminothiazolate were prepared similarly.

2.3. Preparation of $Cu(S_2CNEt_2)$

A colorless solution of $[Cu(NH_3)_2]^+$ was produced as described above. Using a syringe, a solution of $NaS_2CNEt_2\cdot3H_2O$ (7.04 g, 31.3 mmol) in 80 mL H_2O was added. A yellow-brown solid formed immediately. The product was collected via filtration and was washed with H_2O, EtOH, and ether in succession and vacuum-dried. It was recrystallized by dissolving in $CHCl_3$ and precipitating with ether. The golden product was filtered, washed with additional ether, and vacuum dried (3.47 g, 16.4 mmol, 65.3%). Other Cu(I) compounds were prepared similarly using aqueous solutions of $NH_4S_2P(OEt)_2$, Na(CMIT), $Na(BIm_4)$, and $Na_3(C_3N_3S_3)\cdot9H_2O$. These insoluble products were not recrystallized.

2.4. Preparation of $[Cu_2(MBT)_2(DPPE)_3]$

1,2-Bis(diphenylphosphino)ethane (DPPE) (0.520 g, 1.31 mmol) was dissolved in 80 mL MeCN in a thick-walled reaction tube at 85 °C, and Cu(MBT) (0.200 g, 0.870 mmol) was suspended in the mixture. The tube was sealed and heated to 100 °C in an oil bath for 20 h. The cream colored product was collected via filtration and washed with hot MeCN and ether. The solid was vacuum dried (0.542 g, 0.327 mmol, 75.3%). X-ray quality crystals were grown by layering a solution of the product in $CHCl_3$ with ether in a 5-mm i.d. tube.

2.5. Preparation of $[Cu(BIm_4)(PPh_3)]$

Triphenylphosphine (0.325 g, 1.24 mmol) was dissolved in 80 mL CH_3CN in a thick-walled reaction tube and $Cu(BIm_4)$ (0.425 g, 1.24 mmol) was suspended in the mixture. The tube was heated to 100 °C in an oil bath for 18 h. The suspension was filtered, yielding a white solid which was washed with ether and vacuum dried (0.632 g, 1.04 mmol, 51.7%). Other phosphine adducts of Cu(I) salts were prepared similarly.

2.6. X-ray crystallographic study

Data collection was carried out at 173 K on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operating in the ϕ and ω scanning mode. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined riding on the respective carbon bonded atoms. The asymmetric unit consists of two crystallographically independent but chemically similar molecules residing on inversion centers, and a molecule of diethyl ether, one of the recrystallization solvents. All software was part of the Bruker libraries of programs (Bruker-AXS, Madison, WI).

3. Results and discussion

Reduction of $CuSO_4$ in aqueous ammonia solution by hydroxylamine proceeded smoothly when nitrogen was continuously purged directly through the solution. The complete reduction was signaled by the disappearance of the blue Cu(II) color. The resulting solution was sufficiently alkaline that acid substrates, such as thiols, were spontaneously deprotonated, producing the desired products, according to Eq. (2). The products were readily isolated and yields were good to excellent (Table 1). The results of elemental analysis confirmed the expected identity of the products.

The new complexes prepared include the Cu(I) salts of CMIT, BIm_4 [13], 2-aminothiazolate, and TTC ($C_3N_3S_3$). Copper (II) compounds have been reported for the TTC ligand [14]. However, the two TTC compounds reported herein are the first incorporating Cu(I). Thus reaction of three equivalents of Cu(I) with

Table 1
Copper compounds prepared

Compound	Color	Yield, %	Element	% (theory)	% (expt)
CuSPh	pale yellow	89.6	Cu	36.79	36.10
			C	41.73	41.38
			H	2.92	2.89
CuSCy	cream	74.9	Cu	35.55	35.70
			C	40.31	39.46
			H	6.20	6.15
CuS-*n*-$C_{12}H_{25}$	cream	64.2	Cu	23.99	23.80
			C	54.40	54.33
			H	9.51	9.58
Cu(MBT)	orange	71.2	Cu	27.65	27.70
			C	36.59	36.75
			H	1.75	1.76
			N	6.10	6.16
$[Cu_2(MBT)_2(DPPE)_3]$	cream	75.3	Cu	7.68	8.37
			C	66.77	65.99
			H	4.87	4.77
			N	1.69	1.86
$Cu(S_2CNEt_2)$	golden	65.3	Cu	30.00	29.46
			C	28.35	28.54
			H	4.76	4.75
			N	6.61	6.54
$Cu(S_2P(OEt)_2)$	white	64.3	Cu	25.54	25.39
			C	19.31	19.19
			H	4.05	4.02
$Cu(CMIT)\cdot 1/2H_2O$	white	74.2	Cu	34.04	33.22
			C	19.30	18.53
			H	2.70	2.42
			N	22.51	22.54
$Cu(CMIT)(PPh_3)$	white	100	Cu	13.87	14.23
			C	57.33	55.29
			H	4.35	4.27
			N	9.55	9.92
$Cu(CMIT)(PPh_3)_2$	white	86.9	Cu	8.82	9.14
			C	66.70	65.45
			H	4.88	4.85
			N	5.98	6.11
$Cu(CMIT)(DPPE)_{1/2}$	white	86.9	Cu	16.86	16.13
			C	50.99	49.99
			H	4.28	4.28
			N	11.14	9.97
$Cu(BIm_4)$	white	94.4	Cu	18.55	17.95
			C	42.07	41.86
			H	3.53	3.56
			N	32.70	32.55
$Cu(BIm_4)(PPh_3)$	white	84.2	Cu	10.50	10.28
			C	59.57	57.78
			H	4.50	4.38
			N	18.52	18.49
$Cu(BIm_4)(DPPE)_{1/2}$	white	57.9	Cu	11.73	11.51
			C	55.42	53.87
			H	4.46	4.28
			N	20.68	21.01
Cu(2-NH-thiazole)	tan	57.0	Cu	39.06	38.66
			C	22.15	22.11

(*continued on next page*)

Table 1 (*continued*)

Compound	Color	Yield, %	Element	% (theory)	% (expt)
			H	1.86	1.84
			N	17.22	17.03
$Cu_2H(C_3N_3S_3)\cdot H_2O$	brick red	44.8	Cu	39.67	40.16
			C	11.25	11.57
			H	0.94	1.08
			N	13.12	13.54
$Cu_3(C_3N_3S_3)\cdot 3/2H_2O$	red brown	91.7	Cu	48.65	49.63
			C	9.19	9.58
			H	0.77	0.73
			N	10.72	12.14

$Na_3C_3N_3S_3$ produced $Cu_3(C_3N_3S_3)\cdot 1.5H_2O$ and the reaction of two equivalents of Cu(I) with $Na_3C_3N_3S_3$ produced $Cu_2H(C_3N_3S_3)\cdot H_2O$. The use of one equivalent of Cu(I) per TTC ligand yielded an impure product, which did not correspond to a discrete stoichiometry.

Proposed structures for the insoluble complexes of the CMIT, BIm_4, and 2-aminothiazolate anions are shown in Chart 1. The structures of the TTC complexes are likely to be significantly more complicated and therefore speculation is probably not particularly useful.

A non-polymeric Cu(I) thiolate complex was produced by reacting the 2-mercaptobenzothiazolate compound Cu(MBT) with 1,2-bis(diphenylphosphino)-ethane (DPPE) in pressurized acetonitrile or toluene. This reaction produced a 2:3 Cu(MBT):DPPE complex which was structurally characterized as the Et_2O solvate by using X-ray crystallography (Fig. 1). Crystallo-

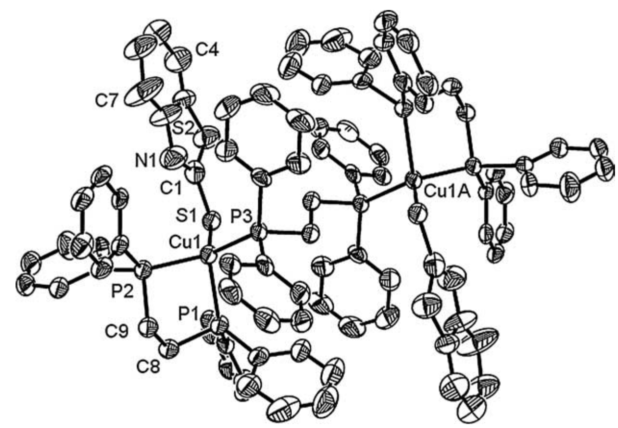

Fig. 1. Molecular structure of $[Cu_2(MBT)_2(DPPE)_3]\cdot Et_2O$. Thermal ellipsoids shown at 50%. One of two independent molecules shown; the solvent molecule omitted. Hydrogen atoms omitted for clarity.

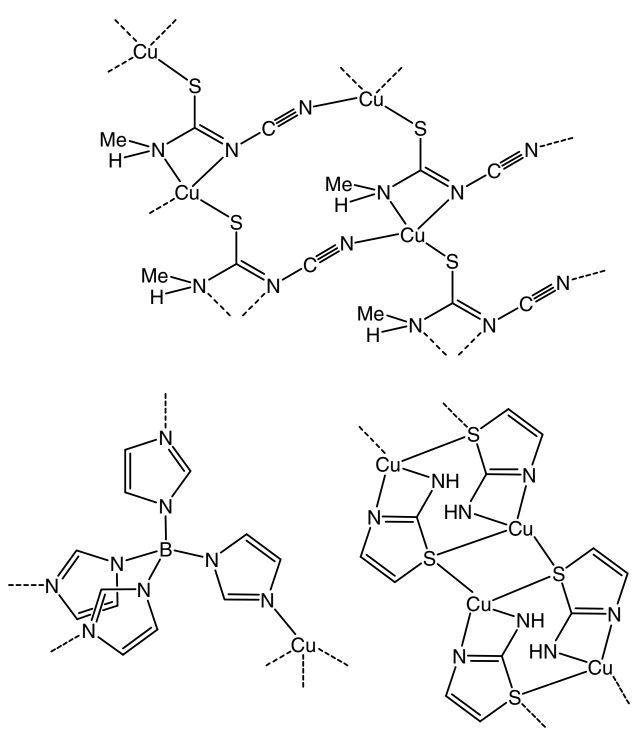

Chart 1.

Table 2
Crystal and structure refinement data for $[Cu_2(MBT)_2(DPPE)_3]\cdot Et_2O$

Formula	$C_{96}H_{90}Cu_2N_2OP_6S_4$
Formula weight	1728.84
T (K)	100
λ (Å)	0.71073
Crystal habit	colorless block
Crystal system	triclinic
Space group	$P\bar{1}$(#2)
a (Å)	16.6420(10)
b (Å)	17.2710(11)
c (Å)	18.3365(11)
α (°)	112.1901(11)
β (°)	90.0859(9)
γ (°)	118.3840(10)
Z	2
V (Å^3)	4186.0(4)
D_{calc} (g cm^{-3})	1.372
Absorption coefficient, μ (mm^{-1})	0.773
Scan technique	ϕ and ω
F(000)	1800
Crystal size, mm	0.25 × 0.20 × 0.10
Residuals:[a] R_1; wR_2	0.068; 0.147
Goodness-of-fit	1.128
θ Range for data collection (°)	1.23–25.00

[a] $R = R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ for observed data only. $R_w = wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data.

Table 3
Selected bond lengths and angles for $[Cu_2(MBT)_2(DPPE)_3]\cdot Et_2O$[a]

Cu(1)–P(1)	2.3313(15), 2.3296(16)	P(1)–Cu(1)–P(2)	89.47(6), 89.44(6)
Cu(1)–P(2)	2.2865(17), 2.2825(16)	P(1)–Cu(1)–P(3)	107.86(6), 107.91(6)
Cu(1)–P(3)	2.2820(14), 2.2789(14)	P(2)–Cu(1)–P(3)	115.65(6), 115.67(6)
C(2)–C(7)	1.352(9), 1.332(10)	P(1)–Cu(1)–S(1)	109.46(6), 108.99(6)
Cu(1)–S(1)	2.3104(17), 2.3086(17)	P(2)–Cu(1)–S(1)	118.59(6), 118.82(6)
C(3)–C(4)	1.348(8), 1.328(10)	P(3)–Cu(1)–S(1)	112.63(6), 112.70(6)
S(1)–C(1)	1.717(6), 1.702(7)	Cu(1)–S(1)–C(1)	106.9(2), 107.2(2)
S(2)–C(1)	1.750(6), 1.759(7)	S(1)–C(1)–S(2)	117.9(4), 117.8(3)
N(1)–C(1)	1.297(8), 1.298(7)	N(1)–C(1)–S(1)	127.4(5), 128.1(6)
S(2)–C(3)	1.693(6), 1.699(6)	N(1)–C(1)–S(2)	114.6(5), 114.2(5)
N(1)–C(2)	1.414(8), 1.414(9)	C(1)–S(2)–C(3)	92.2(3), 92.3(3)
C(2)–C(3)	1.439(9), 1.441(9)	C(1)–N(1)–C(2)	110.3(6), 110.6(6)
C(4)–C(5)	1.392(10), 1.396(9)	N(1)–C(2)–C(3)	115.3(6), 115.5(6)
C(5)–C(6)	1.362(10), 1.362(10)	C(2)–C(3)–S(2)	107.5(4), 107.2(5)
C(6)–C(7)	1.352(9), 1.332(10)		

[a] Data pairs represent independent half molecules. Numbering corresponds to molecule shown in Fig. 1.

graphic and structural data are shown in Tables 2 and 3, respectively. Structurally characterized copper (I) thiolates bearing solubilizing ligand (such as phosphines or pyridines) are fairly rare [3,4]. X-ray analysis revealed two independent half molecules and an ether solvent molecule. The molecular structure of $[Cu_2(MBT)_2(DPPE)_3]\cdot Et_2O$ is composed of two copper centers bridged by a DPPE ligand. A chelating DPPE ligand is coordinated to each copper. A MBT ligand is coordinated to each copper only through the thiolate sulfur atom. This dimeric arrangement is directly analogous to that found for $[Cu_2I_2(DPPE)_3]$ [15] which features terminal iodide rather than terminal thiolate. Somewhat similar is $[Cu_3I_3(DPPE)_3$(2-pyridylthiolate)] [16]. In the latter structure, both terminal and bridging iodides and both chelating and bridging DPPE ligands are present.

The $Cu(BIm_4)$ and Cu(CMIT) salts were also found to coordinate phosphine ligands. When a suspension of $Cu(BIm_4)$ was heated in acetonitrile solution containing PPh_3 or DPPE, the products $[Cu(BIm_4)(PPh_3)]$ and $[Cu(BIm_4)(DPPE)_{1/2}]$ were collected. The addition of a single P(III) ligand per Cu(I) center suggests that the BIm_4 anion coordination can be lowered from four- to three-coordinate. Similarly, $[Cu(CMIT)(PPh_3)]$ and $[Cu(CMIT)(DPPE)_{1/2}]$ have been obtained. Further studies of these new metal-organic networks are on-going.

4. Conclusion

We have presented a simple and apparently general synthesis leading to sulfur- and nitrogen-based salts of copper (I) and have characterized a rare example of a ligand supported copper (I) thiolate salt.

5. Supplementary material

CCDC-252221 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; email: deposit@ccdc.cam.ac.uk].

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