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Hexameric and Tetrameric Copper(I) Thioamidates

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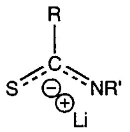
The two copper(I) thioamidates $\{Cu[RCS(NR')]\}_x$ (R = *n*-Bu, R′ = *t*-Bu; R, R′ = Me) are obtained via reaction of copper(I) chloride with lithium thioamidates. Both occur as a mixture of hexamer and tetramer, detectable in solution by ^{1}H NMR spectroscopy. The hexamer is favored for methyl substituents, whereas the tetramer is the major product when bulkier butyl groups are used. These clusters are the first examples of copper(I) thioamidates and are the first metal thioamidates prepared via metathesis. The X-ray structures of $\{Cu[MeCS(NMe)]\}_6$ and $\{Cu[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}_4$ are presented, and a mechanism for their formation based on aggregation of dimeric units is suggested. The core of the tetramer comprises a Cu_4 tetrahedron with short Cu···Cu distances. Each Cu_3 face of the tetrahedron is bridged by a η^1(N),μ_2(S) thioamidate unit. A similar bridging arrangement is seen in the hexamer, but in this case the ligands are organized in a paddle-wheel fashion about a Cu_6S_6 pseudohexagonal prismatic core. In the case of $\{Cu[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}_x$ (x = 4, 6) the two oligomers are easily separated and the tetramer can be converted to the hexamer on heating above 100 °C.

Introduction

Carboxylate anions $[RCO_2]^-$ are ubiquitous, as are a number of other related species such as carbamates $[(NR_2)CO_2]^-$, xanthates $[(OR)CS_2]^-$, dithiocarbamates $[(NR_2)CS_2]^-$, etc. Somewhat less common are isoelectronic analogues that retain the central RC portion of the carboxylate ligature while replacing oxygen with various other main-group centers: e.g., amidinates $[RC(NR')_2]^-$, oxoamidates $[RCO(NR')]^-$, thioamidates $[RCS(NR')]^-$, thiocarboxylates $[RCOS]^-$, dithiocarboxylates $[RCS_2]^-$, etc. Thioamidates are of particular interest due to their ambidentate combination of hard (N) and soft (S) centers.

Investigation of the structural features of alkali-metal heterocarboxylates is an important prelude to understanding their ligand behavior. Prior to our recent work in this area,[1] however, no transition-metal or main-group derivatives of thioamidates had been prepared by metathetical routes (although several were prepared by other means).[2] Following our characterization of three thioamidate ligands as their lithium salts (**1**, R = *n*-Bu, R′ = *t*-Bu; **2**, R = Me, R′ = *t*-Bu; **3**, R, R′ = Me),[3] we wished to show that these reagents could be employed in metathetical reactions.



1: R = *n*-Bu, R′ = *t*-Bu
2: R = Me, R′ = *t*-Bu
3: R, R′ = Me

A number of recent reports have focused on the use of cyanate,[4] thiocyanate,[5] and thiocarboxylate[6] anions as ligands for coinage metals, particularly Cu(I). Much of this interest has stemmed from the discovery of molecular magnetic materials comprised of metal−cyano bridges.[7] Further impetus for the study of copper centers ligated by nitrogen- and sulfur-containing compounds is provided by their biological relevance. For example, blue-copper proteins are well-known to carry out electron transfer using a Cu(I)/Cu(II) redox couple.[8]

The structural consequences of replacing alkali metals with coinage metals in main-group-cluster compounds can be difficult to predict. Wright and co-workers have observed different behavior for $[\{As_2(NCy)_4\}_2M_4]$ (M = Li,[9] Na, Cu[10]) than for the related system $[\{Sb_2$-

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$(NCy)_4\}_2M_4]$ (M = Li,[11] Na,[12] Cu, Ag[13]). In the latter case the lithium derivative differs significantly from the sodium, copper, and silver complexes, all of which have similar structures. The arsenic compound shows similar behavior in the lithium and sodium cases, but the copper derivative exhibits a "dramatic change" in cluster architecture.

Here we describe the synthesis and X-ray structural characterization of two copper(I) thioamidates $\{Cu[RCS(NR')]\}_x$ (**4**, R, R′ = Me; **5**, R = *n*-Bu, R′ = *t*-Bu) prepared via eq 1. Both **4** and **5** occur as a mixture of hexamer

$$\mathrm{CuCl} + \mathrm{Li[RCS(NR')]} \rightarrow {}^{1}/_{x}\{\mathrm{Cu[RCS(NR')]}\}_x + \mathrm{LiCl} \qquad (1)$$

and tetramer (**4a**, **5a**, $x = 4$; **4b**, **5b**, $x = 6$). The formation of these hexameric and tetrameric clusters, and their interconversion, is discussed in the context of related examples from the literature, and a common dimeric precursor is invoked.

Experimental Section

General Procedures. All reactions and manipulations of air- or moisture-sensitive compounds were carried out using standard glovebox and Schlenk techniques under an atmosphere of high-purity, dried argon. Solvents were distilled prior to use by using standard techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories in predried ampules and degassed by using three freeze/thaw cycles prior to use. All solvents were stored over molecular sieves in glass flasks equipped with Teflon needle valves and hose-joint sidearms. The lithium thioamidates **1** and **3** were prepared using previously reported procedures,[3] and CuCl was obtained from Aldrich and used as received.

Preparation of $\{Cu[MeCS(NMe)]\}_x$ (4). Addition of dry acetonitrile (15 mL) to CuCl (0.079 g, 0.80 mmol) produced a clear, pale green solution. This was added dropwise to a stirred yellow solution of Li[MeCS(NMe)] (**3**; 0.076 g, 0.80 mmol) in acetonitrile (15 mL) over several minutes at 23 °C. As addition proceeded, the reaction mixture initially became clear and amber in color, and it finally turned orange and opaque. After 1 h of stirring, the solution was allowed to settle, giving a clear, faintly orange mother liquor over an orange solid. The supernatant liquid was decanted and the solid washed with acetonitrile (2 × 10 mL) and methylene chloride (2 × 10 mL). Removal of solvent from the remaining solid under dynamic vacuum yielded a dry, orange powder identified as $\{Cu[MeCS(NMe)]\}_x$ (**4**; 0.098 mmol, 0.089 g, 72%). Mp: 146−149 °C dec. Anal. Calcd for CuC_3H_6NS: C, 23.75; H, 3.99; N, 9.23. Found: C, 24.10; H, 3.61; N, 8.27.

4a. The tetrameric oligomer $\{Cu[MeCS(NMe)]\}_4$ (**4a**) could not be separated from the hexamer **4b**, and attempts to grow crystals suitable for X-ray diffraction were unsuccessful. It was identified in the bulk product mixture by ^1H NMR (200 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 25 °C): δ 4.27 (s, [MeCS(N*Me*)], 3H), 1.36 (s, [*Me*CS(NMe)], 3H). Yield: 5% (of the recovered product **4**), estimated by ^1H NMR of the bulk mixture.

4b. Storage of the decanted mother liquor from the reaction mixture for 48 h at −14 °C yielded red crystals of $\{Cu[MeCS(NMe)]\}_6$ (**4b**), identified by X-ray diffraction. Yield: 66% (of the recovered product **4**), estimated by ^1H NMR of the bulk mixture. IR (KBr, Nujol mull; ν (cm^{-1})):: 2727, 1574, 1305, 1261, 1169, 1111, 937, 801. ^1H NMR (200 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 25 °C): δ 2.65 (s, [MeCS(N*Me*)], 3H), 1.88 (s, [*Me*CS(NMe)], 3H). ^{13}C NMR (50.288 MHz, δ (TMS in $CDCl_3$); in C_4D_8O at 27 °C): δ 183.12 (s, [Me*C*S(NMe)]), 41.92 (s, [MeCS(N*Me*)]), 24.07 (s, [*Me*CS(NMe)]). LRMS (EI, 70 eV; *m*/*e*): 89, $\{H[MeCS(NMe)]\}^+$, 46%.

Preparation of $\{Cu[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}_x$ (5). A pale green solution of CuCl (0.211 g, 2.12 mmol) in acetonitrile (5 mL) was added dropwise to a stirred slurry of Li[(*n*-Bu)CS(N*t*-Bu)] (**1**; 0.382 g, 2.12 mmol) in acetonitrile (5 mL) over several minutes at 23 °C. An opaque orange reaction mixture ensued, and on cessation of stirring, a white solid was observed to settle out below a clear orange mother liquor. This mixture was stirred for 30 min, during which time no further changes were observed. The orange solution was decanted, and the remaining solid was washed with acetonitrile until the washings became colorless (3 × 5 mL). Removal of residual solvent from the solid material under dynamic vacuum produced a pale yellow powder identified as $\{Cu[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}_4$ (**5a**; 0.359 g, 1.509 mmol, 75%) by X-ray crystallography. The mother liquor and washings were also collected and pumped to dryness, yielding an orange powder. This was washed with CH_2Cl_2 (2 × 5 mL) and again pumped to dryness, producing $\{Cu[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}_6$ (**5b**; 0.075 g, 0.032 mmol, 15%).

5a. An alternative procedure was employed to produce crystals of **5a** suitable for X-ray diffraction and other analyses. The reaction was carried out in *n*-hexane (10 mL) with a few drops of acetonitrile. Removal of solvents in vacuo gave an oily brown solid. Extraction of this product with *n*-hexane (2 × 5 mL) and MeCN (2 × 5 mL) left a dry brown solid on pumping down. Clear, colorless crystals of the tetramer **5a** were obtained from the *n*-hexane washings after storage at −14 °C overnight. Mp: 100−103 °C dec (to a brown solid), 126−130 °C (brown liquid). Anal. Calcd for $CuC_9H_{18}NS$: C, 45.83; H, 7.69; N, 5.94. Found: C, 45.91; H, 7.58; N, 5.90. IR (KBr, Nujol mull; ν (cm^{-1})): 2726, 1558, 1302, 1261, 1231, 1190, 1139, 1101, 1035, 1023, 802, 722. ^1H NMR (200 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 25 °C): δ 2.8−2.6 (m, $[-\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}]$, 2H), 2.2−1.9 (m, $[-\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CH_3}]$, 2H), 1.46 (s, $[\text{-}\mathrm{C(C}\mathit{H}_3)_3]$, 9H), 1.4−1.2 (m, $[-\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}]$, 2H), 0.88 (t, $[-\mathrm{CH_2CH_2CH_2C}\mathit{H}_3]$, 3H). ^{13}C NMR (50.288 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 27 °C): δ 186.3 (s, [(*n*-Bu)*C*S(N-*t*-Bu)]), 58.7, (s, $[-\mathit{C}\mathrm{(CH_3)_3}]$), 41.2 (s, $[-\mathit{C}\mathrm{H_2CH_2CH_2CH_3}]$), 32.9 (s, $[-\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}]$), 31.9 (s, $[-\mathrm{C(}\mathit{C}\mathrm{H_3)_3}]$), 23.7 (s, $[-\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}]$), 14.5 (s, $[-\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}]$). LRMS (EI, 70 eV; *m*/*e*): 173, $\{H[(n\text{-}Bu)CS(N\text{-}t\text{-}Bu)]\}^+$, 39%.

5b. ^1H NMR (200 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 25 °C): δ 2.8−2.6 (m, $[-\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}]$, 2H), 2.3−2.1 (m, $[-\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CH_3}]$, 2H), 1.36 (s, $[-\mathrm{C(C}\mathit{H}_3)_3]$, 9H), 1.3−1.1 (m, $[-\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}]$, 2H), 0.86 (t, $[-\mathrm{CH_2CH_2CH_2C}\mathit{H}_3]$, 3H). ^{13}C NMR (50.288 MHz, δ (TMS in $CDCl_3$); in C_6D_6 at 27 °C): δ 184.5 (s, [(*n*-Bu)*C*S(N-*t*-Bu)]), 57.6, (s, $[-\mathit{C}\mathrm{(CH_3)_3}]$), 40.8 (s, $[-\mathit{C}\mathrm{H_2CH_2CH_2CH_3}]$), 32.6 (s, $[-\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}]$), 32.1 (s, $[-\mathrm{C(}\mathit{C}\mathrm{H_3)_3}]$), 24.0 (s, $[-\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}]$), 14.7 (s, $[-\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}]$).

X-ray Measurements. Data were collected at low temperature using oil (Paratone 8277, Exxon Corp.) or epoxy-coated crystals mounted on glass fibers. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Empirical absorption corrections were applied in each case.[14] Non-hydrogen atoms

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Table 1. Crystallographic Data for 4a and 5a

	4a	**5a**
mol formula	$C_{18}H_{36}N_6S_6Cu_6$	$C_{36}H_{72}N_4S_4Cu_4$
fw	910.16	943.42
cryst syst	monoclinic	tetragonal
space group	$C2/c$ (No. 15)	$I4_1/a$ (No. 88)
a (Å)	18.760(8)	18.157(3)
b (Å)	15.168(9)	
c (Å)	11.757(8)	14.624(5)
V (Å^3)	3238(3)	4821(1)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.867	1.298
abs coeff (cm^{-1})	42.77	19.38
F_{000}	1824	1984
cryst size (mm)	0.50 × 0.20 × 0.03	0.40 × 0.40 × 0.35
$2\theta_{max}$ (deg)	50.1	50.1
no. of rflns collected	6148	1250
no. of indep rflns	5994	1196
R_{int}	0.073	0.000
no. of data ($I > 2\sigma(I)$)/ params	1114/163	470/113
max shift/error in final cycle	0.01	0.000
goodness of fit	1.38	0.973
residuals	$R^a = 0.049$ $R_w{}^b = 0.050$	$R1^c = 0.0416$ $wR2^d = 0.1397$
largest diff peak, hole (e Å^{-3})	0.69, −0.64	0.235, −0.231
max, min transmission factors	0.4895, 1.0000	0.5503, 0.5111

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = [\sigma^2(F_o)]^{-1} = [\sigma_c{}^2(F_o) + 0.25p^2F_o{}^2]^{-1}$, $p = 0.021$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o{}^2 > 2\sigma F_o{}^2$. [d] $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$ (all data); $w = [\sigma(F_o{}^2) + (0.0571p)^2F_o{}^2]^{-1}$, $p = [\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2]/3$.

were refined anisotropically, while hydrogen atoms were included at geometrically idealized positions and not refined. Crystallographic data are presented in Table 1.

4b. The data were corrected for decay (2.99%). The structure was solved by direct methods[15] and expanded using Fourier techniques.[16] Full-matrix least-squares refinement was performed using the teXsan crystallographic software package of Molecular Structure Corp.[17]

5a. The structure was solved by direct methods[18] and refined using the full-matrix least-squares method on F^2.[19] The thermal parameters for C(2)−C(5) (the *n*-butyl group) are higher than would normally be expected due to a small degree of uncertainty in the positions of C(2) and C(3). The maximum and minimum peaks in the final difference Fourier map corresponded to 0.24 and −0.23 e/Å^3, respectively, and the final R1 value was 0.042, confirming that the solution was satisfactory even though the observations/parameter ratio (470/115 = 4:1) was rather low.

Results and Discussion

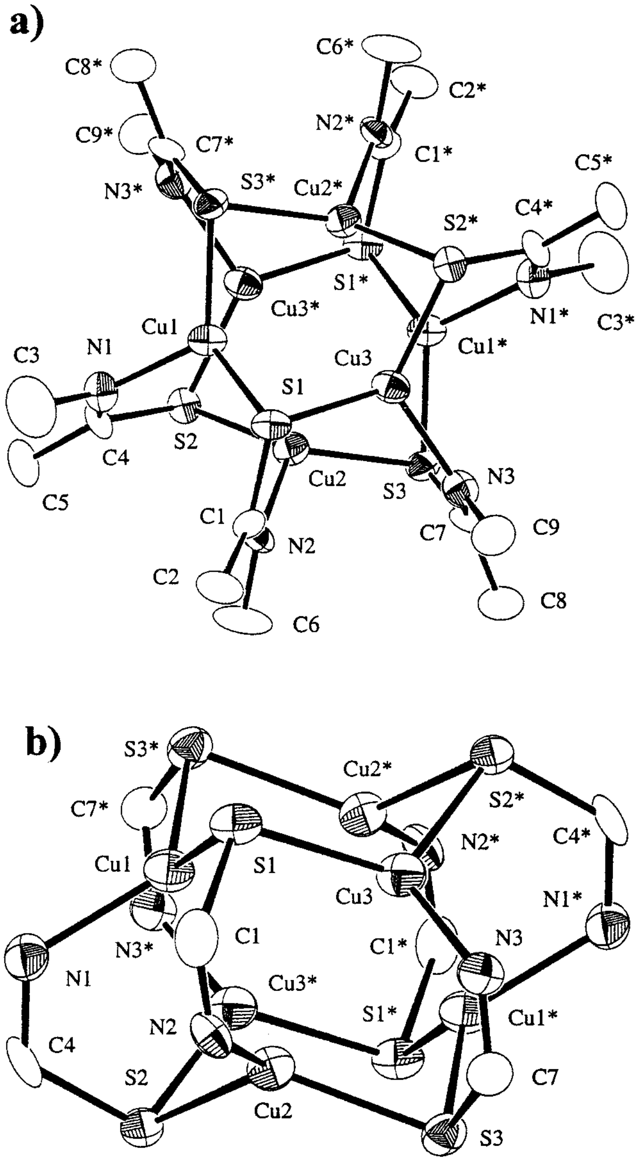

Figure 1. ORTEP diagrams of **4b** showing the atom-labeling scheme: (a) down the C_3 axis of symmetry, with H atoms removed for clarity; (b) down a C_2 axis, with CH_3 groups removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformations used to generate equivalent atoms: (*) $^3/_2 - x$, $^1/_2 - y$, $-z$.

Synthesis of 4a,b and X-ray Structure of 4b. The addition of Li[MeCS(NMe)] (**3**) to an equimolar amount of CuCl in acetonitrile (eq 1: R, R′ = Me) produced an orange solid that was moderately stable in air. CHN analyses were consistent with the empirical formula Cu[MeCS(NMe)], and red plates crystallized from a solution of this product in acetonitrile at −14 °C. An X-ray structural determination of **4b** revealed the hexameric aggregate {Cu[MeCS(NMe)]}$_6$ (see Figure 1). Selected metrical parameters are summarized in Table 2. The thioamidate ligands in **4b** bridge three Cu^+ centers in an η^1(N),μ_2(S) fashion, and six Cu[MeCS(NMe)] units are organized in a paddle-wheel arrangement with D_{3d} symmetry. The core of the molecule consists of a pseudohexagonal prismatic [Cu_6S_6] core, wherein two stacked, chair-shaped Cu_3S_3 rings are joined by the C−N bridges of the thioamidate ligands but not by Cu−S bonding.

The arrangement observed in **4b** is similar to that observed for {Li[(*n*-Bu)CS(N*t*-Bu)]}$_6$ (**1**).[3] In **1**, however, a true hexagonal-prismatic core involving 4-fold coordination of lithium is achieved through the formation of Li−S rungs between the two Li_3S_3 rings (Figure 2).

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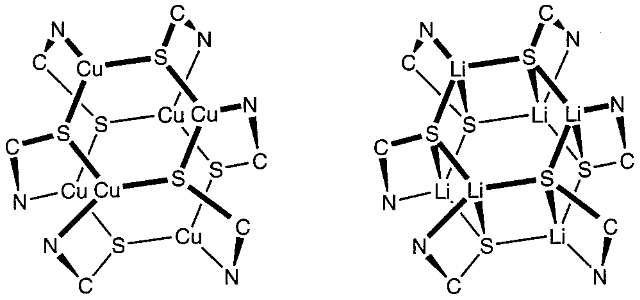


4b **1**

Figure 2. Schematic diagrams of the cores of **4b** (Me groups on C and N removed for clarity) and **1** (*t*-Bu groups on N and *n*-Bu groups on C removed for clarity).

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 4a and 5a

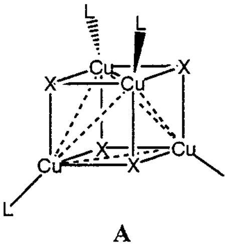
4a		5a	
Cu(1)−S(1)	2.273(5)	Cu(1)−S(1)	2.267(3)
Cu(1)−S(3)*	2.229(4)	Cu(1)−S(1)′	2.282(3)
Cu(2)−S(2)	2.241(5)	Cu(1)−N(1)*	1.994(9)
Cu(2)−S(3)	2.253(4)	S(1)−C(1)	1.776(11)
Cu(3)−S(1)	2.270(4)	N(1)−C(1)	1.286(13)
Cu(3)−S(2)*	2.248(4)	Cu(1)−Cu(1)″	2.592(2)
Cu(1)−N(1)	2.030(12)	Cu(1)−Cu(1)′	2.592(2)
Cu(2)−N(2)	2.019(11)	Cu(1)−Cu(1)*	2.721(3)
Cu(3)−N(3)	2.031(13)		
S(1)−C(1)	1.770(16)		
S(2)−C(4)	1.745(14)		
S(3)−C(7)	1.805(17)		
N(1)−C(4)	1.300(17)		
N(2)−C(1)	1.284(17)		
N(3)−C(7)	1.236(17)		
S(1)−Cu(1)−S(3*)	117.30(17)	S(1)−Cu(1)−S(1)′	121.00(8)
S(2)−Cu(2)−S(3)	123.60(16)	Cu(1)−S(1)−Cu(1)″	69.47(10)
S(1)−Cu(3)−S(2*)	118.51(15)	N(1)−C(1)-S(1)	119.9(10)
Cu(1)−S(1)−Cu(3)	84.46(14)	Cu(1)″−Cu(1)−Cu(1)′	63.32(6)
Cu(2)−S(2)−Cu(3*)	80.14(15)	Cu(1)″−Cu(1)−Cu(1)*	58.34(3)
Cu(1)*−S(3)−Cu(2)	80.82(15)	Cu(1)′−Cu(1)−Cu(1)*	58.34(3)
S(1)−C(1)−N(2)	119.4(11)	C(1)−S(1)−Cu(1)	107.4(4)
S(2)−C(4)−N(1)	119.8(11)	C(1)−S(1)−Cu(1)″	110.7(4)
S(3)−C(7)−N(3)	118.0(13)	C(1)−N(1)−Cu(1)*	116.5(9)
Cu(1)−N(1)−C(4)−S(2)	−6.6(17)	Cu(1)*−N(1)−C(1)−S(1)	−0.2(16)
Cu(2)−N(2)−C(1)−S(1)	−3.2(19)		
Cu(3)−N(3)−C(7)−S(3)	7.4(18)		

The mean Li−S bond distance in **1** was 2.405(7) Å within the Li_3S_3 rings, and 2.638(7) Å for the bridged Li−S bonds. For comparison, the mean Cu−S distance in the Cu_3S_3 rings of **4b** is 2.252(4) Å, whereas the nonbonded Cu−S distances between the two rings are all greater than 3.2 Å. Thus, replacing 4-coordinate lithium with 3-coordinate copper(I) allows the two E_3S_3 rings of the hexamer to move farther apart while the overall hexagonal-prismatic shape of the complex is retained (Figure 2).

Despite the bridging mode of the thioamidate units in **4b**, there is still considerable contraction of the internal bond angle at carbon (|∠SCN| = 119.1(12)°; cf. 126.64(16)° for MeCS(HN-*t*-Bu)[20] and 127.3(7)° for the polymer {Li·2THF[MeCS(NMe)]}$_\infty$ (**3**·2THF), in which the thioamidate is also bridging.[3b] Surprisingly, this parameter does not differ significantly in **1** and **4b**, suggesting that it may arise as a consequence of the paddle-wheel conformation itself rather than from steric pressure applied by bulky substituents and/or intra-ring bonding (viz. bidentate chelation). Accommodation for the increased distance between the two E_3S_3 rings is apparently made at N; the mean internal angle is much larger in **4b** (|∠CuNC| = 123.03(11)°) than in **1** (|∠LiNC| = 105°). The corresponding angle in **3**·2THF (|∠LiNC| = 127.3(7)°) is quite close to that in **4b**, suggesting that the Li−S rungs in **1** are actually responsible for the contraction.

The mean C−N bond length within the NCS unit of **4b** (|*d*(C−N)| = 1.273(17) Å) is similar to those observed in **1** and **3**·2THF (|*d*(C−N)| = 1.268(5) and 1.279(8) Å, respectively). (The Cu−N distances in **4b** (|*d*(Cu−N)| = 2.026(12) Å (cf. a predicted length of 2.06 Å[21] when copper is four-coordinate) are actually quite close to typical Li−N distances (e.g. |*d*(Li−N)| = 1.988(7) Å in **1**). The C−S bond lengths in **4b** and **1** are similar (|*d*(C−S)| = 1.773(16) Å and 1.773(5) Å, respectively) and are elongated with respect to those in **3**·2THF (*d*(C−S) = 1.716(8) Å), providing further evidence that structural changes arising from the lack of inter-ring Cu−S contacts in **4b** are manifested mostly in a change of geometry around nitrogen. For comparison, the corresponding mean bond distances in the chelated complex $NbCl_3[MeCS(NMe)]_2$ are |*d*(C−S)| = 1.732 Å and |*d*(C−N)| = 1.30(2) Å.[2f]

Synthesis of 5a,b and X-ray Structure of 5a. The reaction of **1** with CuCl in acetonitrile (eq 1: R = *n*-Bu, R′ = *t*-Bu) produced pale yellow and brown products in 72% and 15% yields, respectively, both of which were moderately stable in air. The pale yellow product gave colorless crystals from *n*-hexane, and a structural determination by single-crystal X-ray diffraction revealed the unsolvated, tetrameric aggregate {Cu[(*n*-Bu)CS(N-*t*-Bu)]}$_4$ (**5a**) centered around a tetrahedral Cu_4 core (Figure 3). Selected metrical parameters are summarized in Table 2. Each face of the Cu_4 tetrahedron in **5a** is bridged by a η^1(N),μ_2(S) thioamidate unit. This arrangement resembles the more well-known structural archetype **A**, adopted by [CuXL]$_4$ (*X* = halide, L = phosphine, arsine).[22] The tetramer **5a** can be considered an analogue of **A** wherein no ligands L are present and X is a thioamidate rather than a halide.



A

The thioamidate unit in **5a** is almost planar, and the plane of the bridging unit approximately bisects the triangle defined by the three copper centers it bridges. Thus, the torsion angle Cu(1)*−N(1)−C(1)−S(1) is close to zero (τ = −0.2(16)°), and the pertinent Cu−S distances are similar (*d*(Cu(1)−S(1)) = 2.267(3) Å,

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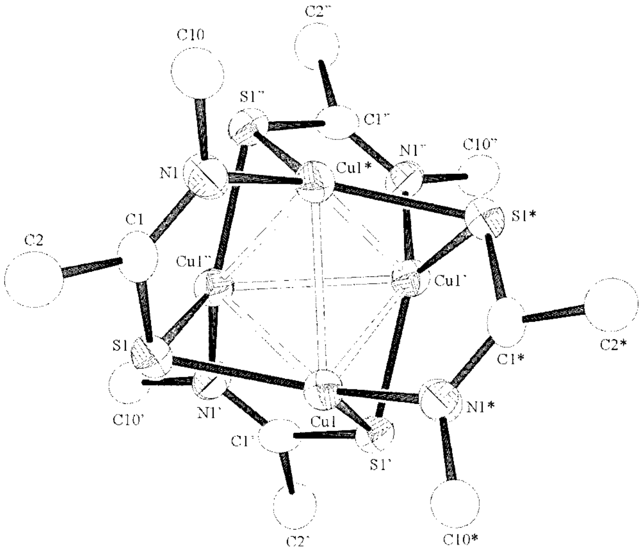


Figure 3. ORTEP diagram of **5a** showing the atom-labeling scheme. Only the α-carbon atoms of the *t*-Bu and *n*-Bu groups on N and C, respectively, are shown. Thermal ellipsoids are drawn at the 30% probability level, and unfilled bonds are used to indicate short Cu···Cu distances. Symmetry transformations used to generate equivalent atoms: (*) $-x$, $^1/_2 - y$, z; (′) $^1/_4 - x$, $y - ^1/_4$, $^5/_4 - z$; (″) $x + ^1/_4$, $^1/_4 - y$, $^5/_4 - z$.

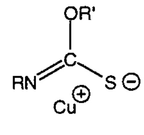
d(Cu(1)−S(1′))= 2.282(3) Å). The corresponding mean torsion angle in **4b** is also very small ($|\tau|$ = 5.7(18)°), and the internal angle of the bridging unit (∠(N(1)−C(1)−S(1)) = 119.1(12)°) is close to that observed for **5a** (119.9(10)°). The internal angle at N is somewhat smaller in **5a** (∠(C(1)−N(1)−Cu(1)*) = 116.5(9)°) than the corresponding parameter in **4b** (123.03(11)°). Bond distances within the thioamidate unit of **5a** do not differ significantly from those observed earlier for similar compounds (e.g. d(C(1)−N(1)) = 1.286(13) Å, d(C(1)−S(1)) = 1.776(11) Å). The Cu−N distance (d(Cu(1)−N(1)*) = 1.994(9) Å) is close to that seen in **4b** ($|d$(Cu−N)$|$ = 2.026 Å) and very close to the mean Li−N distance reported for **1** ($|d$(Li−N)$|$ = 1.988(7) Å).

The tetrahedron formed by the four copper centers in **5a** is fairly regular, with one nominally longer Cu···Cu distance (d(Cu(1)−Cu(1)*) = 2.721(3) Å, d(Cu(1)−Cu(1)′) = 2.592(2) Å, d(Cu(1)−Cu(1)′) = 2.592(2) Å) and Cu···Cu···Cu angles close to 60° (63.32(6), 58.34(3), 58.34(3)°). The issue of Cu···Cu interactions in polynuclear compounds of Cu(I) is a matter of some contention.[23] Reports by Pyykkö and co-workers suggest that “attractive intra- and intermolecular secondary bonding interactions between d^{10} cations lead to formation of dimers, oligomers, chains, and sheets”.[23c] However, more recent work by Cotton et al.[24] has indicated that short Cu···Cu separations are better explained in terms of ligand-imposed cluster geometry.

NMR Studies of the Tetramer to Hexamer Conversion. For both **4** and **5**, NMR spectra of the bulk products in arene solvents indicated mixtures of oligomers. In the case of **4** the predominant species was the hexamer **4b**. This can be isolated from the bulk mixture[25] by fractional crystallization and is readily identified both by its red color and by ^{1}H NMR resonances at 2.65 and 1.88 ppm. A second species, probably the corresponding tetramer **4a**, was identified as a minor product by resonances corresponding to CH_3 groups at 4.27 and 1.36 ppm in the ^{1}H NMR spectrum of the bulk product. Despite numerous attempts, we were unable to obtain crystals of this oligomer suitable for X-ray analysis.

Only two products were present in the bulk mixture of **5**. These could be easily separated on the basis of their different solubilities, and they were identified by their distinctive ^{1}H and ^{13}C NMR spectra. The tetramer **5a** is obtained as a pale yellow powder (colorless when crystalline), whereas the second product, tentatively identified as the hexamer **5b**, is brown. During the melting point determination of **5a** a color change from pale yellow to brown was observed before melting (100−103 °C), suggesting that the conversion of **5a** to **5b** might take place upon heating. Accordingly, variable-temperature proton NMR studies were conducted on a solution of **5a** in d_8-toluene. No changes were observed up to 100 °C; however, above this temperature a second set of signals corresponding to **5b** emerged. When the temperature was lowered to 23 °C, the new signals remained, and the solution had become brown in color. In addition, a solution of **5a** in d_6-benzene was observed by ^{1}H and ^{13}C NMR to convert slowly to **5b** over several days at 23 °C. These observations indicate that the hexamer is favored thermodynamically over the tetramer in this case and that irreversible conversion of the latter to the former takes place in solution. A similar phenomenon has been reported by Samuelson and co-workers for the conversion of the “yellowish” dimer $\{Cu[(OC_6H_4Me\text{-}4)CS(NPh)](PPh_3)_2\}_2$ to the orange hexamer $\{Cu[(OC_6H_4Me\text{-}4)CS(NPh)]\}_6$ free of PPh_3 in a mixture of methylene chloride and acetonitrile (3:2).[26]

Hexameric Cu(I) Aggregates. Although **4** and **5** are the first examples of copper(I) thioamidates and the metathetical route presented here is a new path to metal thioamidate derivatives, the $[Cu_6S_6]$-based paddle-wheel conformation adopted by **4b** is not novel. The copper(I) azaxanthates **6**[26] and **7**[27] were prepared by



6: R = Ph, R' = C_6H_4-4-Me
7: R = Me, R' = C_6H_4-4-Me
8: R = CH_2=$CHCH_2$, R' = Me

insertion of isothiocyanates into the Cu−O bonds of copper(I) aryloxides, while **8**[28] was formed via reaction of the appropriate isothiocyanate with $[Cu(MeCN)_4]ClO_4$ in the presence of methanol. Each adopts an open, hexameric paddle-wheel conformation analogous to that seen in **4b** in the solid state. A number of other bent-

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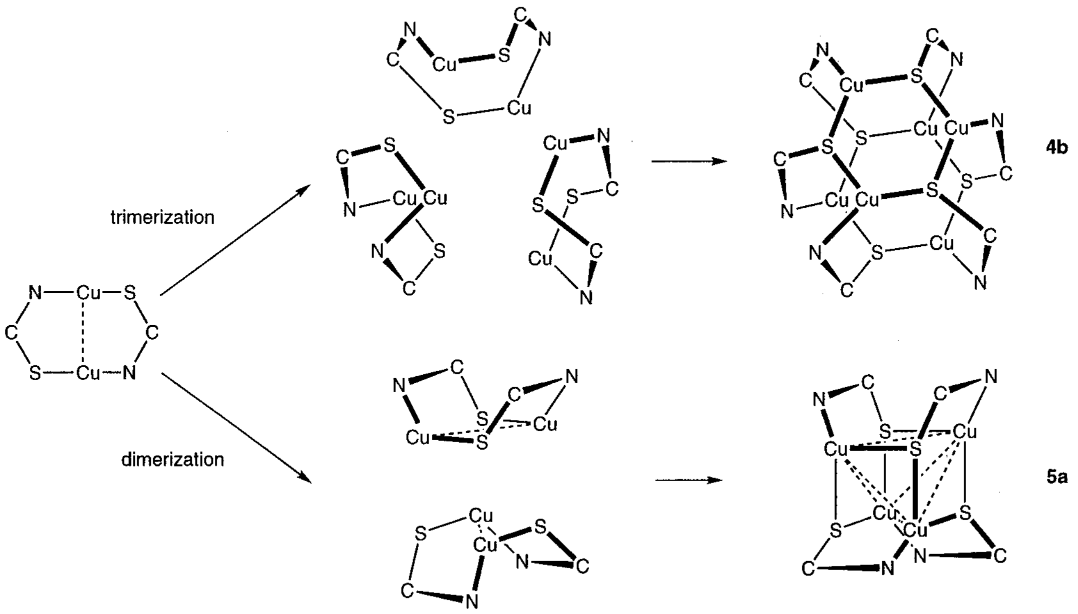

Figure 4. Formation of **4b** and **5a** via dimer aggregation. Dashed lines indicate short Cu···Cu distances. The substituents on carbon and nitrogen have been removed for clarity.

[NCS], anionic ligand systems are also known to form paddle-wheel clusters with Cu(I). These include several pyridine-2-thiolates,[29] a deprotonated thiourea derivative,[30] and two dithiocarbamates.[31]

The formation of **4b** can be visualized as a trimerization of three tub-shaped dimeric Cu(I) thioamidates (Figure 4). This route presents a direct analogy to that suggested for the formation of **1**,[3] except in that case the dimeric unit {Li[(*n*-Bu)CS(N-*t*-Bu)]}$_2$ had transannular Li−S bonds which eventually formed the rungs of the closed paddle-wheel hexamer. An analogous difference is exhibited by lithium and copper(I) amidinates; the former generally occur as laddered dimers, while the latter are eight-membered rings stabilized by weak, transannular metal−metal interactions.[32]

Tetrameric Cu(I) Aggregates. In **5a**, bridging of each Cu$_3$ face of the Cu$_4$ tetrahedron occurs through a η^1(N),μ_2(S) thioamidate unit. This bridging arrangement is precisely that seen in **4b**, and similar molecular architecture is also observed for a number of other systems. The insertion of isothiocyanates into the Cu−O bonds of copper(I) aryl oxides, for example, produces the copper(I) azaxanthates {Cu[(OEt)CS(NMe)]}$_4$[33] (**9**) and {Cu[(OC$_6$H$_3$Me$_2$-2,6)CS(NPh)]}$_4$[34] (**10**), which are isoelectronic with **5a** and isostructural in the solid state. Indeed, all of the tetrameric copper(I) azaxanthates reported to date are either hexameric like **4b** or tetrameric like **5a**, except where monomers and dimers are stabilized by phosphine coordination at copper.[6,28,33,34]

Other anionic ligands which adopt the same bridging mode as thioamidates and produce similar tetrameric copper(I) complexes include an imidazolethiolate,[35] pyridine-2-selenolate,[36] a dithiocarboxylate,[37] a silylphosphide,[38] and a phosphorodithioate.[39] Several examples of adamantane-like Cu$_4$S$_6$ cores containing Cu$_4$ tetrahedra have been observed for complexes of copper(I) with bidentate thiolate ligands (i.e., [Cu$_4$L$_3$]$^{2-}$ where L is a dithiolate).[40] Other bonding modes for similar ligands include the bridging of Cu$_2$ edges instead of faces[41] and the linking of tetrameric aggregates to form decanuclear clusters.[42]

Like the hexameric paddle-wheel systems, tetrahedral tetramers can be understood as aggregates of dimers evolving via the formation of Cu−S interactions between dimeric units (Figure 4). Some variation in Cu···Cu distances is observed in **5a**, with the inter-dimer sepa-

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rations being somewhat shorter than transannular ones (2.590(2) versus 2.719(2) Å). This disparity is likely a consequence of the shorter spans having complementary Cu−S links, whereas the longer ones do not. For comparison, the Cu···Cu distance in the dimeric copper(I) benzamidinate $\{Cu[PhC(NSiMe_3)_2]\}_2$ is 2.45 Å.[43]

Tetramer/Hexamer Competition. Of the five known copper(I) azaxanthates, three (**6**−**8**) are hexameric paddle-wheel aggregates, while the remaining two (**9** and **10**) are tetrameric. Although the observed dependence of oligomerization on substituent factors is familiar for **4** and **5** (i.e. larger substituents favor a smaller oligomer), the same is not true of the azaxanthates. For example, **9** is tetrameric despite its small substituents, while the relatively more hindered systems **6** and **7** are hexameric. Equilibrium between dimeric, tetrameric, and hexameric forms has been suggested previously, but only in the context of examining the effect of coordinating phosphine ligands on the position of such equilibria.[27,34] We add to these preliminary thoughts our observation that both hexamers and the tetramers can be viewed as aggregates of dimers and that product mixtures may contain observable quantities of both oligomers. While steric considerations are certainly expected to influence the relative amounts of each oligomer formed, they may not determine which crystallizes first. Thus, mixtures may previously have been described erroneously as pure hexamer or tetramer based on a single crystal X-ray structure rather than on their actual composition. Some support for this hypothesis may be construed from the observation of Samuelson et al., who isolated a tetramer in low yield despite modeling studies which indicated that a hexamer would be sterically viable; in other cases modeling results accurately predicted the observed oligomer.[27]

Finally, we note a correlation among the color of the copper(I) azaxanthate and thioamidate oligomers: while the hexameric species range from deep yellow to red, the tetramers are all either very pale yellow or white. Copper(I) has no d → d transitions, and its compounds are expected to be colorless; however, many are known with various hues.[21] This is thought to be due to charge transfer (both LMCT and MLCT),[44] the efficacy of which ostensibly depends greatly on ligand geometry and orientation. This being said, colored copper(I) compounds are difficult to predict or rationalize. As Melnik et al. concluded in a review on the subject, "there is evidently no structural rationale for the observed red color" of such species.[44]

Conclusions

A metathetical route has been employed to prepare two novel copper(I) thioamidates from CuCl and the corresponding lithium thioamidates. Both occur as a mixture of hexamer and tetramer. While the molecular architectures are quite different in the two oligomers, both may be viewed as the result of dimer aggregation.

These complexes are the first examples of metal thioamidates prepared via metathesis. In view of the large body of work stemming from metal carboxylates and related species, the general synthetic pathway presented here may be useful in providing access to thioamidate analogues of carboxylates. We are currently exploring the use of these previously underutilized ligands for transition-metal, main-group, and supramolecular applications.

Acknowledgment. We thank the NSERC of Canada for financial support and the University of Calgary for a Silver Anniversary Fellowship (A.D.).

Supporting Information Available: X-ray diffraction data, in CIF format, for **4b** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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