A Mixed (Arenethiolato)copper(I)/Copper Bromide Aggregate: X-ray Structure of Octanuclear $[Cu_8\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}_3Br_5]$

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Introduction

Copper(I) arenethiolate complexes with intramolecular coordination have been reported as catalysts for selective group transfer of RMgX reagents to various substrates, *e.g.* conjugate 1,4-additions to cyclic or acyclic α,β-unsaturated enones.[1] In a previous study, we reported that copper(I) arenethiolate complexes react with alkynyllithium, alkynylcopper(I), and arylcopper reagents to afford the mixed organo(arenethiolato)-copper aggregates $[Cu_3(SAr)_2(C{\equiv}C^tBu)]_2$,[2] $[Cu_4(SAr)_2(Mes)_2]$,[3] and $[Cu_3(SAr)_2(Mes)(PPh_3)]$[3] which are stable species in the solid state as well as in solution. In particular, the arenethiolate complexes $[Cu(SC_6H_4CH(R)NMe_2\text{-}2)]_3$ (R = H, Me)[4a] have been used in catalysis.[1,3]

These arenethiolates are monoanionic *S*,*N*-bidentate chelating ligands that are easily derived from benzylamine precursors.[4] In order to study the influence of *S*,*N*-ligands on the structure and reactivity of such copper complexes, some other bidentate arenethiolate ligands have also been developed and the syntheses of their copper(I) complexes studied; reports of the novel trimeric and nonameric species $[Cu(SC_6H_4NMe_2\text{-}2)]_3$ and $[Cu(S\text{-}1\text{-}C_{10}H_6NMe_2\text{-}8)]_9$ as well as their mixed organo(arenethiolato)-copper aggregates have been presented elsewhere.[5]

In the course of further modeling of the intramolecular coordination in arenethiolates, we have investigated the potentially *N*,*S*,*N*-terdentate ligand $SC_6H_3(CH_2NMe_2)_2\text{-}2,6$ (Figure 1), *i.e.* an arenethiolate anion containing in both *ortho* positions a tertiary amine substituent. This *N*,*S*,*N*-monoanion is closely related to the well-studied *N*,*C*,*N*- and *N*,*O*,*N*-terdentate ligands $C_6H_3(CH_2NMe_2)_2\text{-}2,6$[6] and $OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4$.[7] Here we report the synthesis and characterization of a novel octanuclear mixed (arenethiolato)copper/copper bromide aggregate containing this *N*,*S*,*N*-terdentate ligand, and its unusual structure is discussed.[8]

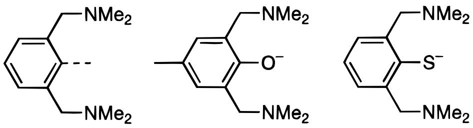

Figure 1. Terdentate *N*,*C*,*N*, *N*,*O*,*N* and *N*,*S*,*N* ligands.

Experimental Section

Syntheses were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Toluene, benzene, hexane, pentane, Et_2O (predried over CaH_2), and THF were carefully dried and distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200P spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Commercial ^nBuLi (1.67 M solution in hexane) was used. $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ was prepared according to literature methods.[8]

Synthesis of $[Cu_8\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}_3Br_5]\cdot CH_2Cl_2$ (4). To a suspension of $CuBr\cdot SMe_2$ (**3**) (2.69 g; 13.09 mmol) in Et_2O (40 mL) cooled at 0 °C was slowly added $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ (**2**) (1.51 g; 6.56 mmol) in Et_2O (40 mL). The initially white suspension slowly became yellow-green upon the addition. The reaction mixture was allowed to warm to room temperature, and after 2 h of stirring, all volatiles were removed *in vacuo*. Extraction with benzene (3 × 50 mL) gave 1.15 g of **4** (59% based on Cu; 33% based on ligand). Continued extraction with CH_2Cl_2 afforded 1.45 g of solid containing $[Li_2\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}Br]$ and a number of unidentified products. Crystallization by slow diffusion of pentane into a concentrated solution of **4** in CH_2Cl_2 afforded 1.02 g (87%) of **4** as yellow-green crystals, mp 176 °C dec. ^1H NMR (CD_2Cl_2, 297 K): δ 2.30 (br s, 12H, NMe_2), 2.5−4.5 (br, 4H, CH_2), 7.09 (br s, 3H, Ar). ^1H NMR (CD_2Cl_2, 217 K): δ 1.5−3.0 (12 × s, NMe), 3.0−5.3 (10 × d, CH_2), 6.8−7.3 (m, Ar). Anal. Calcd for $C_{37}H_{59}Br_5Cl_2Cu_8N_6S_3$: C, 26.73; H, 3.58; N, 5.05. Found: C, 26.78; H, 3.50; N, 5.21.

Crystal Structure Determination of 4. X-ray data were collected (total reflections 16 464; 4938 unique reflections; $R_{av} = 0.11$) on an Enraf-Nonius CAD4T rotating-anode diffractometer for a yellow brick-shaped crystal (0.15 × 0.25 × 0.50 mm) glued on top of a glass fiber. Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 25 well-centered reflections (SET4)[9] in the range $11 < \theta < 14°$. The unit-cell parameters were checked for the presence of higher lattice symmetry.[10] Data were corrected for Lorentz−polarization effects. An empirical absorption correction was applied (DIFABS[11] as implemented in PLATON;[12] correction range

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(1) (a) van Koten, G. *Pure Appl. Chem.* **1994**, *66*, 1455−1462. (b) Lambert, F.; Knotter, D. M.; Janssen, M. D.; van Klaveren, M.; Boersma, J.; van Koten, G. *Tetrahedron: Asymmetry* **1991**, *2*, 1097−1100. (c) van Klaveren, M.; Lambert, F.; Eijkelkamp, D. J. F. M.; Grove, D. M.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6135−6138. (d) Haubrich, A.; van Klaveren, M.; van Koten, G.; Handke, G.; Krause, N. *J. Org. Chem.* **1993**, *58*, 5849−5852. (e) van Klaveren, M.; Persson, E. S. M.; Grove, D. M.; Bäckvall, J.-E.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 5931−5934.

(2) (a) Knotter, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738−1740. (b) Knotter, D. M.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1992**, *11*, 4083−4090.

(3) Knotter, D. M.; Grove, D. M.; Smeets; W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400−3410.

(4) (a) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309−3317. (b) Knotter, D. M.; Janssen, M. D.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 4361−4366.

(5) Janssen, M. D.; Donkervoort, J. G.; van Berlekom, S. B.; Spek, A. L.; Grove, D. M.; van Koten G. *Inorg. Chem.*, in press.

(6) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490−5492. (c) Jastrzebski, J. T. B. H; van Koten, G. *Inorg. Synth.* **1989**, *26*, 150−155.

(7) van der Schaaf, P. A.; Hogerheide, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1703−1705.

(8) Reaction of $[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (**1**) with 1 equiv of elemental sulfur (S_8) in THF at −78 °C and subsequent slow heating within 1 h to 25 °C yields, after evaporation of the volatiles *in vacuo*, the hexameric lithium arenethiolate $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ (**2**) in quantitative yield. Details of the synthesis and characterization of **2** are reported elsewhere: Janssen, M. D.; Rijnberg, E.; de Wolf, C. A.; Hogerheide, M. P.; Kruis, D.; Kooijman, H.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.*, submitted for publication.

(9) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

(10) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(12) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

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Table 1. Crystal Data and Experimental Details for the X-ray Diffraction Study of **4**$\cdot CH_2Cl_2$

formula	$C_{36}H_{57}Br_5Cu_8N_6S_3\cdot CH_2Cl_2$
fw	1662.9
space group	$Pna2_1$ (No. 33)
crystal system	orthorhombic
Z	4
a (Å)	26.5238(15)
b (Å)	16.2318(15)
c (Å)	12.421(4)
V (Å^3)	5347.6(18)
d_{calc} (g cm^{-3})	2.066
μ(Mo Kα) (cm^{-1})	71.0
radiation (λ (Å))	MoKα (0.71073)[a]
T (°C)	−123
R	0.056[b]
wR_2	0.128[c]

[a] Graphite monochromated. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] Refinement on F^2. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

0.47−2.49). The structure was solved by direct methods (SIR92)[13] and subsequent difference Fourier techniques. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93)[14] using no observance criterion. The correct polarity adopted for the structure of **4** was indicated by the Flack-parameter[15] value of 0.01(2). Hydrogen atoms were introduced in calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The hydrogen atoms were refined with fixed isotropic atomic displacement parameters related to the values of the equivalent isotropic atomic displacement parameters of their carrier atoms by a factor of 1.2 for the benzylic and CH_2Cl_2 hydrogens and a factor of 1.5 for the methyl hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 16. Geometrical calculations and production of the illustrations were performed with PLATON.[12] All calculations were carried out on a DEC5000 cluster. Crystal data and numerical details of the structure determination and refinement are collected in Table 1. Selected geometrical details of the structure of **4** are listed in Table 2.

Results

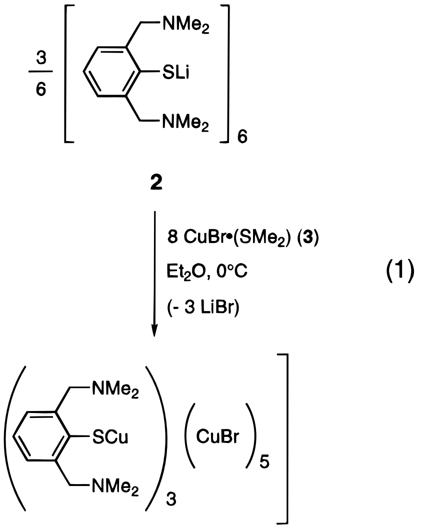
Reaction of $[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (**1**)[6] with 1 equiv of elemental sulfur (S_8) leads to insertion of sulfur into the lithium−carbon bond thereby yielding the hexameric lithium arenethiolate $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ (**2**) in quantitative yield.[8] Subsequent reaction of **2** with 2 equiv of $CuBr\cdot SMe_2$ (**3**) in Et_2O at 0 °C (eq 1) results in a suspension, from which a yellow-green solid complex is isolated. This complex has been identified and characterized as $[Cu_8\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}_3Br_5]$ (**4**) (*vide infra*). The isolated yield of **4** is moderate (59% based on Cu and 33% based on ligand), and other products are also formed, but we have as yet not been able to positively identify these other materials. It is important to note that the formation of **4** is reproducible and is not a single observation.

Mixed aggregate **4** is air-stable for several hours in the solid state. This complex is readily soluble in chlorinated hydrocarbons such as CH_2Cl_2 and $CHCl_3$, sparingly soluble in aromatic solvents, but insoluble in apolar alkanes. Solutions of **4** in CH_2Cl_2 are only slightly air-sensitive, and from this solvent single crystals of **4**$\bullet CH_2Cl_2$ can be obtained.

Table 2. Selected Geometrical Details of $[Cu_8\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}_3Br_5]$ (**4**).[a]

	Bond Distances (Å)		
Cu1−S1	2.213 (6)	Cu2−S3	2.236 (5)
Cu2−S1	2.260 (5)	Cu6−S3	2.221 (5)
Cu3−S1	2.278 (6)	Cu7−S3	2.269 (6)
Cu3−S2	2.242 (5)	Cu8−S3	2.324 (5)
Cu4−S2	2.248 (5)		
Cu5−S2	2.205 (5)		
Cu1−Br4	2.482 (3)	Cu4−Br5	2.418 (3)
Cu4−Br4	2.814 (3)	Cu7−Br5	2.814 (3)
Cu7−Br4	2.390 (3)	Cu8−Br5	2.431 (3)
Cu3−Br2	2.599 (3)	Cu5−Br3	2.335 (3)
Cu6−Br2	2.302 (3)	Cu8−Br3	2.461 (3)
Cu1−Br1	2.293 (3)		
	Bond Angles (deg)		
Cu1−S1−Cu2	76.67 (16)	Cu2−S3−Cu6	71.56 (15)
Cu1−S1−Cu3	137.8 (2)	Cu2−S3−Cu7	94.9 (2)
Cu2−S1−Cu3	91.31 (19)	Cu2−S3−Cu8	133.0 (2)
Cu3−S2−Cu4	124.4 (2)	Cu6−S3−Cu7	144.3 (2)
Cu3−S2−Cu5	117.4 (2)	Cu6−S3−Cu8	96.4 (2)
Cu4−S2−Cu5	97.27 (17)		
Cu1−Br4−Cu4	122.14 (10)	Cu4−Br5−Cu7	65.78 (9)
Cu1−Br4−Cu7	85.58 (11)	Cu4−Br5−Cu8	67.53 (9)
Cu4−Br4−Cu7	66.10 (9)	Cu7−Br5−Cu8	58.39 (9)
Cu3−Br2−Cu6	90.90 (9)	Cu5−Br3−Cu8	63.18 (9)

[a] The estimated standard deviations are given in parentheses.



2

4

(1)

To elucidate fully the structure of **4**$\bullet CH_2Cl_2$, an X-ray crystallographic study was carried out, showing this complex to be an asymmetric octanuclear mixed arenethiolatocopper/copper bromide aggregate (Figure 2). Selected bond lengths and angles are listed in Table 2.

The structure of **4** comprises eight copper atoms, three arenethiolate ligands, and five bromine atoms, with the copper atoms arranged in the form of a heavily distorted square antiprism (Figure 3). In this description Cu1, Cu3, Cu4, and Cu5 form the top square and Cu2, Cu6, Cu7, and Cu8 form the bottom square.

In this complex structure, two different modes for bonding of the arenethiolate ligands are present. The arenethiolate sulfur atoms S1 and S2 are μ_3-bridging over copper atoms of the triangular faces Cu1, Cu2, Cu3 and Cu3, Cu4, Cu5, respectively, whereas the sulfur atom of the third arenethiolate ligand (S3) is μ_4-bonded to the bottom square; this μ_4-bridging of an arenethiolate ligand is unprecedented.[17] The bromine atoms are also variously bonded: whereas Br4 and Br5 are μ_3-bonded to the triangular faces Cu1, Cu4, Cu7 and Cu4, Cu7, Cu8, respectively, the bromine atoms Br2 and Br3 are μ_2-bonded to the edges Cu3, Cu6 and Cu5, Cu8, respectively. Finally, bromine atom Br1 is simply η^1-bonded to Cu1.

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(13) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

(14) Sheldrick, G. M. *SHELXL93*: *Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1993.

(15) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

(16) Wilson, A. J. C., Ed. *International Tables for Crystallography;* Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

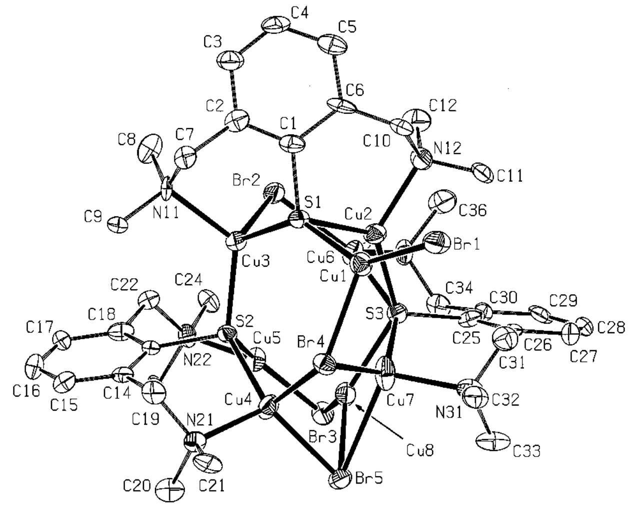

Figure 2. ORTEP drawing of **4** (drawn at 50% probability, with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

In the structure of **4**, the six nitrogen atoms from the arenethiolate ligands all coordinate to a copper atom. However, whereas the nitrogen coordination from the μ_4-bridging arenethiolate ligand occurs on opposite sides of the aromatic plane (*trans*), in the other two ligands this coordination occurs on the same side (*cis*). As a result of the different bondings of the arenethiolate ligands, the bromine atoms, and the nitrogen coordination, both trigonal-planar (Cu1, Cu2, Cu5, Cu6, Cu8) and tetrahedrally coordinated copper atoms (Cu3, Cu4, Cu7) are present.

The Cu−Br distances in the structure of **4** can be categorized by the bonding degree (hapticity) of the bromine atoms and they become longer with increasing hapticity. Thus, while the Cu-Br distance is 2.293(3) Å for the η^1-Br atom, the Cu−Br distances are in the range 2.302(3)−2.599(3) Å for the μ_2-Br atoms and in the range 2.390(3)−2.814(3) Å for the μ_3-Br atoms. A similar feature can be expected to hold also for the Cu−S distances. However, this feature is not very clear, as the Cu−S distances are in the range 2.205(5)−2.278(6) Å for the μ_3-arenethiolate and 2.221(6)−2.324(5) Å for the μ_4-arenethiolate ligands. The Cu−Br−Cu and Cu−S−Cu angles in the structure of **4** cover rather large ranges with differences that probably arise from the differences in bonding degree of the atoms involved.

Discussion

The mixed aggregate **4** is a most unusual complex in many respects and its isolation from the 1:2 reaction of [Li{$SC_6H_3(CH_2NMe_2)_2$-2,6}] (**2**) with CuBr, albeit in moderate yield, is very surprising. On the basis of the reaction stoichiometry, one would expect a much higher yield, but we believe that during the synthesis mixed (arenethiolato)lithium/lithium halide aggregates related to known species such as [Li_2{$SC_6H_3(CH_2NMe_2)_2$-2,6}I(THF)$_2$] (**5**)[8] can be formed. This type of species is expected to have a much lower trans-metalation capability than the pure lithium arenethiolate **2**, and formation of such a species effectively reduces the amount of transferable ligand that is available. Use of excess of **2** unfortunately leads to complications whose origin is probably to be found in the formation of thermodynamically stable and fairly insoluble side products (aggregates).

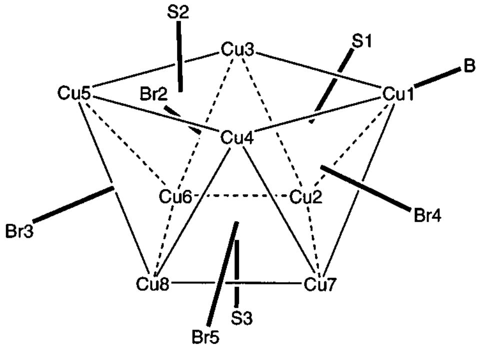

Figure 3. Schematic representation of **4**.

Another example in which the reactivity of a lithium reagent is reduced by formation of a lithium halide adduct comes from related phenolate chemistry; in a particular case, the reaction of 2 equiv of [Li{$OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4}] with 1 equiv of SmI_2 only afforded the lithium iodide adduct [Li_4{$OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4}$_2I_2$] as isolable product.[7]

The structural composition of **4** is unique though it does contain many structural features that have been known from related copper(I) arenethiolate chemistry. The μ_4-S-bonded arenethiolate ligand is to our knowledge unprecedented.[17] One of the most characteristic features that is particularly clear in the $Cu_8(SAr)_3Br_5$ core of **4** is the three Cu_3S_2Br and one Cu_3SBr_2 cyclohexane-like six-membered rings. The Cu1−S1−Cu2−S3−Cu7−Br4 and Cu1−S1−Cu3−S2−Cu4−Br4 six-membered rings are in a chairlike conformation, whereas the Cu3−S1−Cu2−S3−Cu6−Br2 and Cu5−S2−Cu4−Br5−Cu8−Br3 six-membered rings are in a boatlike conformation. Similar cyclohexane-like six-membered rings have been encountered in the structures of copper arenethiolates with intramolecular coordination (Cu_3S_3) and mixed organo(arenethiolato)copper complexes (Cu_3S_2C), and both chairlike conformations (in [$Cu_3(SAr)_3$])[4] and boatlike conformations (in [$Cu_3(SAr)_2(C{\equiv}C^tBu)$]$_2$)[2] have been previously reported. The observation of these structural features with bromide instead of arenethiolate in the structure of **4** indicates that the arenethiolate ligand possesses some pseudohalide character; *i.e.*, it can be replaced by bromide without severe structural changes.

Moreover, in the structure of **4** an eight-membered $Cu_4S_2Br_2$ ring (Cu5−S2−Cu3−Br2−Cu6−S3−Cu8−Br3) and two four-membered Cu_2SBr rings (Cu7−S3−Cu4−Br4 and Cu7−S3−Cu8−Br5) can also be identified. In a similar way, the eight-membered ring can be seen to resemble the $Cu_4S_2C_2$ ring in the mixed organo(arenethiolato)copper aggregate [$Cu_4(SAr)_2(Mes)_2$][3] and in some mixed organocopper/copper bromide aggregates [$Cu_4(R)_2Br_2$].[18] The smaller four-membered rings are unknown for copper(I) arenethiolates with intramolecular coordination but have been reported for copper(I) thiolates in which auxiliary ligands are present.[19]

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(17) μ^2- and μ^3-bridging arenethiolates have been reported. For examples see: (a) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476−2483. (b) Togni, A.; Rihs, G.; Blumer, R. E. *Organometallics* **1992**, *11*, 613−621. (c) Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 1263−1271.

(18) (a) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551−563. (b) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *Inorg. Chem.* **1977**, *16*, 1782−1787. (c) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Rotteveel, M. A.; Stam, C. H. *Organometallics* **1988**, *7*, 1477−1485. (d) Wehman, E.; van Koten, G.; Erkamp, C. J. M.; Knotter, D. M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Organometallics* **1989**, *8*, 94−99.

(19) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

Conclusions

Summarizing, the structure of **4** is unique and quite complicated but, with the exception of the μ_4-thiolate bridge, can be easily rationalized in terms of several structural features which are present in individual complexes like [$Cu_3(SAr)_3$], [$Cu_3(SAr)_2(C{\equiv}C^tBu)]_2$, [$Cu_4(SAr)_2(Mes)_2$], and [$Cu_4(R)_2(Br)_2$].

In our synthetic studies, our inability to prepare the pure copper(I) arenethiolate [$Cu\{SC_6H_3(CH_2NMe_2)_2$-2,6}] from the reaction of [$Li\{SC_6H_3(CH_2NMe_2)_2$-2,6}]$_6$ (**2**) with CuBr suggests that the bromine atoms in **4** are well-retained in this aggregate and not available for easy replacement. At present, this makes the *N*,*S*,*N*-monoanion a less suitable ligand for our (arenethiolato)copper-catalyzed reactions (*vide supra*), since the [$Cu_8(SAr)_3Br_5$] aggregate would provide not only CuSAr entities for the self-assembling process of the kinetically active key intermediates in the catalytic process but also unwanted CuBr units which would give rise to the formation of homo cuprates in which the modifying arenethiolate ligand would be absent. Therefore, the synthesis of pure [$Cu\{SC_6H_3(CH_2NMe_2)_2$-2,6}] from the reaction of **2** with copper salts in which the anion is less strongly coordinating (*e.g.* $CuOSO_2CF_3$) is currently under investigation.

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Supporting Information Available: Tables of structure determination details, atomic coordinates and equivalent isotropic atomic displacement parameters, anisotropic atomic displacement parameters, bond lengths, and bond angles (12 pages). Ordering information is given on any current masthead page.

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