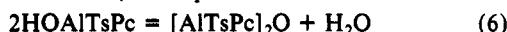


Similar behavior in water is shown by the tetrasulfonate IIA, which shows a broad intense Q_d band immediately on addition to water. The band is enhanced with increased ionic strength.

The tetrasulfonate IIIA, however, shows very different behavior. Its Q_d band forms slowly over 4 h when ionic strength is increased and is substantially narrower than that observed in the other cases. We would like to interpret this "slow dimer formation" as formation of the binuclear μ -oxo species:



Why are IIA [formed by H_2TsPc plus $\text{Al}(\text{acac})_3$] and IIIA [formed by AlCl_3 and sulfophthalic acid] so different? There is some evidence that the acetylacetone ligand is not displaced by a hydroxo ligand. However, attempts to establish the presence of an acetylacetone ligand by mass spectrometry and by NMR and FTIR spectroscopy gave ambiguous results. Both IIA and IIIA are tetrasulfonates, so we believe that a tightly bound ligand is the reason for their different behaviors rather than some subtle difference in the isomer types contained in each sample.

Our results closely parallel those of Wagner et al.,^{9b} who reported on the photochemical activity of selectively sulfonated gallium phthalocyanines. They found that more highly sulfonated phthalocyanines have greater tendency to dimerize and have lower photochemical quantum yields. They did not report on any kinetics for dimer formation, and their spectra suggest that the gallium phthalocyanines form contact dimers rather than μ -oxo binuclear species.

Finally, assuming that the Q_d band of IIIA is indeed due to a binuclear μ -oxo species, we wish to compare its excited-state properties and likely structure to those of the closely related silicon phthalocyanines. An X-ray structure for $[\text{Al}(\text{Pc})]_2\text{O}$ has been reported by Wynne.²⁵ This shows that the phthalocyanine rings

are eclipsed and separated by 4.27 Å. The Al atoms are 0.459 Å above the least-squares plane of the ring. We note that the monomer peak of IIIA is at 677 nm and the Q_d peak at 648 nm, a shift of 660 cm⁻¹. In the very comparable dimer $[\text{Si}(\text{Pc})\text{OR}]_2\text{O}$ with R = Si[C(CH₃)₃](CH₃)₂, studied by Marks and co-workers,²⁶ the Si atoms are planar within the phthalocyanine rings. The rings are also somewhat staggered and separated by 3.33 Å. In this case, the dimer peak is at 635 nm and the monomer peak at 670.5 nm, a shift of 830 cm⁻¹. This larger shift is consistent with a smaller ring-ring separation in the Si dimer. In both dimers, the M-O-M (M = Al or Si) axis is essentially linear and perpendicular to the ring planes. Wheeler et al.²⁷ have reported that $[\text{Si}(\text{Pc})\text{OR}]_2\text{O}$ does not fluoresce, as in our study.

The quenching of fluorescence in these dimers is important for their uses as fluorescence monitors and as photochemical sensitizers. Thus, the report here on the effect of variable sulfonation on the dimerization of aluminum phthalocyaninesulfonates should be valuable to research workers who wish to use the molecules for photochemical purposes. It also poses a challenge to isolate and study the binuclear μ -oxo aluminum tetrasulfonate species suggested by our kinetic spectroscopic observations.

Registry No. IA, 131582-87-1; IIA, 134418-66-9; IIIA, 134391-41-6; IZ, 61569-02-6; IIIZ, 61586-86-5; ClAlPc, 14154-42-8; ZnPc, 14320-04-8; Al(acac)₃, 13963-57-0; Zn(acac)₂, 14024-63-6; H₂TsPc, 7790-94-5; AlCl₃, 7446-70-0; ZnSO₄⁺, 7733-02-0; sulfophthalic acid, 26657-75-0.

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Synthesis and Properties of Trimeric Ortho-Chelated (Arenethiolato)copper(I) Complexes

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Received December 4, 1990

Neutral (arenethiolato)copper(I) complexes $[\text{CuSC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)-2-\text{R}''-3]_3$ ($\text{R}' = \text{H}, \text{R}'' = \text{H}, \text{Cl}; \text{R}' = \text{Me}, \text{R}'' = \text{H}$) with an intramolecularly coordinating ligand have been prepared and characterized. Crystals of $[\text{CuSC}_6\text{H}_4(\text{R}-\text{CH}(\text{Me})\text{NMe}_2)-2]_3\text{THF}$ are hexagonal, space group $P\bar{6}_3$, with $a = 13.743$ (1) Å, $b = 11.248$ (1) Å, $V = 1839.8$ (3) Å³, $Z = 2$, and final $R = 0.054$ for 1448 reflections with $I \geq 2.5\sigma(I)$ and 140 variables. The crystals are triboluminescent. The structure contains a Cu₂S six-membered ring in a chairlike conformation with alternating copper and sulfur atoms, and on each sulfur atom the $\text{C}_6\text{H}_3(\text{R}-\text{CH}(\text{Me})\text{NMe}_2)-2$ group is bonded equatorially with respect to this ring. Coordination of the nitrogen atoms of the *o*-CH(Me)NMe₂ substituents to the copper atoms ($\text{Cu}-\text{N} = 2.077$ (7) Å) provides three six-membered CuSCCN chelate rings. The bridge bonding of the arenethiolate has striking structural features, an acute Cu-S-Cu angle of 79.63 (7)°, Cu-S bond lengths of 2.231 (2) Å and 2.186 (2) Å, and a short Cu-Cu distance of 2.828 (1) Å. These features reflect an electron-deficient two-electron three-center Cu₂S bond in which there is interaction of a sulfur sp² hybrid orbital with a bonding combination of empty orbitals on the two copper atoms. In solution the $[\text{CuSC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)-2-\text{R}''-3]_3$ complexes remain trimeric but exist as two conformers that are in equilibrium through inversion at the bridging sulfur atoms. ¹H and ¹³C NMR studies reveal that the ratio of these two conformers can be influenced by changing R' and R'' in the arenethiolate ligand. The low free activation energy barrier ($\Delta G^* = \pm 50$ kJ/mol) for sulfur inversion is explained by a new mechanism which is based on a rotation (wagging) process around the axis through the sp² hybrid orbital in the electron-deficient Cu₂S unit. Evidence for the occurrence of separate intermolecular exchange processes is presented.

Introduction

Investigations of (thiophenolato)copper(I) complexes¹ in the solid state show them to be polynuclear and to usually contain anionic units of the type $[\text{Cu}_n(\text{SAr})_{n+m}]^{m-}$.²⁻⁴ The structural

features of copper(I) alkanethiolates are quite similar to those of copper(I) arenethiolates.⁴ In general, copper(I) thiolates in

- (1) In this paper (thiophenolato)copper(I) complexes are referred to as copper(I) arenethiolates.
- (2) (a) Dance, I. G.; Calabrese, J. C. *Inorg. Chim. Acta* 1976, 19, L41. (b) Dance, I. G. *J. Chem. Soc., Chem. Commun.* 1976, 103. (c) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *Ibid.* 1983, 546. (d) Dance, I. G.; Scudder, M. L.; Fitzpatrick, L. J. *Inorg. Chem.* 1985, 24, 2547.

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the solid state contain tetrahedrally coordinated sulfur atoms that bridge two or three trigonally coordinated copper atoms. However, there are no reports on the structure of copper(I) thiolates and their behavior in solution; this is due in part to the fact that most copper(I) thiolates are insoluble and thus difficult to study.

Copper(I) thiolates (CuSR_n), and metal thiolates in general are of fundamental chemical interest.⁵ Depending on the R group bound to the sulfur atom and on the presence of extra ligands like phosphines at the metal center, these complexes can display a diversity of structures. The advantage of RS^- over the comparable sulfido ligand (S^{2-}) is the potential it provides to tune the redox potential of the metal atom to which it is bound. Moreover, by the use of a suitable R group the environment around the metal atom can be designed to effect specific coordination of a substrate molecule. In this way models can be made that mimic, for example, the "blue" copper protein and metallothionein proteins.⁶ The combination of copper(I) thiolates with molybdenum complexes has also been investigated for its biological relevance.⁷

Our specific interest in copper(I) arenethiolates is their use in synthetic organic chemistry. Posner et al. used copper(I) thiolates to prepare heterocuprates $\text{CuLi}(\text{SR})(\text{R}')$, in which R' is an organo group, and they found that these compounds have improved thermal stability over classical homocuprates yet still retain enough reactivity for their use as reagents in organic reactions.⁸ These heterocuprates $\text{CuLi}(\text{SR})(\text{R}')$ are of interest because in various organic reactions the organo group R' is exclusively transferred to the substrate. Furthermore, by variation of the R group in CuSR species it is possible to tune the reactivity and selectivity of the reagent over a wide range.

Until recently copper(I) arenethiolates with potentially intramolecularly coordinating ligands were unknown.⁹ Intramolecular coordination can give rise to extra stabilization of these compounds and to a better defined structure. Furthermore, such ligands can coordinate to vacant sites during the reaction processes of the derived heterocuprates and help stabilize intermediate species. The introduction of a stereogenic $-\text{CH}(\text{R})\text{NMe}_2$ group at the ortho position of an arenethiolato anion not only meets the requirements for intramolecular coordination but can also be an excellent probe for the detection and monitoring of asymmetry in its complexes.¹⁰ We have already shown that this approach leads to copper(I) thiolates that are excellent starting materials for the preparation of novel chiral heterocuprates, which are useful in asymmetric organic synthesis.¹¹ Here, we wish to report the preparation, solid-state structure, and solution properties of copper(I) arenethiolate derivatives with an intramoleculerly coordinating group: $[\text{CuSC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)-2-\text{R}''-3]_n$, (R' = H, Cl; R' = Me, R'' = H).

Experimental Section

Syntheses were carried out by using standard Schlenk techniques

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- (13) (a) Abbreviations and techniques used in the text include the following: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; COSY = correlation spectroscopy;^{13b} Eyring equation, $\Delta G^* = -RT \ln [2\pi h(\Delta\nu)/kT_c \sqrt{3}]$ with ΔG^* = free energy of activation (J); T_c = coalescence temperature (K); $\Delta\nu$ = chemical shift difference (Hz). The other symbols have their usual meaning. (b) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
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under an atmosphere of dry, oxygen-free nitrogen. Solvents were carefully dried and distilled prior to use. Commercial Cu_2O , *n*-BuLi (1.56 M in hexane), and *t*-BuLi (1.67 M in pentane) were used. [2-[(Dimethylamino)methyl]phenyl]lithium was prepared according to a literature method.¹²

¹H NMR spectra were recorded on a Bruker AC-200P or a Varian EM 360A NMR spectrometer,¹³ and IR spectra were measured on a Perkin-Elmer 283 IR spectrophotometer. Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen. Elemental analyses were carried out by the Section of Elemental Analysis of ITC/TNO, Zeist, The Netherlands. GC/MS analyses were carried out at the Analytical Chemical Laboratory of the University of Utrecht.

Synthesis of 2-Chloro-1-[(dimethylamino)methyl]benzene (1d).¹⁴ To dimethylamine (100 mL, 1.5 mol) in benzene (200 mL) at 0 °C was slowly added pure 2-chlorobenzyl chloride (119 g, 0.75 mol). During the addition a reflux condenser filled with crushed ice was connected to the reaction vessel. After 2 days at room temperature, an aqueous solution of 100 mL of 6 M HCl was added whereafter the organic layer was separated and the aqueous layer was extracted twice with 50-mL portions of pentane. The aqueous layer was made basic with an aqueous solution of 10 M NaOH, and the product was extracted three times with 100-mL portions of pentane. The combined organic extracts were dried over MgSO_4 , and the product was distilled in vacuo (40 mmHg) at 114 °C; yield 100.4 g (79%); n_D^{20} 1.5249. ¹H NMR (60 MHz, C_6D_6): δ 7.25 (m, 4 H, Ar H), 3.35 (s, 2 H, CH_2), 2.07 (s, 6 H, NMe_2).

Improved Synthesis of [2-(*(R*)-1-(Dimethylamino)ethyl]phenyl]lithium (2b).¹⁵ To {(*R*)-1-(dimethylamino)ethyl}benzene (35 g, 0.23 mol) dissolved in pentane (75 mL) was added a solution of 1.64 M *t*-BuLi in pentane (140 mL, 0.23 mol) at room temperature and the mixture stirred for 16 h. The precipitate of white solid 2b that formed was separated from the solution by centrifugation and decantation. The solid was washed twice with 75 mL of pentane and dried in vacuo. Yield: 28 g (0.18 mol, 76%) of 2b.

Synthesis of [3-Chloro-2-[(dimethylamino)methyl]phenyl]lithium (2d). To 2-chloro-[(dimethylamino)methyl]benzene (25 g, 0.15 mol) in pentane (100 mL) was added a solution of 1.56 M *n*-BuLi in hexane (96 mL, 0.15 mol) and the mixture stirred for 18 h. The white solid of 2d that formed was separated from the solvent by centrifugation and decantation. The solid was washed twice with 75 mL of pentane and dried in vacuo. Yield: 23.3 g (90%) of pyrophoric 2d.

Synthesis of 2-[(Dimethylamino)methyl]thiophenol (3a). [2-[(dimethylamino)methyl]phenyl]lithium (18.8 g, 0.13 mol) dissolved in THF (150 mL) was slowly added to a suspension of sublimed sulfur (4.27 g, 0.13 mol) in THF (50 mL) at -50 °C. The solution was warmed to room temperature, and 13 mL of 10 M aqueous hydrochloric acid was added. A light yellow oil separated on the bottom of the flask, and all volatiles (THF and H_2O) were evaporated in vacuo at 50 °C. Double sublimation of the residue at 80 °C in vacuo (0.1 mmHg) yielded white crystals (17.1 g, 77%) of 3a, mp 103 °C. ¹H NMR (acetone- d_6): δ 7.70 (dd, 1 H, J = 6 and 1.5 Hz, Ar *o*-H), 7.2 (m, 3 H, Ar H), 3.52 (s, 2 H, ArCH_2), 2.65 (s, 1 H, SH), 2.20 (s, 6 H, NMe_2). IR (KBr pellet; cm⁻¹): $\nu_{\text{S-H}}$, 2360. Mass spectrum [*m/z* (relative intensity)]: 167 (57) [M⁺, calcd 167], 44 (100). Anal. Calcd for $\text{C}_9\text{H}_{13}\text{NS}$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.99; H, 7.68; N, 8.00.

Synthesis of 2-[(*R*)-1-(Dimethylamino)ethyl]thiophenol (3b). [2-[(*R*)-1-(dimethylamino)ethyl]phenyl]lithium (28 g, 0.18 mol) dissolved in THF (200 mL) was slowly added to a suspension of sublimed sulfur (5.7 g, 0.18 mol) in THF (50 mL) at -50 °C. The solution was warmed to room temperature, and 18 mL of 10 M aqueous hydrochloric acid was added. A light yellow oil separated on the bottom of the flask. All volatiles (THF and H_2O) were evaporated in vacuo at 50 °C, and sublimation of the residue at 120 °C in vacuo (0.1 mmHg) yielded white crystals of 3b (21.2 g, 65%), mp 133 °C (dec pt >140 °C). ¹H NMR (acetone- d_6): δ 7.30 (dd, 1 H, J = 6 Hz and 1.5 Hz, Ar *o*-H), 6.8 (m, 3 H, Ar H), 4.31 (q, 1 H, J = 7 Hz, ArCH_2), 2.64 (s, 6 H, NMe_2), 1.68 (d, 3 H, J = 7 Hz, $\alpha\text{-CH}_3$). IR (KBr pellet; cm⁻¹): $\nu_{\text{S-H}}$, 2020, 2350.

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- (13) (a) Abbreviations and techniques used in the text include the following: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; COSY = correlation spectroscopy;^{13b} Eyring equation, $\Delta G^* = -RT \ln [2\pi h(\Delta\nu)/kT_c \sqrt{3}]$ with ΔG^* = free energy of activation (J); T_c = coalescence temperature (K); $\Delta\nu$ = chemical shift difference (Hz). The other symbols have their usual meaning. (b) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
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Table I. Crystallographic Data for [CuSC₆H₄(R-CH(Me)NMe₂)-2]₃·THF^a

formula	C ₃₄ H ₅₀ Cu ₃ N ₃ OS ₃
fw	1607.25
temp, K	100
space group	P6 ₃
<i>a</i> , Å	13.743 (1)
<i>c</i> , Å	11.248 (1)
<i>V</i> , Å ³	1839.8 (3)
molecules/unit cell	2
<i>ρ</i> (calcd), g cm ⁻³	1.451
<i>F</i> (000)	836
<i>μ</i> , cm ⁻¹	19.8
radiation	Mo Kα (Zr filtered) (0.71073)
diffractometer	Enraf-Nonius CAD4
no. of colld obsd data	1448 [<i>I</i> ≥ 2.5σ(<i>I</i>)]
no. of variables	140
<i>R</i>	0.054
<i>R</i> _w [<i>w</i> = 1/σ ² (<i>F</i>)]	0.067

Mass spectrum [*m/z* (relative intensity)]: 181 (6) [M⁺, calcd 181], 135 (100). Anal. Calcd for C₁₀H₁₅NS: C, 66.25; H, 8.34; N, 7.73; S, 17.69. Found: C, 66.03; H, 8.44; N, 7.73; S, 17.54.

Synthesis of 3-Chloro-2-[(dimethylamino)methyl]thiophenol (3d). The synthesis is the same as that described for 3b but starting with 2d and without the sublimation procedure.

Synthesis of [2-((Dimethylamino)methyl)thiophenolato]copper(I) (4a). A mixture of arenethiol 3a (10.0 g, 60 mmol) and Cu₂O (3.68 g; 30 mmol) in absolute ethanol (200 mL) was heated at reflux for 18 h. The solid material was collected by filtration and washed twice with ethanol. The product was extracted from the solid with five 100-mL portions of benzene. The combined benzene extracts were concentrated to 50 mL by distillation at atmospheric pressure and then evaporated to dryness in vacuo. The resulting crude product was crystallized twice from CH₂Cl₂/MeOH to afford 4a as a voluminous white solid, which was dried in vacuo (0.07 mmHg) at 100 °C: yield 10.5 g (76%); mp 168 °C (slight dec.). Anal. Calcd for (C₉H₁₂CuNS)₃: C, 47.04; H, 5.26; N, 6.09. Found: C, 46.94; H, 5.36; N, 5.96. Molecular weight: found (corrected for incorporated solvent), 597 (640) (calcd for trimeric unit, 689). ¹H NMR data are presented in Table V.

Synthesis of [2-((R)-1-(Dimethylamino)ethyl)thiophenolato]copper(I) (4b). To crude unsublimed arenethiol 3b was added Cu₂O (13.0 g; 0.091 mol) and absolute ethanol (300 mL) and the mixture heated at reflux for 16 h. The solid material (lithium salts and excess Cu₂O) was then filtered off and washed with 150 mL of benzene. The combined organic solutions were concentrated by distillation at atmospheric pressure to 45 mL and then evaporated to dryness in vacuo (0.1 mmHg) for 1 h at 90 °C. The solid was extracted with hexane under a nitrogen atmosphere for 50 h in a Soxhlet apparatus. The hexane extract was cooled to -78 °C, and the solid that formed was filtered off and washed with 50 mL of pentane. The yellow solid was dried in vacuo and stored under a nitrogen atmosphere. Yield of 4b: 36.3 g (83%). The compound crystallizes out of a THF solution as a trimeric THF solvate 4b' (mp 148 °C). Anal. Calcd for (C₁₀H₁₄CuNS)₃·THF: C, 50.82; H, 6.27; N, 5.23; S, 11.97. Found: C, 50.25; H, 6.17; N, 5.10; S, 12.02. Molecular weight: found (corrected for incorporated solvent), 416 (760) (calcd for trimeric unit, 731). ¹H NMR data are presented in Table V.

Synthesis of [2-((±)-1-(Dimethylamino)ethyl)thiophenolato]copper(I) (4c). The syntheses is the same as that described for 4b but starting from racemic [2-[(dimethylamino)methyl]phenyl]lithium. Yield: 65%. ¹H NMR data are presented in Table V.

Synthesis of [3-Chloro-2-[(dimethylamino)methyl]thiophenolato]copper(I) (4d). The crude arenethiol 3d was reacted with Cu₂O as described for the synthesis of 4b with a reaction time of 2.5 h. Workup was identical: overall yield 11.5 g (33%); mp >170 °C dec. Anal. Calcd for (C₉H₁₁ClCuNS)₃: C, 40.91; H, 4.20; N, 5.30. Found: C, 40.34; H, 4.49; N, 5.04. Molecular weight: found (corrected for incorporated solvent), 700 (770) (calcd for trimeric unit, 792). ¹H NMR data are presented in Table V.

Collection and Reduction of X-ray Data and Solution and Refinement of the Structure of 4b. Crystals of 4b suitable for X-ray analysis were prepared by recrystallization of 4b out of a warm (68 °C) saturated THF solution on cooling over 2 days in a 3-L Dewar flask initially filled with water at 68 °C. The crystal data and experimental details of the structure determination are given in Table I. For a full description of the experimental details of the methods used for the structure solution, see ref 9. The crystal did not exhibit significant decay under X-ray irradiation. Tables II and III list atomic positional parameters and selected bond lengths and angles.

Table II. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [CuSC₆H₄(R-CH(Me)NMe₂)-2]₃·THF^a

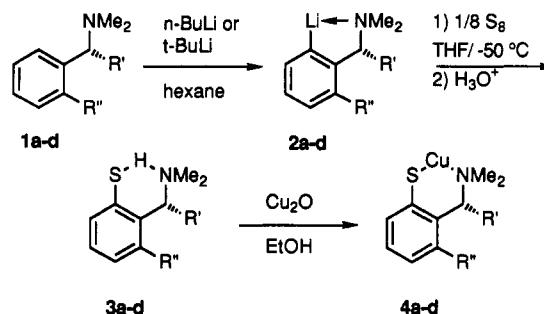
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), ^b Å ²
Cu	0.45855 (6)	0.68074 (6)	0.49990 ^c	0.0183 (2)
S	0.3502 (1)	0.5086 (1)	0.4262 (2)	0.0176 (4)
N	0.5384 (5)	0.6492 (5)	0.6389 (5)	0.020 (2)
C1	0.3666 (6)	0.4119 (6)	0.5205 (6)	0.018 (2)
C2	0.2835 (6)	0.3012 (5)	0.5151 (7)	0.020 (2)
C3	0.2863 (7)	0.2189 (6)	0.5811 (8)	0.030 (2)
C4	0.3775 (7)	0.2488 (7)	0.6553 (8)	0.033 (3)
C5	0.4633 (7)	0.3595 (7)	0.6621 (7)	0.028 (2)
C6	0.4601 (6)	0.4421 (6)	0.5936 (6)	0.019 (2)
C7	0.5641 (6)	0.5583 (6)	0.6031 (6)	0.023 (2)
C8	0.6347 (6)	0.5907 (7)	0.4876 (8)	0.033 (2)
C9	0.4647 (6)	0.6094 (6)	0.7443 (6)	0.020 (2)
C10	0.6440 (7)	0.7490 (6)	0.6749 (7)	0.027 (2)

^aThe estimated standard deviations of the last significant digits are shown in parentheses. ^b*U*(eq) = one third of the trace of the orthogonalized *U* tensor. ^cFixed.

Table III. Relevant Bond Distances (Å) and Bond Angles (deg) in [CuSC₆H₄(R-CH(Me)NMe₂)-2]₃·THF^a

Cu-S	2.231 (2)	Cu-S(B)	2.186 (2)
Cu-N	2.077 (7)	S-C1	1.801 (8)
Cu...Cu(A)	2.828 (1)	S...S(A)	3.977 (3)
S-Cu-S(B)	128.44 (8)	S-Cu-N	101.6 (2)
S(B)-Cu-N	129.3 (2)	Cu-S-Cu(A)	79.63 (7)
Cu-S-C1	107.5 (3)	Cu(A)-S-C1	109.9 (3)
Cu-N-C7	109.7 (4)	Cu-N-C9	110.2 (5)
Cu-N-C10	113.0 (5)	C9-N-C10	107.4 (6)
S-C1-C2	116.7 (6)	S-C1-C6	124.2 (6)

^aThe estimated standard deviations of the last significant digits are shown in parentheses. Coordinates for A = -1 + *y*, 1 - *x*, *z*; coordinates for B = 1 - *y*, 1 + *x* - *y*, *z*.

Scheme I

a, R' = R'' = H; b, R' = Me, R'' = H, (R) configuration;

c, R' = Me, R'' = H, racemic; d, R' = H, R'' = Cl.

Results

The copper(I) arenethiolates [CuSC₆H₄(CH(R')NMe₂)-2R''-]₃ (R' = H, R'' = H, Cl; R' = Me, R'' = H) (**4a-d**) were prepared from C₆H₄(CH(R')NMe₂)-R''-2 (**1a-d**), sulfur, and Cu₂O as outlined in Scheme I. The use of *n*-BuLi or *t*-BuLi in the metalation of the *N,N*-dimethylbenzylamine (H-dmba) derivatives (**1a-d**) depends on the aryl and benzylic carbon atom substituents.¹⁰ This reaction step afforded the pure organolithium compounds [Li(dmba)]_n (**2a-d**) in about 75–90% yield (see Experimental Section). The synthesis of the lithium arenethiolates from the reaction of **2a-d** with elemental sulfur were carried out at temperatures below -40 °C. After hydrolysis of the lithium arenethiolates, the resulting arenethiols **3a-d** could be isolated in 50–60% yield by sublimation out of the crude reaction product. Care was taken during this sublimation that the temperature did not exceed 120 °C, above which slow decomposition of the thiophenols takes place. The reaction of the arenethiols with copper(I) oxide resulted in the formation of the copper arenethiolates **4a-d** in almost quantitative yields. (It was also possible to obtain pure **4a-d** from the crude, unsublimed, arenethiolates

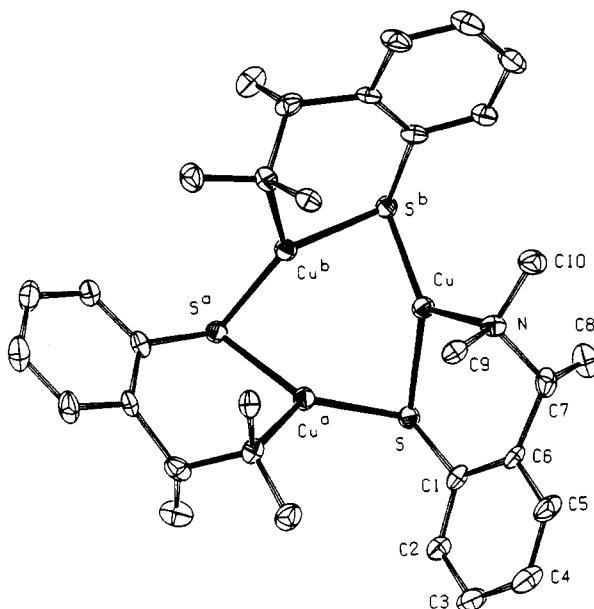


Figure 1. ORTEP drawing (50% probability level) of trinuclear [2-(*R*)-1-(dimethylamino)ethyl]thiophenolato)copper(I) (**4b**) (with the exclusion of the hydrogen atoms and the disordered THF molecule) with the atom-labeling scheme.

3a-d obtained after the hydrolysis step.) The formation of **4a-d** could be monitored with IR spectra (in KBr), since these complexes lack the broad (400 cm^{-1}) vibration band $\nu(\text{SH})$ at 2360 cm^{-1} that is characteristic for arenethiols.

Compound **4b** is soluble in almost all common polar and nonpolar organic solvents with the exception of acetonitrile. The solubilities of **4a,c,d** are less, and the general order of decreasing solubility if **4b** > **4c** > **4a** ≈ **4d**. It appeared impossible to obtain the copper(I) arenethiolates totally solvent free by crystallization from pentane, THF, diethyl ether, or dichloromethane. Powders of **4a-d** that were heated for 1 day at 100°C in vacuo still contained solvents.

Compounds **4a-d** have melting points around $150\text{--}160^\circ\text{C}$ without decomposition (see Experimental Section); i.e., they have considerable thermal stability. Upon exposure to air for a few hours the color of **4a,c,d** turns from white to slightly green/black. Complex **4b** is exceptional, it shows almost no color change even after exposure to air for 1 day. In contrast to this reasonable air stability of the solid compounds, solutions of **4a-d** decompose within a few minutes upon exposure to air. Notably, the copper arenethiolates dissolved in benzene are stable to 0.1 M aqueous hydrochloric acid for several days under a nitrogen atmosphere. Compared to copper(I) thiolates and copper(I) alcoholates, it is apparent that these ortho-chelated copper(I) arenethiolates are remarkably stable, both chemically and thermally.⁸

Interestingly, crystals of **4b** are triboluminescent, and when the compound is mechanically disrupted (e.g. by shaking in a bottle) green flashes are visible even in broad daylight.¹⁶

Structure of 4b in the Solid State. To determine the state of aggregation of complexes **4a-d** in the solid state and the exact geometry of this new type of copper arenethiolate, an X-ray single-crystal determination on **4b** was carried out.

Crystals of the THF solvate ($[\text{CuSAr}_3]\text{THF}$), **4b'**, were obtained by cooling a saturated THF solution of **4b**. Figure 1 shows the molecular geometry of **4b** with the adopted numbering scheme, and a schematic representation of the structure is given in Figure 2. The unit cell comprises two identical trimeric copper arenethiolates that have a crystallographic C_3 -rotation axis as their only symmetry element and two disordered THF molecules. The molecular structure of **4b** is based on a six-membered cyclohexane-like Cu_3S_3 ring in a chair conformation with alternating

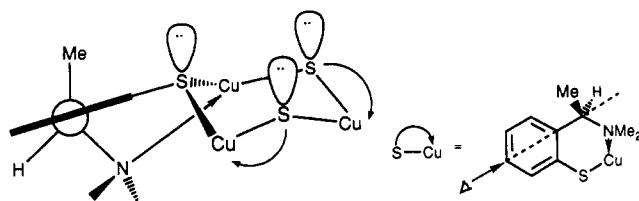


Figure 2. Schematic drawing of [2-(*R*)-1-(dimethylamino)ethyl]thiophenolato)copper(I) (**4b**) with a Newman projection viewed along the benzylic carbon to ortho aromatic carbon axis.

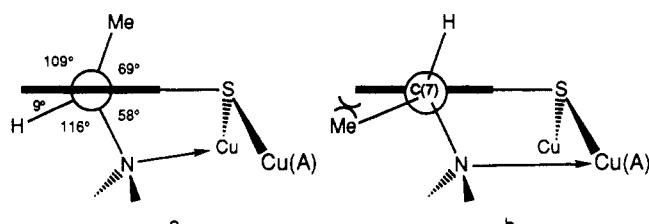


Figure 3. Newman projection of the copper(I) arenethiolate **4b**: (a) actual geometry in solid state with torsion angles corresponding to a left-hand turn of the *R*-CH(Me)NMe₂ substituent; (b) coordination of the amine in the alternative stereoisomer with a right-hand turn (not observed).

copper and sulfur atoms. Each sulfur atom of the arenethiolates bridges two copper atoms, and all the aryl groups are in an equatorial position relative to the Cu_3S_3 ring. Similar Cu_3S_3 six-membered rings in chairlike conformations (see Figure 2) have been found in complexes of the trimeric copper(I) chloride adducts $[\text{CuCl}|\text{S}=\text{C}(\text{Me})\text{NH}_2]_3$ and $[\text{CuCl}|\text{S}=\text{PMe}_3]_3$.¹⁷ Since the sulfur atoms in **4b** are three-coordinate, one coordination site on each sulfur atom is occupied by a stereochemically active lone pair that is in an axial position with respect to the Cu_3S_3 ring. Each nitrogen atom of the *o*-CH(Me)NMe₂ function (the "arm" of the arenethiolate) coordinates intramolecularly to a copper atom and occupies a bisectinal position with respect to the Cu_3S_3 ring. Thus, each copper atom is three-coordinate with two sulfur atoms and one nitrogen atom in its coordination sphere. The geometry around the copper atoms is trigonal (the sum of angles around copper is 359.3°); since the bite angle of the arenethiolate group is smaller than 120° (i.e., $\text{S}-\text{Cu}-\text{N} = 101.6(2)^\circ$), the $\text{S}-\text{Cu}-\text{S(B)}$ and $\text{S(B)}-\text{Cu}-\text{N}$ angles are a little larger than 120° (see Table III).

There are two very different sides to the trinuclear copper molecule. One "organic side", where all the aromatic groups are exposed, protects the copper atoms, and there is one "inorganic side" with the three sulfur atoms exposed. Looking at the molecule from its "organic side", the *o*-CH(Me)NMe₂ arms of the arenethiolate groups all turn to the left. The benzylic methyl group C8 on the methylenic carbon C7 is placed out of the aryl C1-C6 ring plane (the torsion angle C(5)C(6)C(7)C(8) is $109.0(8)^\circ$ (see Figure 3a)). The benzylic proton H5 is in a sterically unfavorable position almost in the plane of the aromatic ring (the C(5)C(6)C(7)H(5) torsion angle is $-9(1)^\circ$ (see Figure 3a)). There appears to be some steric strain in this molecule, which is induced by the amino methyl groups. One of the methyl groups C10 is close to the aromatic ring of the neighboring ligand ($\text{C}10\cdots\text{C}2\text{B} = 3.42\text{ \AA}$), and in parallel the geminal methyl group C9 is pushed toward the same aromatic group ($\text{C}9\cdots\text{C}1 = 3.44\text{ \AA}$).

The Cu-N bond distance in **4b** of $2.077(7)\text{ \AA}$ is short for a tertiary amine group bound to a copper(I) ion.^{13,18-21} The sulfur

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Table IV. Cu...Cu Distances (Å) and Cu-S-Cu Angles (deg) of Copper-Sulfur Complexes

compd	Cu...Cu; (av)	Cu-S-Cu; (av)	ref
[Cu ₄ (SPh) ₆] ²⁻	2.639–2.846; (2.76)	70.2–76.7; (74.3)	2a
[Cu ₄ (SPh) ₆] ²⁻	2.692–2.772; (2.75)	(73.9)	3a
[Cu ₄ (SPh) ₆] ²⁻	2.679–2.806; (2.74)	71.3–75.5; (73.4)	24
[Cu ₅ (SPh) ₇] ²⁻	2.65–3.12	75.0–88.0; (80.8)	2b
[Cu ₈ (SC ₆ H ₂ Pr ⁱ) ₈] ⁻	(2.705)	77.2–92.5	3b
[Cu ₅ (SBu ⁱ) ₆] ⁻	2.698–2.741; (2.72)	74.5–76.3; (75.4)	4b
[Cu ₅ (SBu ⁱ) ₆] ⁻	2.667–2.875; (2.77)	73.4–80.9; (77.0)	25
Cu ₄ (SMe) ₆] ²⁻	2.673–2.791; (2.72)	72.0–74.8; (73.3)	24
[Cu ₄ {o-(SCH ₂) ₂ C ₆ H ₄] ₃] ²⁻	2.698–2.739; (2.73)	72.4–74.8; (73.7)	4c
[Cu ₃ (SPh) ₃ (PPh ₃) ₄]	3.13	87	2c
[Cu ₄ (SPh) ₄ (PPh ₃) ₄]	2.782–3.404	70.8–88.0	2d
[Cu ₂ (SC ₆ H ₄ Me-o)(phen) ₂]	2.613	67.8; 68.1	26
[Cu ₃ (SAr) ₃] ^a	2.828	79.63	d
[Cu ₁₂ (SC ₆ H ₄ o-SiMe ₃) ₁₂] ^b	2.748–3.329	75.9–95.6	3c
[Cu ₆ (SC ₆ H ₃ N(SiMe ₃) ₃) ₆] ^c	3.139	82.6–88.5	44
[Cu ₄ [SC ₆ H ₃ (SiMe ₃) ₂ -2,6] ₄] ^f	f	82.9; 83.7 92.3; 92.4	45
[Cu ₃ (SAr) ₂ (C ₆ H ₂ Me ₃ -2,4,6)(PPh ₃)] ^b	2.8056; 2.7525	76.87; 75.13	11c
[Cu ₆ (SAr) ₄ (C≡CBu ⁱ) ₂] ^c	2.841; 3.026	84.4; 77.1	11a
[Cu ₄ (SAr) ₂ (C ₆ H ₂ Me ₃ -2,4,6) ₂] ^c	2.698; 2.796	78.1; 74.8	e
[Cu ₄ (SBu ⁱ) ₄ (PPh ₃) ₂] ^c	2.834–3.113; (2.94)	79.9–89.9; (83.7)	4a
[Cu ₈ (SC ₅ H ₁₁) ₄ (S ₂ CSC ₅ H ₁₁) ₄] ^b	2.652–3.201; (2.88)	71.5–98.7; (78.8)	27
[Cu ₄ (S ₂ CC ₆ H ₄ Me-p) ₄ (PPh ₃) ₂] ^c	2.574; 2.653; 2.766	68.5–95.5; (76.6)	28
[Cu ₆ (C ₅ H ₄ NS) ₆] ^c	2.795–2.853; (2.83) 3.009–3.160; (3.07)	84.98–89.10; (86.6)	43
[Cu ₂ (SPh) ₂ (PPh ₃) ₄] ^c	3.662	98.63; 102.75	29
[Cu ₃ (SPh) ₃ (PPh ₃) ₄] ^c	3.70	105	2c
[Cu ₃ (S=PMe ₃) ₃ Cl ₃] ^c	3.545; 3.610	103.0; 105.8 (108.5)	17b
[Cu ₃ (S ₃ MoO) ₃ Cl ₃] ^c	3.583	120	7b
[Cu ₄ (S ₂ CC ₆ H ₄ Me-p) ₄ [CH ₂ (PPh ₂) ₂]] ^c	3.843	120	30
[Cu ₈ (SC ₅ H ₁₁) ₄ (S ₂ CSC ₅ H ₁₁) ₄] ^b	3.89–3.91; (3.90)	120	27
[Cu ₃ (SPh) ₃ (PPh ₃) ₄] ^c	4.09	124	2c
[Cu ₄ (SPh) ₄ (PPh ₃) ₄] ^c	4.289	130.1	29
[Cu ₃ (S=C(CH ₃)N(H ₂) ₃ Cl ₃] ^c	3.982	125.9	17a
[Cu ₁₂ (SC ₆ H ₄ o-SiMe ₃) ₁₂] ^c	4.172–4.208	131.4–135.5	3c

^aSAr = SC₆H₄(R-CH(Me)NMe₂)-2. ^bSAr = SC₆H₃(CH₂NMe₂)-2-Cl-3. ^cSAr = SC₆H₄(CH₂NMe₂)-2. ^dThis work. ^eUnpublished results.

^fNot reported.

in **4b** is slightly asymmetrically bridging between the two copper atoms with Cu-S bond distances of 2.231 (2) Å (Cu-S(A)) and 2.186 (2) Å (Cu-S(B)). The Cu-S bond distances are within the ranges expected for two- and three-coordinate copper atoms.^{22,23}

With the exception of the rather acute Cu-S-Cu bond angle (79.63 (7)°) the other bond angles around the sulfur atom are close to that expected for a tetrahedral coordination geometry (i.e. 109.9 (4) and 107.5 (3)°). The Cu-S-Cu bond angle in **4b** is not exceptional for (arenethiolato)copper complexes and is in the range found for this angle in complexes where sulfur bridges two copper atoms (see Table IV).² The Cu...Cu distance of 2.828

(1) Å in **4b** is normal for a copper thiolate (see Table IV).

Structure in Solution. Cryoscopic molecular weight determinations of all compounds (**4a–d**) in benzene (0.15–0.015 mol/kg of benzene) indicate a trimeric aggregation state that is independent of the solute concentration. The measured values have been corrected for the amount of solvent found by ¹H NMR spectroscopy to be incorporated in the solid materials. These data are consistent with single-crystal X-ray study of a representative compound **4b**, *vide supra*, that shows it to have trimeric aggregation in the solid state.

At room temperature or higher the ¹H NMR spectrum (200 MHz, toluene-*d*₈) of [CuSC₆H₄(R-CH(Me)NMe₂)-2]₃ (**4b**) displays a simple pattern. Characteristic features are as follows: the doublet at 1.35 ppm for the methyl group on the benzylic carbon; one singlet at 2.02 ppm for the methyl groups on the nitrogen atom; the quartet at 3.10 ppm for the proton on the benzylic carbon; the low-field pattern (doublet of doublets at 7.53 ppm) for the aromatic proton ortho to the sulfur atom.

Upon cooling of the solution, the ¹H NMR signals become broader and decoalesce into a complicated spectrum at 203 K. The reversibility of this process indicates that fluxional processes take place in **4b**. The line widths at 203 K ($\Delta_{1/2} = 12$ –20 Hz) of the signals for the amino methyl groups made it difficult to interpret the standard one-dimensional ¹H NMR spectrum. With a ¹H, ¹H COSY phase-sensitive 2D experiment,^{13b} the situation was significantly improved and four different CH(Me)NMe₂ groupings in the 1D spectrum could be identified. Most evident are four quartets, in a 9/2/2/2 ratio, found for the proton on the benzylic carbon at 2.57, 2.50, 2.63, 4.48 ppm, respectively. These signals correlate with four doublets for the methyl group on the benzylic carbon at 1.86, 0.72, 1.76, and 0.63 ppm, respectively.

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- (23) Copper-sulfur bond distances are dependent on the coordination number of the copper atom and distinct ranges can be discerned: 2.14–2.17 Å for two-coordinate copper atoms,^{3b,4a,b} 2.22–2.33 Å for three-coordinate copper atoms,^{2,3a,4,27,17} and 2.33–2.48 Å for four-coordinate copper atoms.^{2c,d,29}
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Table V. Temperature-Dependent ^1H NMR Spectral Data (200 MHz)^a for Copper(I) Arenethiolates $[\text{CuSC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)\text{-2-R''-3}]_n$ (**4a-d**)

no.	R'	R''	T, K	conformer	NMe (s)	CMe (d)	CH_2/CH (s/d)/q	Ar o-H (dd)	Ar H
4a	H	H	298	<i>b</i>	2.04		3.51	7.68	6.71 (dd), 6.83 (dt), 6.96 (dt)
			203	C_3^c	1-3		5.15, 3.4	7.38	6.5-7.2
				C_1^d	1.5-2.5		4.76, 4.53, 3.38, 2.36, 2.83, 2.55	7.59, 7.79, 7.95	6.6-7.2
4b	Me	H	358	<i>b</i>	2.02	1.35	3.10	7.53	6.5-6.9
			223	C_3^c	1-3	1.86	2.57	7.62	6.5-7.3
				C_1^d	1-3	0.63, 0.72, 1.76	4.48, 2.50, 2.63	7.49, 7.63, 8.04	6.5-7.3
4c	Me	H	343	<i>b</i>	2.02	1.86	3.52	7.81	6.5-6.95
				C_1^d	1-3	1-3	4.65, 1-3	7.59, 7.89, 8.32	6.3-7.3
4d	H	Cl	303	<i>b</i>	2.26		4.04	7.72	6.80 (t), 7.06 (dd)
			203	C_1^d	2-3		3.98, 4.23, 4.38, 4.81, 3.72	7.50, 7.84, 8.11	6.5-7.2

^a δ in ppm relative to TMS. Solvent is toluene- d_6 . For broad signals that are not separated from other signals the range is given. ^b Fast-exchange limit. ^c See Figure 2. ^d See Figure 6.

Table VI. C_3/C_1 Conformer Ratio of the Copper(I) Arenethiolates and ΔG^\ddagger Values for C_3/C_1 Interconversion^a

no.	C_3/C_1^b	$T_c, ^\circ\text{C}$	$\Delta\nu, ^\text{d}$ Hz	$\Delta G^\ddagger, ^\text{e}$ kJ mol $^{-1}$
4a	1/9	235	32, 41	48, 47
4b	3/2	270	84	53
		250	26	51
4c	<1/100	270	60, 86	54, 53
4d	<1/100	235	55	47
		248	69	49

^a Calculated from temperature-dependent NMR data. ^b Estimated from the integral ratio of the ortho aromatic protons. ^c Temperature where one doublet (of the ortho aromatic protons) coalesces with one or two others. ^d Chemical shift difference of the coalescing protons in the slow-exchange limit. ^e Calculated by using the Eyring equation.¹³

(the supplementary material includes the 1D spectrum and 2D plot). Furthermore, in the one-dimensional ^1H NMR spectrum only three doublets of doublets are visible for the aromatic protons ortho to the sulfur atoms. However, in the 2D experiment a fourth doublet also becomes discernible. With a heteronuclear (^{13}C , ^1H) COSY 2D experiment in CDCl_3 at 203 K all of the eight different amino methyl groups were identified and correlated ($\delta(^1\text{H})$ ($\delta(^{13}\text{C})$) (ppm): 2.01 (20.5); 2.02 (34.7); 2.08 (31.9); 2.10 (26.7); 2.33 (26.7); 2.37 (34.7); 2.40 (18.7); 2.44 (18.3)).

These NMR results are consistent with the presence of two trimeric species of different symmetry, one species with C_3 symmetry (one ligand pattern) and one with C_1 symmetry, which is responsible for three ligand patterns in the same ratio. The C_3 conformer is almost certainly a species with a Cu_3S_3 ring in the chair conformation as in the crystal structure of **4b**, though for the C_1 conformer there are three alternative structures (Figure 5) that must be considered when the fluxional behavior is interpreted; see Discussion.

The same phenomenon of coalescence and decoalescence was found for the other copper arenethiolates **4a,c,d**. The variable-temperature NMR data of these compounds are given in Table V. A general observation for the ^1H NMR spectra of all the copper arenethiolates **4a-d** is that at room temperature and higher they display a single ligand pattern, while at 213 K they display four ligand patterns, three patterns from a trimer with C_1 symmetry and one ligand pattern from a C_3 conformer.

The complexes show different $C_3:C_1$ ratios that are a reflection of the substituents of the arenethiolato group, and these data are listed in Table VI. These ratios are neither concentration nor solvent dependent. Furthermore, the coalescence behavior for all signals did not change when the concentration of the copper arenethiolate was changed by a factor of 100. The fluxional process is therefore of zero-order. The behavior is also independent of the prepared batch of **4** or addition of $[\text{t-BuS}]^-[\text{NEt}_4]^+$. Consequently, we conclude that intermolecular processes proceeding via a $[\text{Cu}_3(\text{SR})_4]^-$ intermediate (a potential impurity) can be excluded and that the C_3/C_1 equilibrium/fluxionality is solely an intramolecular process.

The best discernible ^1H NMR signals of the copper arenethiolates are those of the ortho protons to low field of the aromatic signals. The three equally intense doublets (from the C_1 conformer) found in the slow-exchange limit ($T < 235$ K) become

one doublet in the fast-exchange limit ($T > 270$ K). In this temperature range two coalescence points can be identified, where the central doublets of the C_3 conformer (that overlaps with one of the signals of the C_1 conformer) coalesces with one and then the other flanking doublet. The coalescence temperatures (T_c) of some of the ortho aromatic protons with estimated ΔG^\ddagger values (Eyring equation¹³) for this C_3/C_1 process are given in Table VI. For all compounds **4a-d** a ΔG^\ddagger was found of approximately 50 kJ mol $^{-1}$.

The low-temperature (213 K) NMR spectrum of **4c**, which contains the racemic $\text{SC}_6\text{H}_4(\text{CH}(\text{Me})\text{NMe}_2)\text{-2}$ ligand, is more complicated than that of **4b** synthesized with the $\text{SC}_6\text{H}_4(R\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}$ enantiomer. For **4c** one can theoretically expect a number of species. First, one can expect trimers that are based on ligands with either all the *R* configuration (*RRR*) or all the *S* configuration (*SSS*). These enantiomeric trimers are NMR identical but can exist in either the C_3 or the C_1 conformation as was seen for **4b**. Second, one can have trimers of the *SSR* and *RRS* type for which there are a number of conformers possible. The actual spectrum of **4c** shows (see Table V) at low temperature (213 K) C_3/C_1 forms of the *SSS/RRR* enantiomers together with only one of the *SSR/RRS* conformers as the major species (see Table VI).

If solutions containing the pure *RRR* and *SSS* enantiomers of $[\text{CuSC}_6\text{H}_4(\text{CH}(\text{Me})\text{NMe}_2)\text{-2}]_3$ are mixed, then within a few minutes the same ^1H NMR spectrum is obtained as from **4c** prepared from the racemic form of $\text{C}_6\text{H}_5\text{CH}(\text{Me})\text{NMe}_2$ (**1c**). This is evidence for ligand scrambling between the different trimers, an interaggregate exchange process (eq 1) that takes place on the laboratory time scale.



Discussion

Structure and Bonding of Copper Arenethiolates in the Solid State. In X-ray structures of copper thiolates the bonding mode of the RS^- thiolate anion shows little variation and the anion usually bridges through sulfur over either two or three copper atoms. The distinct structural differences of the copper thiolates are primarily related to the geometry of the $\text{Cu}(\text{SR})\text{Cu}$ units.

Table IV gives an almost complete survey of Cu...Cu distances and Cu-S-Cu angles in reported copper-sulfur complexes containing a sulfur-copper bond. There are three types of sulfur bridges: (i) bridges with an acute Cu-S-Cu angle; (ii) bridges with an obtuse Cu-S-Cu angle of approximately 104°; (iii) bridges with an obtuse Cu-S-Cu angle of more than 120°. The Cu...Cu distances for sulfur bridges of type i are between 2.57 and 3.40 Å, with the most common distance being ca. 2.76 Å. The spread in the Cu...Cu distances when sulfur is bridging according type ii or iii is less; type ii gives values from 3.55 to 3.70 Å, and type iii, from 3.84 to 4.20 Å.

Compound **4b** is a copper thiolate having a type i bridge. Most copper(I) thiolates have this type of bridge, and it is remarkable that in the literature there is no satisfactory explanation given for the acute Cu-S-Cu bond angle and the accompanying short Cu...Cu distance. At first sight these geometric features do seem to be unexpected. Since copper(I) has a closed d 10 shell, there is hardly any direct metal-metal interaction between the copper(I)

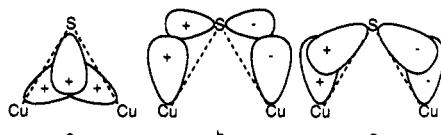


Figure 4. Proposed three-center two-electron bonding mode of sulfur-bridged copper atoms, where the dotted lines are the vectors connecting the copper and sulfur atoms and defining the acute Cu-S-Cu bond angle: (a) three-center two-electron bonding sulfur electron pair; (b) π -electron donation of sulfur p orbital to empty copper orbitals; (c) π -electron back-donation from filled copper d orbitals to empty sulfur d orbitals.

ions.^{31,32} Moreover, for tetragonally coordinated sulfur the copper cations are bound to it via four-electron three-center (4e–3c) bonds and the only force between the copper cations would be repulsive (Coulomb). One therefore expects a Cu–S–Cu angle larger than 109.4° and a Cu…Cu distance that is larger than $1.632 \times d_{\text{Cu-S}}$ (i.e. 3.60 Å with a $d_{\text{Cu-S}}$ of 2.21 Å). These values fall in the range of found for type ii sulfur bridges. For trigonally coordinated bridging sulfur ($\angle \text{Cu-S-Cu} = 120^\circ$) with the copper cations bound to it via 2e–2c bonds, the minimum Cu…Cu distance would be $\sqrt{3} \times d_{\text{Cu-S}}$ (i.e. 3.83 Å with $d_{\text{Cu-S}}$ of 2.21 Å). This latter value for the Cu…Cu distance is in the range of type iii sulfur bridges.

The short Cu…Cu contacts and the acute Cu–S–Cu bond angle in **4b** and other copper thiolates (type i) have parallels in the geometries of the carbon-bridged units Cu_2C .^{32,33} Therefore, the Cu_2S bonding can probably be explained in terms of a ligand-assisted metal–metal interaction in an electron-deficient two-electron three-center (2e–3c) bond. Moreover, from extended Hückel calculations (EHT) it has been concluded that large, polarizable bridging anions prefer a bonding type close to that of a 2e–3c bond.³⁴

In this model the bridging sulfur atom in the electron-deficient Cu_2S bond has sp^2 hybridization, which is not unprecedented for sulfur atoms in thiolates and thioethers.³⁵ One of the filled sp^2 hybrid orbitals overlaps with one empty orbital of each of the two copper atoms to form a 2e–3c bridge bond (Figure 4a). Since the two copper orbitals are bonding with respect to each other, one obtains sulfur-assisted metal–metal bonding and the copper–copper distance is shortened.³¹ Consequently, the observed Cu–S–Cu angle is acute. With sp^2 hybridization for sulfur the filled p_z orbital is parallel to the Cu–Cu vector and can donate electron density into empty orbitals of both copper atoms via a π -type bond (Figure 4b). This π interaction is bonding in the Cu–S bond but nonbonding between the two copper atoms and can cause a slight lengthening of the copper–copper distance. A further positive contribution to the Cu–S bond from π back-donation from filled copper orbitals to empty sulfur orbitals cannot be excluded (Figure 4c).

The 2e–3c Cu_2S bonding just described has a close analogy to the 2e–3c bonding of aryl groups in arylcopper compounds. In such a Cu_2C unit a carbon atom bridges two copper atoms with a filled sp^2 hybrid orbital and its p_z orbital, which is part of the aromatic π system, donates electron density via a π interaction of the two copper atoms. Because of the latter interaction the plane of a bridging aryl group is almost always perpendicular to the Cu…Cu vector.

In the 2e–3c Cu_2S bonding description the nonbonding lone-pair electrons on the sulfur atom are of an sp^2 hybrid type. This lone pair and the organic substituent occupy positions on the sulfur atom, which are in the trigonal plane perpendicular to the Cu…Cu vector (see Figure 7). The sp^2 lone pair on sulfur has, thus, a

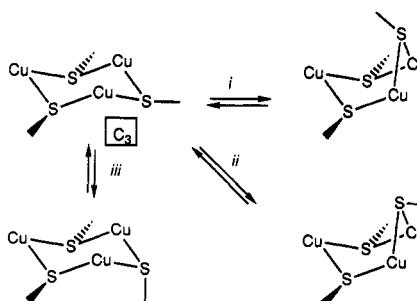


Figure 5. Schematic drawing of the C_3 species and the three possible structures of the C_1 species. The C_1 species are derived from the C_3 species by intramolecular processes i–iii; (i) a chair-to-boat flip; (ii) a concerted chair-to-boat flip and an inversion of the sulfur configuration; (iii) an inversion of the sulfur configuration.

stereochemical identity, and the position of the lone pair is important in the following discussion of the fluxional behavior of **4a–d**.

In copper thiolates the existence of different sulfur bridge bonding types (i.e. (i) Cu_2S (sp^2) 2e–3c, (ii) Cu_2S (sp^3) 4e–3c, and (iii) Cu_2S (sp^2) 4e–3c) provides a rationale for the large variation in the Cu…Cu distances found (Table IV). This variation is due to a combination of several factors, namely (a) the difference in orbital overlap between the bonding MO's as well as the extent of the Cu–S π interaction, (b) the coordination number of the copper and sulfur atoms participating in the Cu_2S bond, and (c) steric constraints of the ligands bonded to the copper and sulfur atom in the Cu_2S unit. The electron-deficient bonded (2e–3c) Cu_2S unit is more sensitive to these factors (especially factor a), since it is more compact than the 4e–3c systems. Consequently, the Cu–S–Cu bond angle and the Cu…Cu distance vary the most in the electron-deficient Cu_2S units.

Structural Aspects and Fluxional Behavior of Trinuclear Copper Arenethiolates in Solution. In solution one of the fluxional processes that can be investigated with NMR spectroscopy is the Cu–N bond association/dissociation process. In an earlier study of copper and tin complexes, we showed that ^1H NMR data of the $\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2$ -2 ligand system can probe the metal–nitrogen interaction because the benzylic carbon is a stereogenic center.^{10,15} The amino nitrogen is then a prosteriotropic center when coordinated to the metal center and an achiral center when not coordinated. In the case of $[\text{CuSC}_6\text{H}_4(\text{R-CH}(\text{Me})\text{NMe}_2)_2]_3$ (**4b**), when the copper nitrogen bond is stable on the NMR time scale, then one expects two singlet resonances for the diastereotopic methyl groups of the NMe_2 unit. However, the ^1H NMR spectrum of **4b** at 353 K shows one signal for these methyl groups and this indicates that there is rapid copper–nitrogen bond dissociation/association at room temperature on the NMR time scale; rapid inversion of configuration of the noncoordinated nitrogen (25 kJ mol^{-1})³⁶ then provides isochronous amino methyl groups. At lower temperatures the Cu–N bond does become stable on the NMR time scale and for each ligand pattern there are two signals for each NMe_2 unit. The same conclusion can be reached for **4c** containing the racemic $\text{SC}_6\text{H}_4(\text{CH}(\text{Me})\text{NMe}_2)$ -2 ligand. The use of this ligand system allowed us also to conclude that interaggregate exchange processes take place on the laboratory time scale (cf. eq 1).

There are two points regarding the trimeric copper arenethiolates in solution that require some discussion. Namely, what are the likely structures of the C_3 and C_1 conformers and what is the process by which they are interconverted? To aid us, there is an accumulation of useful physical and spectroscopic data, and it is worth summarizing these.

The most characteristic feature of the C_3/C_1 conformers is that their ratio in solution is dependent on the benzylic carbon substituents; it ranges from 3/2 for $\text{R-CH}(\text{Me})\text{NMe}_2$ (**4b**) to 1/9

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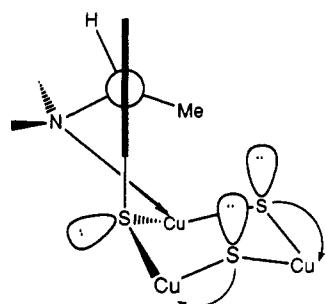


Figure 6. Schematic drawing of the species with C_1 symmetry of [2-(*R*)-1-(dimethylamino)ethyl]thiophenolato]copper(I) (**4b**) with a Newmann projection viewed along the benzylic carbon to ortho aromatic carbon axis (compare Figure 2) after an inversion of the sulfur configuration.

for CH_2NMe_2 (**4a**); i.e., the conformers are energetically not very different. The ^1H NMR shifts of the benzylic substituents (H/Me) are particularly characteristic (see Table V). The C_3/C_1 conformers have different physicochemical properties, including solubility and sensitivity toward air, and further studies show them to contain different chromophores.¹⁶ The interconversion ($\Delta G^\ddagger = 50 \text{ kJ mol}^{-1}$) is a low-energy process during which Cu-N coordination is probably retained.³⁸ Finally, the X-ray structure of **4b** has a trimeric C_3 structure and this seems to be a logical model for the C_3 conformer in solution. It is also important to remember that the sp^2 lone pair on sulfur has a stereochemical identity and occupies in this conformer an axial position.

For the C_1 conformer the forms to be discriminated are (see Figure 5) (i) a Cu_3S_3 ring in the boat conformation with two equatorially and one axially bonded aromatic groups, related to the C_3 conformer by a chair-to-boat flip of the Cu_3S_3 ring (without inversion of configuration at sulfur), (ii) a Cu_3S_3 ring in the chair conformation but with one aromatic group in the axial position, related to the C_3 conformer by an inversion of configuration at the sulfur atom bearing this group, or (iii) a Cu_3S_3 ring in the boat conformation with all aromatic groups in the equatorial position, related to the C_3 conformer by a chair-to-boat flip with inversion of configuration of one of the sulfur atoms in the Cu_3S_3 ring.

The first possible structure (i) whereby a chair-to-boat flip with retention of the sulfur configuration occurred is unlikely. The C_3 conformer has, as pointed out above, an organically crowded side, and in a C_1 boat form the situation here is worse. Furthermore, by analogy to cyclohexane, the presence of bulky axial substituents on the Cu_3S_3 ring would make a chair-to-boat flip a high-energy process. The second C_1 conformer can be seen as a species in which the equatorial aryl group and the axial lone pair on one sulfur atom have exchanged positions. This releases some steric strain in the "equatorial plane" of the C_3 conformer by moving the aryl system to the "inorganic" side, but this is held in balance by more crowding under the Cu_3S_3 ring on the "organic" side. The most important aspect of this conformer (best seen with molecular models) is the position that the benzylic carbon of this aryl system now occupies. First, it is placed so that it is within the through-space sphere of influence of two sulfur atoms, and second, it is positioned close to a neighboring "equatorial" aryl ring. These features can be used to easily explain both the low-field chemical shift of benzylic protons in for example the ^1H NMR spectrum of **4b** (C_1 conformer) and the increased percentage of the C_1 conformer when both benzylic substituents are protons (**4a**). In the third possible conformer there do not appear to be any steric advantages over the C_3 form; in fact, there are now some new unattractive interligand steric interactions. The benzylic carbon substituents in this conformer are not in special positions and are unlikely to have a significant influence on C_3/C_1 ratios.

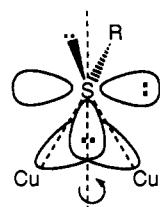


Figure 7. Schematic drawing of the electron-deficient thiolate-S bridge bond in copper(I) thiolates showing the position of the stereochemically active sulfur lone pair and the R group relative to the $\text{Cu}\cdots\text{Cu}$ vector.

Consequently, we conclude that the structure of the C_1 species is the one with the Cu_3S_3 chair and two aromatic rings in equatorial positions and one in an axial position (see Figure 6). A compound that has structural analogy to the proposed C_1 species is $[(\text{BX}_2)_3(\text{SR}_3)]$.³⁷ This C_1 conformer allows us to readily explain why the *SSR* and *RRS* enantiomers of complex **4c** with the racemic arenethiolate groups exist as only one conformer. Compared to the C_1 structure of **4b**, that of **4c** has the position of the methyl group and the proton interchanged on the axially positioned ligand; this leads to a decreased steric interaction. On the other hand, the other possible conformer (analogous to the C_3 conformer of **4b**) gains some extra steric interaction through the positioning of a methyl group in the plane of its aromatic ring (Figure 3b). Both points favor formation of the former conformer for the *RRS/SSR* diastereoisomer.

The interconversion of the C_1 and C_3 conformers of **4a** and **4b** that has been followed by NMR spectroscopy is a process that primarily involves inversion of configuration at a single sulfur atom. The ΔG^\ddagger found is a very rough estimate that gives the order of magnitude for this process in copper(I) arenethiolates having a 2e–3c bridging sulfur atom. A similar process ($\Delta G^\ddagger = 49 \text{ kJ mol}^{-1}$) has also been recently observed by us in the new compounds $[\text{Cu}_3(\text{SAr})_2(\text{R})(\text{L})]$ and $[\text{Cu}_4(\text{SAr})_2\text{R}_2]$ (R is an organic group and L is a phosphine ligand).^{9,38}

The ΔG^\ddagger values are lower than those for sulfur inversion reported for sulfur bonded to group 6 and 8 transition metals (60–72 kJ for W, Fe, Ru)³⁹ but in the range for platinum(II) and palladium(II) complexes (48–79 kJ).⁴⁰ In those cases where the metal atoms have empty d orbitals the low ΔG^\ddagger was ascribed to some electron donation from filled sulfur orbitals to these empty metal orbitals.⁴¹ This explanation for the low-energy barrier is clearly not correct for our species in which Cu(I) has a filled d shell. Consequently, it is likely that the "sulfur inversion" mechanism in copper thiolates is different.

We propose that the analogy between the bonding mode of the sulfur atom in the copper thiolates and the bonding of C_{ipso} in arylcopper compounds can be extended to explain their fluxional behavior in solution. We therefore conclude that the copper-binding sp^2 hybrid sulfur orbital can function as a rotation (wagging) axis (Figure 7) in the same way that the C_{ipso} sp^2 orbital allows bridging aryl groups to rotate in arylcopper compounds.¹⁰ This type of rotation (wagging) easily allows the stereochemically active sp^2 lone pair and the aryl group to exchange their positions on the sulfur atom; this can be seen as sulfur inversion. In our copper thiolates this rotation is limited by the chelating nature of the arenethiolate, and this results in a wagging movement of the aryl group from axial to equatorial positions. There is also a close similarity in ΔG^\ddagger for rotation process of the aryl group in arylcopper compounds and that in the copper arenethiolates (i.e. 50 kJ mol^{-1}).^{18,42} The ΔG^\ddagger value for both processes is low

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because in the transition state the dominant 2e-3c bond of the Cu-S-Cu unit and Cu-C-Cu unit remains intact, while only the contribution of the π -bonding to the Cu-S bond is lost.

Conclusion

The use of the novel monoanionic, bidentate amine-thiolate ligands $\text{SC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)\text{-2-R''-3}$ ($\text{R}' = \text{H}, \text{R}'' = \text{H}, \text{Cl}; \text{R}' = \text{Me}, \text{R}'' = \text{H}$) resulted in the synthesis and characterization of trinuclear copper arenethiolates $[\text{CuSC}_6\text{H}_3(\text{CH}(\text{R}')\text{NMe}_2)\text{-2-R''-3}]_3$. These copper arenethiolates are soluble, and this has allowed a detailed study of their fluxional behavior in solution. The structural features of these copper arenethiolates indicate that

in copper thiolates with acute Cu-S-Cu angles the likely bonding description of the Cu_2S unit is an sp^2 -hybridized sulfur atom bridging two copper atoms in an electron-deficient three-center two-electron interaction. In copper thiolates this type of bonding allows the organic group and the sulfur lone pair to exchange positions and thus provides "sulfur inversion" with a low-energy barrier.

Acknowledgment. This work was supported in part (A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Tables S1-S6, listing fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal parameters, ^1H NMR spectra at 223 and 353 K of **4a-d** (Figure S1a-d), and a COSY 2D spectrum of **4b** (Figure S2) (8 pages); a listing of observed and calculated structure factor amplitudes for **4b** (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the New Quaternary One-Dimensional Chain Materials $\text{K}_2\text{CuNbSe}_4$ and $\text{K}_3\text{CuNb}_2\text{Se}_{12}$

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Received November 9, 1990

The one-dimensional chain materials $\text{K}_2\text{CuNbSe}_4$ and $\text{K}_3\text{CuNb}_2\text{Se}_{12}$ have been synthesized at 800 and 870 °C, respectively, through the use of molten alkali-metal selenides as reactive fluxes. $\text{K}_2\text{CuNbSe}_4$ crystallizes in space group $D_{2h}^{24}\text{-Fddd}$ of the orthorhombic system with eight formula units in a cell of dimensions $a = 5.745$ (1), $b = 13.444$ (1), and $c = 23.907$ (3) Å. The structure consists of infinite linear chains separated from the K^+ ions. These chains, which are along the c axis, consist of edge sharing of alternating NbSe_4 and CuSe_4 tetrahedra. The structural motif thus represents an elaboration of that in KFeS_2 . There are no short Se...Se interactions and so formal oxidation states of K(I) , Cu(I) , Nb(V) , and Se(-II) are assigned. The compound is a poor conductor, having a resistance greater than 10 MΩ cm at room temperature. $\text{K}_3\text{CuNb}_2\text{Se}_{12}$ crystallizes in space group $C_{2h}^{24}\text{-P}2_1/n$ of the monoclinic system with four formula units in a cell with dimensions $a = 9.510$ (6), $b = 13.390$ (9), and $c = 15.334$ (10) Å and $\beta = 96.09$ (4)°. The structure consists of an infinite $\text{Cu}/\text{Nb}/\text{Se}$ chain separated from K^+ cations. The infinite chain can be formulated as $[\text{CuNb}_2(\text{Se})_2(\text{Se}_2)_3(\text{Se}_4)^3]$ or alternatively as $[\text{CuNb}_2(\text{Se})_3(\text{Se}_2)_3(\text{Se}_3)^3]$ depending upon the choice of a cutoff for the length of an Se-Se bond. In the former instance the chain contains Cu(I) and Nb(IV) centers while in the latter instance it contains Cu(I) and Nb(V) centers. The two crystallographically distinct Nb atoms are seven-coordinate and the Cu atom is tetrahedral.

Introduction

Molten salts and high-temperature solvents have been extensively used as fluxes in the temperature range 300–1800 °C to promote crystal growth.¹ The majority of the compounds crystallized from these high-temperature solvents have been elements, binaries, or ternary oxides; however, binary and ternary chalcogenides have been crystallized from molten salts of the type A_2Q_n (A = alkali metal, Q = S, Se).^{2,3} In general, these A_2Q_n fluxes are unreactive, and A is not incorporated into the final product. The use of a reactive flux does not appear to be a standard preparative method⁴ for the synthesis of new compounds. But, as we first described for the $\text{K}_2\text{S}/\text{S}$ system,⁵ the use of a reactive flux takes advantage of low-melting A/Q systems (A = alkali metal; Q = S, Se, Te) and uses the reactive poly-chalcogenides A_2Q_n not only as classic fluxes but also as reactants so that the alkali metal and chalcogen and often the polychalcogen

are incorporated into the final product. This reactive flux method appears to be a general solid-state route to preparing new compounds containing polychalcogenide species.⁵

Until recently the new compounds synthesized with this preparative method were ternary sulfides and selenides, often with unusual structural features. These typically include chalcogen-chalcogen bonding, as in $\text{K}_4\text{Ti}_3\text{S}_{14}$ ⁵ (S^{2-}), $\text{Na}_2\text{Ti}_2\text{Se}_8$ ⁶ (Se^{2-}), KCuS_4 ⁷ (S^{2-}), and KAuSe_5 ⁸ (Se_5^{2-}), one-dimensional chains,⁵⁻⁹ three-dimensional structures,⁹ and molecular species.¹⁰ While many of these reactions have been carried out at low temperatures (200–500 °C), some have been carried out at temperatures as high as 900 °C. Compounds containing polychalcogenide ligands have been made over the entire temperature range, although they may be more prevalent among the low-temperature syntheses.

In an attempt to delineate the applicability of the reactive flux method, we continue to investigate a number of potential new systems. In so doing, we have recently demonstrated that the

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