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Coordination Chemistry of Sterically Hindered Thiolate Ligands. Preparation and Structural Characterization of the Oligomeric Homoleptic Complexes $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ and $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ and a Comparison to the Structure of the Mononuclear Species $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$

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The ligand 2-(trimethylsilyl)benzenethiol may be prepared by treatment of 2-(phenylthio)tetrahydropyran with *tert*-butyllithium in THF/HMPA at −90 °C followed by chlorotrimethylsilane and then mercuric chloride/hydrogen sulfide. Alternatively, conversion of thiophenol to lithium 2-lithiobenzenethiolate followed by quenching at −78 °C with an equivalent of chlorotrimethylsilane affords the ligand 2-(trimethylsilyl) benzenethiol. A cadmium salt of structure $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$ (I) (as determined by X-ray crystallography) and copper and silver salts of structures $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II) and $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ (III), respectively, can be prepared from reactions of the ligand with the appropriate metal precursors. Crystal data for $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$: monoclinic space group $P2_1/n$ with $a = 17.219$ (2) Å, $b = 30.563$ (4) Å, $c = 27.446$ (3) Å, $\beta = 93.58$ (2)°, $V = 14416.0$ (18) Å^3, and $Z = 4$; structure solution and refinement based on 5645 reflections with $F_o \geq 6\sigma(F_o)$ to give $R = 0.064$. Crystal data for $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$: monoclinic space group $A2$ with $a = 11.923$ (2) Å, $b = 14.761$ (2) Å, $c = 26.618$ (4) Å, $\beta = 98.30$ (1)°, $V = 4635.6$ (12) Å^3, and $Z = 4$; structure solution and refinement based on 2954 reflections with $F_o \geq 6\sigma(F_o)$ to give $R = 0.062$. Crystal data for $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$: hexagonal space group $P6_122$ with $a = b = 17.501$ (3) Å, $c = 39.100$ (5) Å, $V = 10371.3$ (18) Å^3, and $Z = 6$; structure solution and refinement based on 1991 reflections with $F_o \geq 6\sigma(F_o)$ to give $R = 0.0675$.

Introduction

Metal–thiolate coordination chemistry is of fundamental chemical interest in view of the structural diversity displayed and the relevance to the metal sites of a variety of redox-active metalloproteins.[1] Furthermore, in metal complexes, the RS^- group can be compared with the sulfido ligand S^{2-}, with the advantage that the substituent R can be manipulated to effect steric and electronic control of ligating ability and to engineer the environment about the metal site, thus affording metal–thiolate sites accessible to small substrate molecules.

As part of our continuing investigations of the chemistry of novel sterically hindered thiolate ligands,[2-7] we have prepared the thiols **1** and **2** (Schemes I and II).[8,9] The silylated thiols are of interest as representatives of a new class of hindered ligands with "tunable" steric demand. Variation in both the silyl substituent and the number of silyl groups should lead to a corresponding variation in the steric cone angle[10] of the ligand. Furthermore, the 2-(triorganosilyl)thiophenols **1** and 2,6-bis(triorganosilyl)thiophenols may provide synthetic precursors for calixarene-like[11] cyclic polythiophenols capable of snugly accommodating a metal while providing a cavity accessible to small linear molecules.

In this paper, we report the coordinating properties of 2-(trimethylsilyl)thiophenol with the group IIb metal Cd and the group Ib metals Cu and Ag. This choice was dictated in part by the well-documented propensity of Cu^+, Ag^+, and Cd^{2+} to form polymeric or oligomeric species with sterically innocent thiolate ligands. Furthermore, the chemistry of Cd^{2+} with thiolate ligands is of some interest in modeling the metal binding sites of metallothioneins,[12] while copper thiolate chemistry provides analogies for cysteinyl ligation of this metal in "blue" copper proteins and metallothionein proteins.[15] The ligand 2-(trimethylsilyl)thiophenol was found to exhibit contrasting behavior with the various metal cations, yielding the mononuclear complex $(Et_4N)_2[Cd(SR)_4]$ and the polynuclear species $[Cu(SR)]_{12}$ and $[\{Ag(SR)_4\}]_2$. The structures of these homoleptic metal thiolates are discussed herein.

Experimental Section

The ligand 2-(trimethylsilyl)thiophenol was prepared as previously described.[14] ^1H NMR spectra were recorded on a Varian XL-300 NMR spectrometer and were referenced to internal TMS. The X-ray studies were performed on a Nicolet R3M/V diffractometer using MICROVAX II mounted program packages.

Elemental analysis were performed by Desert Analytics, Tucson, AZ.

$(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$ (I). To sodium metal (0.048 g, 2.1 mmol) dissolved in ethanol (5 mL) was added 2-(trimethylsilyl)benzenethiol (0.383 g, 2.1 mmol) in acetonitrile (5 mL). After ca. 5 min of stirring, $CdCl_2$ (0.128 g, 0.7 mmol) was added with efficient stirring. The mixture was stirred for 1 h, and Et_4NCl (0.232 g, 1.4 mmol) was added. After the mixture was stirred for 48 h, NaCl was removed by filtration. Ether (0.5 mL) was added to the filtrate, and the solution was maintained at room temperature for several days. The crystals were collected by filtration, washed with ether twice, and dried in air. The product was obtained as colorless, hexagonal-shaped crystals (0.147 g, 22% yield), mp 183 °C. ^1H NMR (D_2O): δ 0.30 ($Si(CH_3)_3$), 1.12 (CH_3), 1.98 (CH_2), 7.30 ($-C_6H_4$). IR (KBr): 3015, 2940, 2885, 1565, 1480, 1440, 1410, 1250, 1240, 1170, 1120, 1100, 840, 750, 725, 675, 615, 440, 330 cm^{-1}. Anal. Calcd for $C_{52}H_{92}N_2S_4Si_4Cd$: C, 56.87; H, 8.44; N, 2.55. Found: C, 56.76; H, 8.84; N, 2.47.

Attempts to synthesize oligomeric species such as $[Cd_2(SR)_6]^{2-}$ or $[Cd_4(SR)_{10}]^{2-}$ proved unsuccessful. Variations of ligand/metal ratios in the range 1:1–4:1 yielded compound I in diminished yields (ca. 10%). Variations in reaction solvent, employing chloroform, acetone, or methanol, also resulted in the isolation of I, again in low yield. No other compositions were observed under the range of conditions employed.

$[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II). A solution was prepared of $[Cu(CH_3CN)_4]PF_6$ (0.745 g, 2 mmol) in methanol (10 mL). Upon addition of 2-(trimethylsilyl)benzenethiol 0.383 g, 2.1 mmol) in methanol (3 mL),

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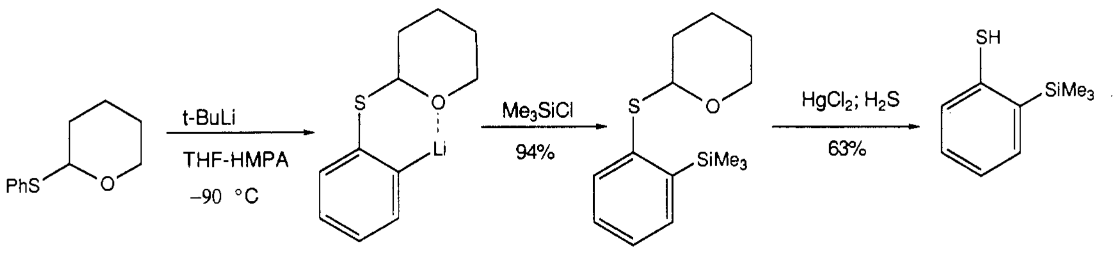
Scheme I



Scheme II

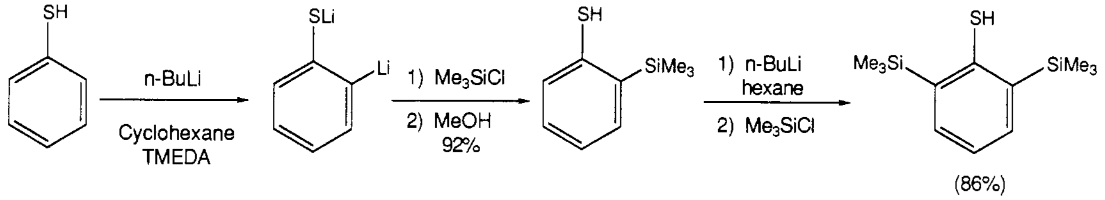


Table I. Summary of Experimental Details for the X-ray Diffraction Studies of $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$, $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$, and $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$

	$(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$	$[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$	$[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$
	(A) Crystal Parameters at 296 K[a]		
formula	$CdS_4Si_4N_2C_{52}H_{92}$	$Cu_{12}S_{12}Si_{12}C_{108}H_{156}$	$Ag_4S_4Si_4C_{36}H_{52}$
fw	1096.9	2936	1155.7
a, Å	17.501 (3)	17.219 (4)	11.923 (2)
b, Å	17.501 (3)	30.563 (5)	14.761 (2)
c, Å	39.100 (5)	27.446 (5)	26.618 (4)
α, deg	90.00	90.00	90.00
β, deg	90.00	93.58 (2)	98.30 (1)
γ, deg	120.00	90.00	90.00
V, Å^3	10371.3 (18)	14416.8 (18)	4635.6 (11)
space group	$P6_122$	$P2_1/n$	$A2$
Z	6	4	4
ρ_{calc}, g·cm^{-3}	1.03	1.35	1.66
ρ_{obs}, g·cm^{-3}	1.07	1.33	1.64
	(B) Summary of Structural Solution Data		
no. of reflcns collcd	3211 ($\pm h,+k,+l$)	12499 ($\pm h,+k,+l$)	2954 ($+h,+k,\pm l$)
no. of reflcns used in solution ($F_o \geq 6\sigma(F_o)$)	1991	5645	1646
abs coeff, cm^{-1}	8.21	20.11	19.48
T_{max}/T_{min}	1.09	1.05	1.21
final discrepancy factors[b]			
R	0.0675	0.0675	0.0621
R_w	0.0689	0.0732	0.0618
goodness of fit[c]	1.446	1.798	1.165

[a] From the fitting of 25 reflections with $2\theta \geq 25°$. [b] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in: Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1979. Atom scattering factors are from: Cromer, D. T.; And Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321. All nonhydrogen atoms corrected for effect of anomalous dispersion by using: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1962; Vol. III. [c] $R = \sum[|F_o| - F_c|/\sum|F_o|]$; $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o + g^*(F_o)$; $g = 0.005$; GOF $= [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables.

a brownish yellow solid precipitated immediately. After the mixture was stirred for 1 h at room temperature, the solvent was decanted and the solid collected and dried in vacuo. The solid was dissolved in warm CH_2Cl_2 (ca. 10 mL) to which solution methanol (5 mL) was added dropwise. The solution was kept at room temperature for 2 weeks, and the red crystals were collected by filtration, washed with methanol (2×), and dried in air. The title compounds was obtained as red rhombic crystals (0.232 g, 47%), mp 250 °C. ^1H NMR (CD_2Cl_2): δ 8.28, 7.67, 7.28, 6.99, 6.88, 6.80, 6.46, 0.39, -0.14. ^{13}C NMR (CD_2Cl_2): δ 142.43, 142.02, 141.73, 140.27, 137.89, 136.76, 135.92, 134.75, 130.45, 129.01, 126.90, 124.36, 2.18, -0.03. IR (KBr): 3040, 2945, 1555, 1410, 1245, 1100, 1030, 825, 740, 710, 615, 440, 330 cm^{-1}. Anal. Calcd for $C_{108}H_{156}S_{12}Si_{12}Cu_{12}$: C, 44.14; H, 5.35. Found: C, 44.05; H, 5.43.

$[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ (III). A solution containing 2-(trimethylsilyl)benzenethiol (0.364 g, 2.0 mmol) and triethylamine (0.212 g, 2.1 mmol) in acetonitrile (10 mL) was prepared at room temperature. To this was added a solution of $AgNO_3$ (0.357 g, 2.0 mmol) in acetonitrile (10 mL) with vigorous stirring at ambient temperature. A yellow solid was produced immediately. After 2 h of stirring, the resultant solution was concentrated to give a pale pink solid. The solid was dissolved in hot chloroform (30 mL), and the solution was filtered to remove impurities and diluted with methanol (10 mL). After several days, a pale yellow powder was produced. Recrystallization from hot chloroform/toluene/methanol (20 mL/1 mL/20 mL) afforded pale yellow pink crystals of needle habit (0.180 g, 31% yield). The crystals were collected by filtration, washed with methanol, and dried in air; mp 208–210 °C dec. ^1H NMR: δ 0.30 ($Si(CH_3)_3$), 7.00 (C_6H_4). IR (KBr): 3040, 2940, 1565, 1410, 1245, 1100, 1030, 840, 745, 710, 615, 440 cm^{-1}. Anal. Calcd for $C_9H_{13}SSiAg$: C, 37.37; H, 4.53. Found: C, 36.41; H, 4.52.

Attempted Synthesis of Other Oligomers of Cu^+ and Ag^+ with $HSC_6H_4\text{-}o\text{-}SiMe_3$. A range of reaction conditions were employed in attempts to isolate a variety of oligomers of the type $[M(SR)]_n$ (M = Cu, Ag; n other than 12 for Cu or 8 for Ag). The stoichiometries of the reactants were varied in the range 1:1–6:1 for the ligand:metal ratio. The reactions were carried out in chloroform, acetone, methanol, and acetonitrile in order to assess solvent influence on oligomer formation. A variety of recrystallization techniques were employed, including slow evaporation, vapor diffusion, and cooling to -20 °C. In no case was a composition other than II or III isolated, although yields were generally greatly diminished (ca. 10%).

Collection and Reduction of X-ray Data and Solution and Refinement of the Structure. The crystal data and experimental details of the

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$ (I)

atom	x	y	z	U_{eq}
Cd(1)	9437 (1)	4719 (1)	833	72 (1)[a]
S(1)	10598 (3)	6014 (3)	491 (1)	97 (3)[a]
S(2)	8302 (3)	3372 (3)	518 (1)	85 (3)[a]
Si(1)	11599 (5)	7852 (5)	56 (2)	112 (5)[a]
Si(2)	7201 (5)	1870 (4)	−78 (1)	100 (4)[a]
C(11)	10355 (9)	6020 (10)	57 (4)	83 (5)
C(12)	10829 (12)	6818 (12)	−103 (4)	109 (6)
C(13)	10590 (15)	6741 (15)	−480 (5)	144 (7)
C(14)	10017 (14)	6017 (15)	−632 (5)	149 (7)
C(15)	9566 (12)	5189 (13)	−458 (4)	128 (7)
C(16)	9751 (10)	5259 (11)	−101 (4)	94 (5)
C(21)	8612 (11)	2608 (11)	416 (4)	88 (5)
C(22)	8142 (11)	1951 (11)	151 (4)	91 (5)
C(23)	8437 (12)	1383 (12)	90 (4)	104 (5)
C(24)	9110 (13)	1368 (13)	272 (4)	132 (7)
C(25)	9544 (14)	1962 (14)	543 (5)	142 (7)
C(26)	9280 (12)	2600 (13)	604 (4)	116 (6)
C(17)	11146 (17)	8274 (14)	369 (5)	188 (19)[a]
C(18)	12084 (26)	8826 (19)	−231 (7)	219 (31)[a]
C(19)	12625 (21)	7856 (15)	193 (6)	301 (29)[a]
C(27)	7410 (21)	2859 (15)	−314 (4)	110 (29)[a]
C(28)	6237 (14)	1533 (14)	195 (5)	1148 (17)[a]
C(29)	6895 (18)	980 (13)	−431 (5)	152 (20)[a]
N(1)	7395 (11)	5696 (11)	120 (4)	129 (5)
C(1)	7313 (15)	4941 (15)	303 (6)	150 (8)
C(2)	6454 (15)	4296 (16)	382 (6)	195 (11)
C(3)	7016 (18)	6166 (17)	316 (6)	201 (11)
C(4)	7331 (20)	6536 (21)	638 (6)	89 (9)
C(5)	6932 (14)	5427 (15)	−202 (5)	141 (7)
C(6)	7168 (20)	4950 (19)	−432 (7)	188 (14)
C(7)	8402 (16)	6298 (16)	68 (6)	166 (9)
C(8)	8673 (26)	7069 (23)	−54 (7)	171 (18)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$ (I)

Cd–S(1)	2.540 (4)	Cd–S(2)	2.518 (4)
Cd–S(1′)	2.540 (3)	Cd–S(2′)	2.518 (3)
S(1)–Cd–S(2)	118.8 (1)	S(1)–Cd–S(1′)	92.3 (2)
S(2)–Cd–S(1′)	117.7 (2)	S(1)–Cd–S(2′)	117.7 (2)
S(2)–Cd–S(2′)	93.8 (2)	S(1′)–Cd–S(2′)	118.8 (1)

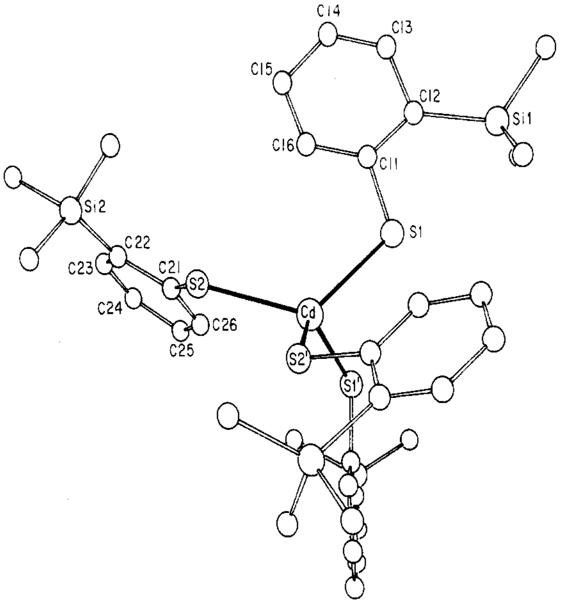


Figure 1. ORTEP view of the structure of $[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]^{2-}$, showing the labeling of the coordination sphere.

structure determinations are given in Table I. A full description of the experimental details of the methods of structure solution may be found in Table S15 (supplementary material) and ref 8. None of the crystals exhibited significant decay under X-ray irradiation. Tables II and III list atomic positional parameters and selected bond lengths and angles for $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$, while Tables V–VIII present these data for the structures of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]^{12}$ and $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$.

Results and Discussions

The synthesis of complexes $[Cu(SR)]_{12}$, $\{[Ag(SR)]_4\}_2$, and $[Cd(SR)_4]^{2-}$ was readily effected by direct addition of a solution of the ligand or of the sodium salt of the ligand to a solution of the metal salt in acetonitrile. Variations in reaction conditions yielded the same products in diminished yields but gave no evidence of the formation of higher oligomers or of other compositions.

Description of the Structure of $(Et_4N)_2[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]$ (I). The most significant feature of the structure is the discrete mononuclear nature of the anion, illustrated in Figure 1. The Cd(II) ion is four coordinate, displaying distorted tetrahedral geometry, common to $[M(II)(SR)_4]^{n-}$ complexes.[15] The major distortion consists of a compression of the tetrahedron along one

Table IV. Comparison of Selected Structure Parameters for $[Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4]^{2-}$ (I) and Related $[M(SC_6H_5)_4]^{2-}$ Complexes

(a) Dihedral Angles (deg) between Ligand Rings

		limiting conformations			
	I	A	B	$[Fe(SC_6H_5)_4]^{2-}$	
C(11)–C(16); C(11′)–C(16′)	86.0	0.0	60.0	50.8	ring 1–ring 2
C(21)–C(26); C(21′)–C(26′)	84.1	0.0	60.0	3.4	ring 3–ring 4
C(11)–C(16); C(21)–C(26)	66.2	90.0	90.0	70.7	ring 1–ring 3
C(11′)–C(16′); C(21′)–C(26′)	66.2	90.0	60.0	78.0	ring 2–ring 4
C(11)–C(16); C(21′)–C(26′)	54.9	90.0	30.0	67.3	ring 1–ring 4
C(11′)–C(16′); C(21)–C(26)	54.9	90.0	30.0	80.1	ring 2–ring 3

(b) Interactions of the Ring Ortho Hydrogen Atom (Å)

	I	$[Cd(SC_6H_5)_4]^{2-}$	$[Fe(SC_6H_5)_4]^{2-}$
M–H	3.10 (9)	2.95 (10)	2.98 (8)
H–S′[a]	2.88 (9)	3.00 (9)	2.94 (6)
H–S″	4.85 (14)	3.66 (20)	3.55 (16)
H–S‴	2.78 (9)	2.86 (9)	2.86 (4)

(c) Selected Angular Distortions (deg)

	I	$[Cd(SC_6H_5)_4]^{2-}$	$[Fe(SC_6H_5)_4]^{2-}$
M–S–C	115.5 (9)	109	111 (2)
S–C–C	118.6 (11)	121.5	121.9 (6)

[a] H–S′, average distance of the ortho hydrogen atoms to the sulfur of the nearest neighboring ligand unit; H–S″, average distance of the ortho hydrogen atoms to the sulfur atoms of two remaining neighboring ligand units; H–S‴, average distance of the ortho hydrogen atoms to the sulfur atoms of the same ligand unit. Corresponding designators in ref 14: H–S′, H–S(a); H–S″, H–S(a′); H–S‴, H–S(b) and H–S(b′).

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II)

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Cu(1)	6429 (2)	2023 (1)	5614 (1)	64 (1)	C(71)	8576 (15)	2709 (8)	4011 (10)	63 (8)
Cu(2)	6788 (2)	1538 (1)	6554 (1)	81 (2)	C(72)	8199 (15)	2813 (9)	3559 (11)	69 (8)
Cu(3)	8383 (2)	1825 (1)	6529 (1)	65 (2)	C(73)	8684 (18)	2940 (10)	3181 (11)	90 (10)
Cu(4)	7984 (2)	1806 (1)	4525 (1)	65 (1)	C(74)	9513 (19)	2935 (10)	3266 (12)	96 (11)
Cu(5)	9585 (2)	1594 (1)	4486 (1)	82 (2)	C(75)	9842 (18)	2792 (10)	3718 (13)	98 (11)
Cu(6)	9920 (2)	2085 (1)	5441 (1)	65 (1)	C(76)	9388 (15)	2702 (8)	4097 (10)	67 (8)
Cu(7)	7374 (2)	3088 (1)	4909 (1)	65 (1)	C(81)	10277 (16)	3206 (9)	5375 (10)	66 (8)
Cu(8)	8026 (3)	3785 (1)	5494 (2)	49 (2)	C(82)	11036 (17)	3317 (10)	5538 (11)	85 (10)
Cu(9)	8836 (2)	3118 (1)	6126 (1)	66 (1)	C(83)	11376 (17)	3658 (10)	5243 (12)	90 (10)
Cu(10)	8187 (2)	1748 (1)	5526 (1)	72 (1)	C(84)	10985 (20)	3890 (11)	4881 (13)	104 (11)
Cu(11)	8758 (2)	2642 (1)	5163 (1)	64 (1)	C(85)	10224 (19)	3787 (11)	4700 (12)	101 (11)
Cu(12)	7545 (2)	2608 (1)	5910 (1)	63 (1)	C(86)	9859 (16)	3431 (10)	4995 (11)	82 (9)
S(1)	5773 (4)	1556 (3)	6050 (3)	73 (3)	C(91)	7533 (16)	4058 (9)	4431 (10)	72 (9)
S(2)	7727 (5)	1535 (3)	7116 (3)	81 (4)	C(92)	7187 (20)	4471 (12)	4272 (13)	97 (12)
S(3)	7116 (4)	1617 (2)	5072 (3)	61 (3)	C(93)	7465 (28)	4647 (16)	3787 (19)	112 (17)
S(4)	9272 (4)	1673 (2)	5988 (3)	65 (3)	C(94)	8065 (25)	4439 (15)	3560 (16)	115 (15)
S(5)	8647 (4)	1533 (3)	3927 (3)	76 (3)	C(95)	8419 (18)	4058 (11)	3736 (12)	103 (11)
S(6)	10599 (4)	1651 (2)	4991 (3)	71 (3)	C(96)	8107 (16)	3894 (9)	4178 (11)	74 (9)
S(7)	7977 (4)	2559 (2)	4509 (3)	54 (3)	C(101)	8565 (17)	4120 (10)	6570 (11)	84 (10)
S(8)	9767 (4)	2788 (2)	5676 (3)	60 (3)	C(102)	8893 (19)	4545 (12)	6688 (13)	92 (11)
S(9)	7117 (5)	3795 (3)	4924 (3)	57 (4)	C(103)	8609 (22)	4743 (12)	7094 (15)	90 (12)
S(10)	8952 (5)	3833 (3)	6059 (3)	60 (4)	C(104)	8055 (23)	4550 (14)	7366 (15)	122 (14)
S(11)	6535 (4)	2728 (2)	5401 (3)	58 (3)	C(105)	7733 (19)	4147 (12)	7241 (13)	108 (12)
S(12)	8336 (4)	2578 (2)	6574 (3)	59 (3)	C(106)	7984 (17)	3928 (10)	6825 (12)	87 (10)
Si(1)	4490 (7)	951 (4)	6601 (5)	112 (6)	C(111)	5982 (14)	3155 (8)	5708 (9)	58 (8)
Si(2)	7663 (8)	1168 (4)	8232 (4)	65 (6)	C(112)	5224 (14)	3228 (8)	5539 (9)	55 (7)
Si(3)	5730 (5)	1051 (3)	4351 (4)	92 (4)	C(113)	4853 (15)	3575 (9)	5807 (10)	71 (9)
Si(4)	10633 (6)	1170 (4)	6791 (4)	108 (5)	C(114)	5239 (16)	3809 (9)	6196 (10)	74 (9)
Si(5)	8662 (10)	1087 (5)	2814 (4)	109 (7)	C(115)	5997 (18)	3710 (10)	6345 (11)	90 (10)
Si(6)	11904 (7)	1080 (3)	4392 (5)	77 (5)	C(116)	6394 (15)	3363 (9)	6073 (10)	68 (8)
Si(7)	7118 (5)	2825 (3)	3365 (3)	84 (4)	C(121)	7745 (13)	2730 (7)	7065 (9)	45 (7)
Si(8)	11663 (5)	3059 (3)	6045 (3)	91 (4)	C(122)	8069 (15)	2903 (9)	7482 (10)	65 (8)
Si(9)	6346 (9)	4748 (5)	4560 (7)	127 (8)	C(123)	7539 (17)	2999 (9)	7852 (11)	78 (9)
Si(10)	9646 (8)	4808 (4)	6298 (7)	97 (8)	C(124)	6739 (19)	2930 (10)	7795 (12)	98 (11)
Si(11)	4601 (5)	2968 (3)	5020 (3)	83 (4)	C(125)	6433 (16)	2731 (9)	7359 (11)	78 (9)
Si(12)	9145 (5)	2965 (3)	7688 (3)	81 (4)	C(126)	6955 (15)	2635 (9)	6970 (10)	69 (8)
C(11)	5084 (14)	1825 (9)	6396 (9)	61 (8)	C(17)	5501 (23)	693 (13)	6854 (15)	128 (15)
C(12)	4504 (16)	1571 (9)	6603 (11)	77 (9)	C(18)	3701 (28)	748 (16)	7022 (19)	90 (17)
C(13)	3913 (17)	1812 (11)	6852 (11)	89 (10)	C(19)	4233 (27)	737 (15)	5925 (18)	113 (17)
C(14)	3946 (19)	2257 (12)	6867 (12)	105 (11)	C(27)	7713 (29)	792 (16)	8815 (19)	127 (18)
C(15)	4461 (18)	2523 (10)	6638 (12)	89 (10)	C(28)	8374 (23)	1625 (14)	8339 (15)	112 (15)
C(16)	5071 (14)	2280 (9)	6400 (9)	62 (8)	C(29)	6702 (23)	1385 (13)	8112 (15)	108 (14)
C(21)	8024 (15)	975 (9)	7232 (11)	70 (9)	C(37)	4964 (24)	634 (14)	4184 (15)	114 (15)
C(22)	7980 (17)	824 (11)	7722 (12)	95 (11)	C(38)	5188 (19)	1540 (12)	4567 (13)	104 (12)
C(23)	8277 (22)	409 (13)	7817 (15)	92 (13)	C(39)	6354 (20)	1162 (11)	3806 (13)	101 (12)
C(24)	8532 (21)	156 (12)	7455 (15)	87 (13)	C(47)	10002 (22)	1381 (12)	7254 (14)	96 (13)
C(25)	8603 (18)	301 (11)	6986 (13)	87 (11)	C(48)	11140 (28)	1666 (16)	6574 (19)	93 (17)
C(26)	8313 (16)	741 (10)	6863 (11)	83 (10)	C(49)	11267 (32)	724 (18)	7174 (21)	87 (19)
C(31)	6891 (14)	1050 (8)	5203 (10)	59 (8)	C(57)	8088 (25)	1598 (15)	2698 (17)	104 (16)
C(32)	6347 (14)	832 (9)	4883 (10)	63 (8)	C(58)	9648 (34)	1298 (19)	2857 (22)	90 (20)
C(33)	6177 (17)	353 (11)	4996 (12)	96 (11)	C(59)	8444 (41)	686 (23)	2294 (27)	87 (25)
C(34)	6585 (18)	179 (10)	5426 (13)	97 (11)	C(67)	12659 (22)	931 (13)	3969 (15)	107 (14)
C(35)	7103 (19)	404 (11)	5718 (12)	101 (11)	C(68)	10969 (27)	846 (15)	4100 (18)	110 (17)
C(36)	7247 (16)	872 (10)	5616 (11)	76 (9)	C(69)	12152 (30)	888 (18)	5003 (21)	80 (18)
C(41)	9568 (14)	1104 (8)	5917 (10)	53 (7)	C(77)	6597 (17)	3337 (10)	3533 (12)	102 (11)
C(42)	10116 (16)	917 (10)	6264 (11)	77 (9)	C(78)	7011 (19)	2826 (11)	2667 (13)	119 (12)
C(43)	10332 (19)	487 (12)	6168 (13)	112 (12)	C(79)	6648 (17)	2320 (10)	3562 (11)	91 (10)
C(44)	9971 (18)	237 (10)	5762 (12)	93 (10)	C(87)	12007 (19)	2509 (12)	5818 (13)	117 (12)
C(45)	9406 (18)	457 (11)	5405 (12)	95 (10)	C(88)	11136 (19)	3022 (11)	6620 (12)	110 (12)
C(46)	9225 (16)	905 (10)	5503 (11)	79 (9)	C(89)	12517 (22)	3470 (13)	6187 (15)	107 (14)
C(51)	8385 (15)	954 (9)	3860 (11)	74 (9)	C(97)	6665 (34)	4880 (20)	5203 (24)	126 (22)
C(52)	8383 (17)	788 (11)	3362 (12)	96 (11)	C(98)	5516 (29)	4404 (17)	4481 (19)	124 (18)
C(53)	8079 (20)	336 (13)	3376 (14)	116 (12)	C(99)	5984 (38)	5240 (22)	4145 (26)	121 (25)
C(54)	7856 (19)	90 (11)	3750 (14)	108 (12)	C(107)	9340 (35)	4871 (20)	5633 (24)	102 (22)
C(55)	7907 (17)	299 (11)	4208 (12)	91 (10)	C(108)	10580 (26)	4459 (15)	6397 (18)	112 (17)
C(56)	8185 (15)	728 (9)	4261 (10)	69 (9)	C(109)	9798 (30)	5440 (18)	6458 (21)	110 (19)
C(61)	11277 (14)	1939 (9)	4661 (9)	57 (8)	C(117)	3727 (17)	3345 (10)	4850 (12)	98 (11)
C(62)	11838 (17)	1688 (8)	4415 (11)	72 (8)	C(118)	5164 (17)	2903 (10)	4455 (11)	93 (10)
C(63)	12413 (17)	1945 (11)	4211 (11)	87 (10)	C(119)	4236 (17)	2419 (10)	5226 (11)	95 (10)
C(64)	12415 (17)	2407 (11)	4194 (11)	87 (10)	C(127)	9697 (23)	2453 (14)	7515 (16)	114 (15)
C(65)	11822 (17)	2630 (9)	4392 (11)	78 (9)	C(128)	9273 (25)	3054 (14)	8380 (17)	123 (16)
C(66)	11289 (16)	2389 (10)	4658 (11)	77 (9)	C(129)	9630 (20)	3440 (12)	7407 (13)	102 (12)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of the 2-fold axes, resulting in approximate D_{2d} site symmetry. The range of S–Cd–S angles, 92.3 (2)–118.8 (1)°, is similar to that observed for $[Cd(SC_6H_5)_4]^{2-}$[7] and $[Cd(SCH_2CH_2S)_2]^{2-}$,[16] which display ranges of 98.7 (2)–120.0 (2)° and 89.5 (1)–124.3

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II)

Cu(1)–S(1)	2.218 (8)	Cu(1)–S(3)	2.317 (7)
Cu(1)–S(11)	2.243 (7)	Cu(2)–S(1)	2.160 (9)
Cu(2)–S(2)	2.164 (9)	Cu(3)–S(2)	2.211 (8)
Cu(3)–S(4)	2.247 (7)	Cu(3)–S(12)	2.306 (8)
Cu(4)–S(3)	2.259 (7)	Cu(4)–S(5)	2.220 (8)
Cu(4)–S(7)	2.303 (8)	Cu(5)–S(5)	2.165 (9)
Cu(5)–S(6)	2.169 (9)	Cu(6)–S(4)	2.301 (7)
Cu(6)–S(6)	2.198 (8)	Cu(6)–S(8)	2.263 (8)
Cu(7)–S(7)	2.243 (7)	Cu(7)–S(9)	2.209 (8)
Cu(7)–S(11)	2.315 (7)	Cu(8)–S(9)	2.142 (11)
Cu(8)–S(10)	2.159 (10)	Cu(9)–S(8)	2.314 (7)
Cu(9)–S(10)	2.204 (9)	Cu(9)–S(12)	2.259 (8)
Cu(10)–S(3)	2.198 (8)	Cu(10)–S(4)	2.203 (9)
Cu(11)–S(7)	2.189 (8)	Cu(11)–S(8)	2.212 (8)
Cu(12)–S(11)	2.191 (8)	Cu(12)–S(12)	2.209 (8)
S(3)–Cu(1)–S(1)	107.4 (3)	S(11)–Cu(1)–S(1)	144.4 (3)
S(11)–Cu(1)–S(3)	107.1 (3)	S(2)–Cu(2)–S(1)	174.3 (3)
S(4)–Cu(3)–S(2)	143.0 (3)	S(12)–Cu(3)–S(2)	109.8 (8)
S(12)–Cu(3)–S(4)	105.7 (3)	S(5)–Cu(4)–S(3)	142.0 (3)
S(7)—Cu(4)–S(3)	105.3 (3)	S(7)–Cu(4)–S(5)	111.4 (3)
S(6)–Cu(5)–S(5)	174.7 (3)	S(6)–Cu(6)–S(4)	109.5 (3)
S(8)–Cu(6)–S(4)	105.3 (3)	S(8)–Cu(6)–S(6)	143.9 (3)
S(9)–Cu(7)–S(7)	144.4 (3)	S(11)–Cu(7)–S(7)	105.6 (3)
S(11)–Cu(7)–S(9)	108.7 (3)	S(10)–Cu(8)–S(9)	175.2 (3)
S(10)–Cu(9)–S(8)	108.6 (3)	S(12)–Cu(9)–S(8)	105.9 (3)
S(12)–Cu(9)–S(10)	143.9 (3)	S(4)–Cu(10)–S(3)	163.5 (3)
S(8)–Cu(11)–S(7)	164.3 (3)	S(12)–Cu(12)–S(11)	163.1 (3)
Cu(2)–S(1)–Cu(1)	86.7 (3)	Cu(3)–S(2)–Cu(2)	82.6 (3)
Cu(4)–S(3)–Cu(1)	132.5 (3)	Cu(10)–S(3)–Cu(1)	89.0 (3)
Cu(10)–S(3)–Cu(4)	76.3 (2)	Cu(10)–S(4)–Cu(3)	76.7 (3)
Cu(6)–S(4)–Cu(3)	134.1 (3)	Cu(6)–S(6)–Cu(5)	88.4 (3)
Cu(10)–S(4)–Cu(6)	89.7 (3)	Cu(11)–S(7)–Cu(4)	95.6 (3)
Cu(5)–S(5)–Cu(4)	80.7 (3)	Cu(11)–S(8)–Cu(6)	74.2 (3)
Cu(7)–S(7)–Cu(4)	135.5 (3)	Cu(9)–S(10)–Cu(8)	85.8 (3)
Cu(11)–S(7)–Cu(7)	78.1 (3)	Cu(12)–S(11)–Cu(1)	75.4 (3)
Cu(9)–S(8)–Cu(6)	131.4 (3)	Cu(12)–S(12)–Cu(3)	91.0 (3)
Cu(11)–S(8)–Cu(9)	83.4 (3)	Cu(8)–S(9)–Cu(7)	82.0 (3)
Cu(7)–S(11)–Cu(1)	132.2 (3)	Cu(12)–S(11)–Cu(7)	87.3 (3)
Cu(9)–S(12)–Cu(3)	133.0 (3)	Cu(12)–S(12)–Cu(9)	75.9 (3)

(1)°, respectively. The considerable variation in the Cd–S bond distances, 2.518 (5)–2.540 (4) Å, also appears to be characteristic of $[Cd(SR)_4]^{2-}$ structures. Thus, $[Cd(SC_6H_5)_4]^{2-}$ displays Cd–S bond lengths in the range of 2.517 (3)–2.546 (4) Å, while $[Cd(SCH_2CH_2S)_2]^{2-}$ exhibits a similar nonequivalence, 2.508 (1)–2.547 (1) Å. The deviation of the CdS_4 unit from T_d symmetry is also evident in the dihedral angles between the S-Cd-S planes, 89.3, 73.9, and 106.8°, compared to values of 94.8, 83.7, and 102.0° for the corresponding planes in $[Cd(SC_6H_5)_4]^{2-}$. Distorted CdS_4 sites are also observed for $[Cd(\text{toluene-3,4-dithiolate})_2]^{2-}$[17] and for the binuclear and polymeric Cd–thiolate complexes $[Cd_2(SC_2H_5)_6]^{2-}$[18] and $[Cd(SCH_2CH_2OH)_2]_\infty$,[19] respectively.

Table VII. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ (III)

atom	x	y	z	U_{eq}
Ag(1)	2034 (2)	221	5063 (1)	68 (1)[a]
Ag(2)	85 (2)	−914 (2)	5580 (1)	59 (1)[a]
Ag(3)	1637 (2)	−2538 (2)	5434 (1)	61 (1)[a]
Ag(4)	3608 (2)	−1437 (2)	4978 (1)	66 (1)[a]
S(1)	700 (7)	623 (6)	5613 (3)	56 (3)[a]
S(2)	−281 (6)	−2492 (6)	5630 (3)	50 (3)[a]
S(3)	3619 (7)	−2813 (6)	5437 (3)	52 (3)[a]
S(4)	3572 (8)	17 (7)	4592 (3)	66 (4)[a]
Si(1)	816 (7)	2553 (7)	6250 (4)	67 (4)[a]
Si(2)	−1747 (8)	−4202 (7)	6060 (4)	62 (4)[a]
Si(3)	3757 (7)	−4455 (6)	6324 (4)	62 (4)[a]
Si(4)	4113 (8)	1703 (7)	3862 (4)	56 (4)[a]
C(11)	1544 (24)	652 (20)	6227 (10)	46 (8)
C(12)	2189 (26)	−108 (23)	6410 (12)	61 (10)
C(13)	2790 (29)	−70 (25)	6903 (12)	72 (11)
C(14)	2845 (32)	716 (27)	7176 (14)	81 (11)
C(15)	2182 (26)	1440 (24)	6982 (12)	60 (9)
C(16)	1547 (23)	1464 (20)	6503 (10)	43 (8)
C(17)	−763 (30)	2372 (30)	6053 (14)	100 (13)
C(18)	1051 (35)	3430 (30)	6762 (15)	106 (14)
C(19)	1456 (34)	2945 (30)	5690 (15)	103 (14)
C(21)	−76 (24)	−2747 (20)	6279 (11)	48 (8)
C(22)	713 (27)	−2237 (25)	6631 (12)	70 (11)
C(23)	898 (29)	−2508 (27)	7138 (13)	75 (10)
C(24)	244 (33)	−3222 (26)	7313 (15)	82 (12)
C(25)	−420 (29)	−3693 (27)	6985 (12)	72 (11)
C(26)	−649 (23)	−3481 (19)	6481 (10)	38 (7)
C(27)	−1182 (30)	−4686 (27)	5495 (12)	83 (11)
C(28)	−2245 (31)	−5146 (25)	6442 (13)	87 (12)
C(29)	−2964 (26)	−3467 (23)	5842 (12)	62 (10)
C(31)	4246 (22)	−2529 (20)	6102 (10)	40 (7)
C(32)	4699 (23)	−1720 (21)	6222 (10)	44 (8)
C(33)	5213 (25)	−1574 (25)	6712 (11)	60 (9)
C(34)	5298 (29)	−2216 (24)	7049 (13)	73 (11)
C(35)	4882 (26)	−3062 (22)	6939 (11)	55 (9)
C(36)	4310 (24)	−3272 (20)	6453 (10)	44 (8)
C(37)	4328 (32)	−5077 (27)	5811 (13)	88 (13)
C(38)	4281 (32)	−5141 (26)	6910 (13)	90 (12)
C(39)	2148 (31)	−4459 (30)	6185 (14)	102 (14)
C(41)	2923 (22)	6 (20)	3955 (10)	38 (8)
C(42)	2276 (24)	−694 (22)	3762 (12)	54 (9)
C(43)	1749 (27)	−750 (26)	3268 (12)	62 (10)
C(44)	1978 (29)	−76 (24)	2948 (14)	73 (11)
C(45)	2678 (28)	655 (24)	3128 (12)	70 (10)
C(46)	3153 (28)	727 (24)	3657 (12)	65 (10)
C(47)	3692 (27)	2320 (23)	4397 (11)	69 (10)
C(48)	3941 (34)	2523 (30)	3316 (14)	106 (14)
C(49)	5548 (34)	1264 (33)	4045 (16)	118 (16)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ (III)

Ag(1)–Ag(2)	3.320 (4)	Ag(1)–Ag(4)	3.111 (4)
Ag(1)–S(1)	2.388 (9)	Ag(1)–S(4)	2.385 (10)
Ag(1)–Ag(2′)	3.298 (3)	Ag(2)–Ag(3)	3.086 (4)
Ag(2)–S(1)	2.383 (10)	Ag(2)–S(2)	2.377 (10)
Ag(2)–Ag(1′)	3.298 (3)	Ag(2)–Ag(2′)	3.065 (5)
Ag(3)–Ag(4)	3.234 (4)	Ag(3)–S(2)	2.419 (8)
Ag(3)–S(3)	2.396 (8)	Ag(3)–S(2′)	3.053 (7)
Ag(4)–S(3)	2.369 (9)	Ag(4)–S(4)	2.377 (10)
Ag(4)–Ag(4′)	3.304 (6)	S(2)–Ag(3′)	3.053 (7)
S(1)–Ag(1)–S(4)	170.0 (3)	S(1)–Ag(2)–S(2)	171.6 (3)
S(2)–Ag(3)–S(2′)	79.0 (3)	S(2)–Ag(3)–S(3)	165.1 (3)
S(3)–Ag(3)–S(2′)	113.4 (3)	S(3)–Ag(4)–S(4)	174.5 (3)
Ag(1)–S(1)–Ag(2)	88.2 (3)	Ag(2)–S(2)–Ag(3)	80.1 (3)
Ag(2)–S(2)–Ag(3′)	92.7 (3)	At(3)–S(2)–Ag(3′)	100.9 (3)
Ag(3)–S(3)–Ag(4)	85.5 (3)	Ag(1)–S(4)–Ag(4)	81.6 (3)

The ligand conformation adopted by I is distinct from those observed for the $[M(SPh)_4]^{2-}$ class of complexes (M = Mn, Fe, Co, Ni, Zn, and Cd), whose geometries have been analyzed in detail by Coucouvanis et al.[14] The latter complexes display nearly planer MSC_6H_5 units, resulting in the adoption of two equivalent conformations of the phenyl rings in the $[M(SC_6H_5)_4]^{2-}$ anions. In type A the phenyl groups attached to two sulfur atoms lie in one plane that is orthogonal to the plane defined by the remaining two phenyl groups and sulfur atoms. The second conformation (B) is obtained by rotating two $-SC_6H_5$ groups about the M–S bonds by ca. ±120°. One consequence of this arrangement is that the proximal ortho hydrogen atoms of the rings nestle between the metal atom and one of the sulfur atoms in the arrangement illustrated in Figure 2a. In contrast, the phenyl rings of I adopt a conformation in which the phenyl group attached to S(1) is nearly perpendicular to that attached to S(1′) and the phenyl group on S(2) is perpendicular to that on S(2′), while the rings on S(1) and S(2) deviate considerably from coplanarity, as illustrated in Table VI. As a consequence, the rings do not adopt either of the

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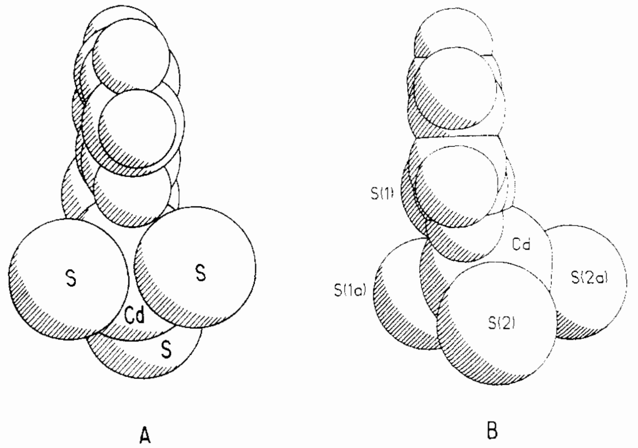

Figure 2. (a) ORTEP plot of the structure of $[\mathrm{Cd(SC_6H_5)_4}]^{2-}$ with atoms drawn to scale with the appropriate covalent radii. Three of the phenyl rings have been omitted for clarity. (b) Similar plot of the structure of $[\mathrm{Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4}]^{2-}$ (I) illustrating the unique orientation of the rings in I.

conformations observed for the $[\mathrm{M(SC_6H_5)_4}]^{2-}$ class of complexes. Furthermore, the ortho hydrogens of the rings exhibit an even more pronounced preference to orient toward one of the sulfur atoms, as shown in Figure 2b. For each ring this configuration gives rise to close contacts between the ortho hydrogens and the sulfur atoms, which result in an expansion of the Cd–S–C angles to 115.5° (average) from the value of 109° observed for the $[\mathrm{Cd(SC_6H_5)_4}]^{2-}$.

The distortions in the ring conformation of I relative to those adopted by the $[\mathrm{M(SC_6H_5)_4}]^{2-}$ complexes appear to be consequences of the introduction of the sterically demanding $-\mathrm{SiMe_3}$ groups in the ortho positions of the rings. Adoption by I of the conformations exhibited by the complexes with the sterically "innocent" thiophenolate ligand would result in significant contact interactions between the protons of the $-\mathrm{SiMe_3}$ groups and either the ring protons or the methyl protons of the adjacent ligands. In fact, the ring conformation adopted by I results in no significantly close nonbonding distances; no H–H distances are significantly shorter than the sum of the van der Waals radii of two hydrogen atoms, 2.4 Å, suggesting that the observed conformation effectively minimizes steric interactions.

Structural types characterized for Cd complexes with thiolate ligands include discrete molecular structures, ranging in size from mononuclear $[\mathrm{Cd(SR)_4}]^{2-}$[18-20] through tetranuclear $[\mathrm{Cd_4(SR)_{10}}]^{2-}$,[21] to octanuclear $[\mathrm{ICd_8(SCH_2CH_2OH)_{12}}]^{3+}$[22] and decanuclear $[\mathrm{Cd_{10}(SCH_2CH_2OH)_{16}}]^{4+}$[23] and $[\mathrm{Cd_{10}S_4(SPh)_{16}}]^{4-}$.[24] Nonmolecular types include the one-dimensional nonmolecular structure $\{\mathrm{Cd[SCH(CH_2CH_2)_2NHCH_3]_2}^{2+}\}_\infty$,[25] the two-dimensionally nonmolecular $[\mathrm{Cd(SCH_2CH_2OH)_2}]_\infty$,[26] and the three-dimensionally nonmolecular polyadamantanoid structure of $[\mathrm{Cd(SPh)_2}]_\infty$.[27] Although a family of the three species $[\mathrm{Cd(SR)_4}]^{2-}$, $[\mathrm{Cd_2(SR)_6}]^{2-}$, and $[\mathrm{Cd_4(SR)_{10}}]^{2-}$ has been isolated and structurally characterized for R = $-\mathrm{C_2H_6}$ and/or $-\mathrm{C_6H_5}$, $[\mathrm{Cd(SC_6H_4\text{-}o\text{-}SiMe_3)_4}]^{2-}$ is unique for the sterically hindered thiolate complex under all reaction conditions. This observation is consistent with the general ability of bulky ligands to stabilize mononuclear species or small oligomers.

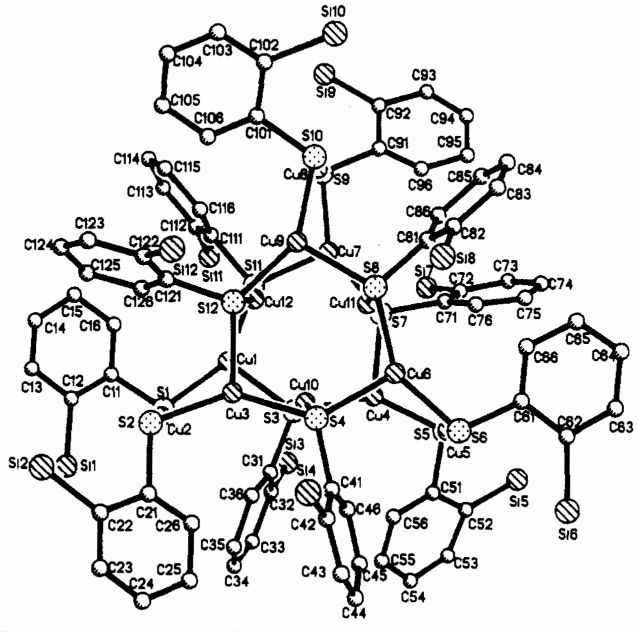

Figure 3. ORTEP view of the structure of $[\mathrm{Cu(SC_6H_4\text{-}o\text{-}SiMe_3)}]_{12}$, showing the atom-labeling scheme.

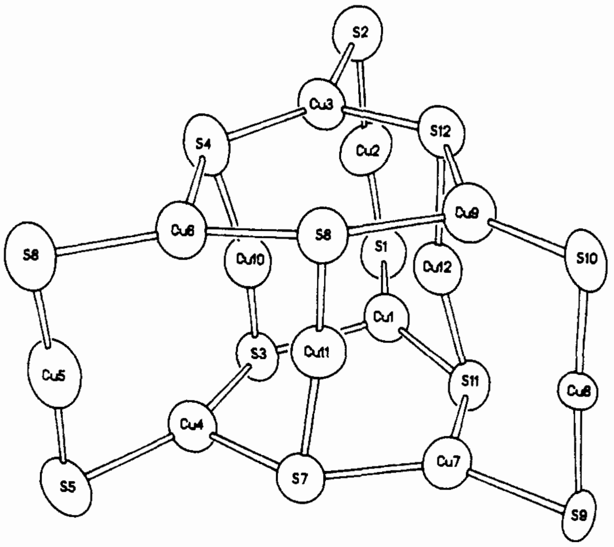

Figure 4. $\mathrm{Cu_{12}S_{12}}$ core, highlighting the eight-membered $\mathrm{Cu_4S_4}$ cycles.

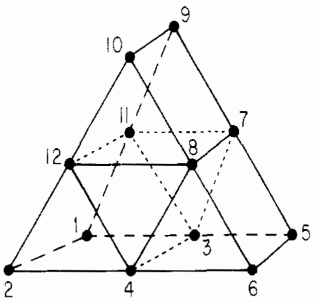

Figure 5. Schematic view of the S atom arrangement of $[\mathrm{Cu(SC_6H_4\text{-}o\text{-}SiMe_3)}]_{12}$, illustrating the exterior trigonal prism (faces 2,6,10 and 1,5,9) and the interior trigonal prism (faces 4,8,12 and 3,7,11).

Description of the Structure of the $[\mathrm{Cu(SC_6H_4\text{-}o\text{-}SiMe_3)}]_{12}$ (II). As shown in Figure 3, the structure of $[\mathrm{Cu(SC_6H_4\text{-}o\text{-}SiMe_3)}]_{12}$ consists of discrete dodecanuclear clusters of unique molecular geometry. The structure is best described as a molecular paddle wheel with the $\mathrm{Cu_{12}S_{12}}$ core arranged as illustrated in Figure 4. The two nearly parallel but staggered (ca 10°) $\mathrm{Cu_3S_3}$ rings and the bridging Cu(10), Cu(11), and Cu(12) atoms provide the central cylinder of the paddle wheel, while the paddles are con-

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Table IX. Ranges of Bond Distances (Å) and Angles (deg) for the $Cu_{12}S_{12}$ Core of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II)

bond type	Cu–S or S–Cu–S range
digonal Cu–doubly bridging S (Cu(2)–S(1), Cu(2)–S(2), Cu(5)–S(5), Cu(5)–S(6), Cu(8)–S(9), Cu(8)–S(10))	2.142 (10)–2.169 (10)
digonal Cu–triply bridging S (Cu(10)–S(3), Cu(10)–S(4), Cu(11)–S(7), Cu(11)–S(8), Cu(12)–S(11), Cu(12)–S(12))	2.189 (9)–2.212 (8)
trigonal-planar Cu–doubly bridging S (Cu(1)–S(1), Cu(3)–S(2), Cu(4)–S(5), Cu(6)–S(6), Cu(7)–S(9), Cu(9)–S(10))	2.198 (8)–2.220 (8)
trigonal-planar Cu–triply bridging S (Cu(1)–S(11), Cu(4)–S(3), Cu(7)–S(7), Cu(3)–S(4), Cu(6)–S(8), Cu(9)–S(12))	2.243 (8)–2.263 (8)
trigonal-planar Cu–triply bridging S (Cu(1)–S(3), Cu(4)–S(7), Cu(7)–S(11), Cu(3)–S(12), Cu(6)–S(4), Cu(9)–S(8))	2.301 (7)–2.315 (7)
S–Cu–S (digonal Cu sites Cu(2), Cu(5), Cu(8))	174.3 (3)–175.2 (3)
S–Cu–S (digonal Cu sites C(10), C(11), C(12))	163.1 (3)–163.5 (3)
S–Cu–S (trigonal planar Cu)	142.0 (3)–144.4 (3), 105.3 (3)–111.4 (3)
Cu–S–Cu (interior ring angle)	131.5 (9)–135.4 (8)
C–S–C (ring sulfur)	74.1 (9)–78.1 (10), 83.3 (8)–95.6 (9), 118.6 (9)–121.9 (8)

structed from the exocyclic $[Cu(SR)_2]^-$ groups that bridge the two hexanuclear rings. In gross geometry, the $Cu_{12}S_{12}$ core is reminiscent of the structure of $[2_3](1,3,5)$cyclophane.[28] Alternatively, the structure may be described as an expanded trigonal prism of thiolate sulfur atoms (S(1), S(2), S(5), S(6), S(9), S(10)) enclosing an interior S_6 trigonal prism (S(3), S(4), S(7), S(8), S(11), S(12)), with the vertices of the interior prism located virtually at the midpoints of the edges defining the triangular faces of the exterior prism. An idealized view of the arrangement of sulfur atoms is presented in Figure 5. The thiolate sulfur atoms are bridged by six digonal Cu atoms located approximately at the midpoints of the rectangular faces of the inner and outer trigonal prisms and by six digonal planar Cu atoms situated on the triangular faces so as to leave vacant only the central inner triangles of the opposing faces. Thus, the $Cu_{12}S_{12}$ core possesses approximate 3-fold symmetry.

There are three distinct copper geometries associated with the $Cu_{12}S_{12}$ core. The six Cu centers of the interior Cu_3S_3 heterocycles display distorted-trigonal-planar geometry, while the three Cu atoms bridging the opposing triangular faces of the exterior exhibit a trigonal-prism geometry and the three Cu atoms bridging the triangular faces of the interior prisms exhibit digonal coordination. The bond lengths and angles associated with these distinct copper geometries are tabulated in Table IX.

The set of digonal Cu centers Cu(2), Cu(5), and Cu(8) displays unremarkable geometry with an average Cu–S bond distance of 2.160 (9) Å and a S–Cu–S valence angle of 174.7 (5)°. On the other hand, the Cu centers spanning the faces of the interior prism, Cu(10), Cu(11), and Cu(12), are significantly distorted from idealized digonal geometry, as illustrated by the S–Cu–S angle of 163.3 (6)°. All three Cu atoms are displaced toward the interior of the prism, with a concomitant increase in the Cu–S bond lengths to 2.200 (9) Å (average) from a value of 2.160 (9) Å for the exterior digonal Cu sites. We can offer no convincing rationalization (vide infra) for this observation as there do not appear to be significant secondary Cu–S interactions or S- - -S interactions within the core. The Cu sites associated with the Cu_3S_3 rings display a number of distortions from the idealized trigonal-planar geometry. There are three distinct Cu–S bond distances associated with each trigonal Cu site: 2.210 (10) Å for the bond length to the doubly bridging S atoms of the exterior prism and 2.309 (10) and 2.253 (10) Å for the distances to the triply bridging S atoms of the interior prism and the Cu_3S_3 heterocycles. The bond distances with the Cu_3S_3 rings display a long–short alternation. The valence angles at the trigonal Cu centers are also distorted such that two of the angles are equivalent at 107.5 (9)° while the third presents a value of 143.6 (8)°. The enlarged angles are exterior to the Cu_3S_3 rings and produces a skewed geometry for the paddles, as shown in Figure 4.

Although both linear and trigonal-planar geometries are known for copper–thiolate clusters,[29] it is unusual to find *both* types of coordination in the same molecule. In complexes studied to date, sterically encumbered ligands have been shown to favor linear coordination for Cu(I), not an unanticipated consequence of the ligand design.[30] However, the structure of $[Cu(SC_6H_4\text{-}o\text{-}Sime_3)]_{12}$ demonstrates that modification of the electronic and/or steric properties of the substituents may effect pronounced structural changes.

The substituted rings of the $-SC_6H\text{-}o\text{-}SiMe_3$ ligands adopt a conformation that orients the ring planes of the groups attached to the interior S_6 prism nearly perpendicular to the Cu_3S_3 best planes, while the rings associated with the exterior S_6 trigonal prism are aligned closely parallel to the Cu_3S_3 planes. One consequence of this conformation is the expansion of one of the exterior S–Cu–S angles at each of the Cu centers in order to minimize nonbonding interactions between adjacent pairs of interior and exterior ligand groups. Furthermore, the adjacent exterior C–S–Cu angle at each of the Cu_3S_3 ring S atoms also expands to an average of 119.6 (20)° as a result of this particular ligand conformation. Thus, two of the angles at the ring S atoms are expanded from limiting tetrahedral values: the interior Cu–S–Cu angle to 131.3 (12)° and the exterior C–S–Cu angle to 119.6 (20)°. To compensate for this angle expansion, the two Cu–S–Cu angles to the diagonal Cu centers bridging the Cu_3S_3 rings contract to average values of 76.1 (18) and 89.3 (17)°. Consequently, the S–Cu–S angles at Cu(10), Cu(11), and Cu(12) deviate considerably from the diagonal limit of 180° and may dictate the displacement of these Cu centers toward the interior of the central cylinder.

Since there are no significant intramolecular H···H contacts (less than 2.5 Å), the observed ring conformation effectively minimized steric interactions between the ligands. There are a number of significant intermolecular H···H contacts, listed in Table X, which arise from the nestling of rings in adjacent clusters in the structure. The observed ligand conformation may also serve to effect efficient packing of clusters.

Description of the Structure of the $[Ag(SC_6H_4\text{-}o\text{-}SiMe_3)]_4$ Dimer (III). As illustrated in Figure 6a, the structure of $[Ag(SC_6H_4\text{-}o\text{-}SiMe_3)]_4$ consists of a eight-membered cycle of alternating silver and sulfur atoms, Ag_4S_4, which is distinctly nonplanar, as a consequence of folding along the S(1)–S(3) axis to produce a dihedral angle of 139.4° between the best planes through S(1)Ag(1)S(4)Ag(4)S(3) and S(3)Ag(3)S(2)Ag(2)S(1). The steric influence of the thiolate ligand $-SC_6H_4\text{-}o\text{-}SiMe_3$ is insufficient to prevent close approach of $[Ag_4S_4]$ units, thus allowing the formation of secondary Ag(3)–S(2′) interactions with a distance of 3.053 (7) Å and producing the bis-cyclic structure $[\{AgSC_6H_4\text{-}o\text{-}SiMe_3\}_4]_2$, illustrated in Figure 6b.

The geometry at Ag(1), Ag(2), and Ag(4) is effectively linear with an average Ag–S bond distance of 2.380 (14) Å. In contrast, the geometry about Ag(3) is distinctly "T"-shaped, rather than trigonal planar, with an average Ag(3)–S bond distance of 2.408 (12) Å within the Ag_4S_4 cycle.

The $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ structure is a member of the general class of neutral $[AgSR]_n$ structural types. The degree of aggregation of these silver thiolate species appears to depend intimately upon the nature of thiolate ligands, such that there is an inverse relationship between the value of *n* and the steric bulk of the ligand. Akerstrom[31] has argued that the degree of asso-

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Table X. Close Nonbonding Contacts (Å) in $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (II)[a]

H(37C)···H(34)[a]	2.423	H(129I)···H(63)[e]	2.332	H(127B)···H(78C)[g]	2.413
H(49A)···H(54)[b]	2.336	H(281B)···H(64)[e]	2.572	H(128F)···H(38C)[g]	2.467
H(67C)···H(35)[b]	2.545	H(128D)···H(64)[e]	2.586	H(128F)···H(79B)[g]	2.538
H(109A)···H(95)[c]	2.550	H(78B)···H(48B)[b]	2.374	H(127B)···H(79B)[g]	2.548
H(78A)···H(14)[d]	2.594	H(78C)···H(48B)[b]	2.418		

[a] Molecules are related by the following symmetry operations: (a) $1.0 - x, -y, 1.0 - z$; (b) $2.0 - x, -y, 1.0 - z$; (c) $2.0 - x, 1.0 - y, 1.0 - z$; (d) $0.5 + x, 0.5 - y, -0.5 + z$; (e) $-0.5 + x, 0.5 - y, 0.5 + z$; (f) $-0.5 + x, 0.5 - y, -0.5 + z$; (g) $0.5 + x, 0.5 - y, 0.5 + z$.

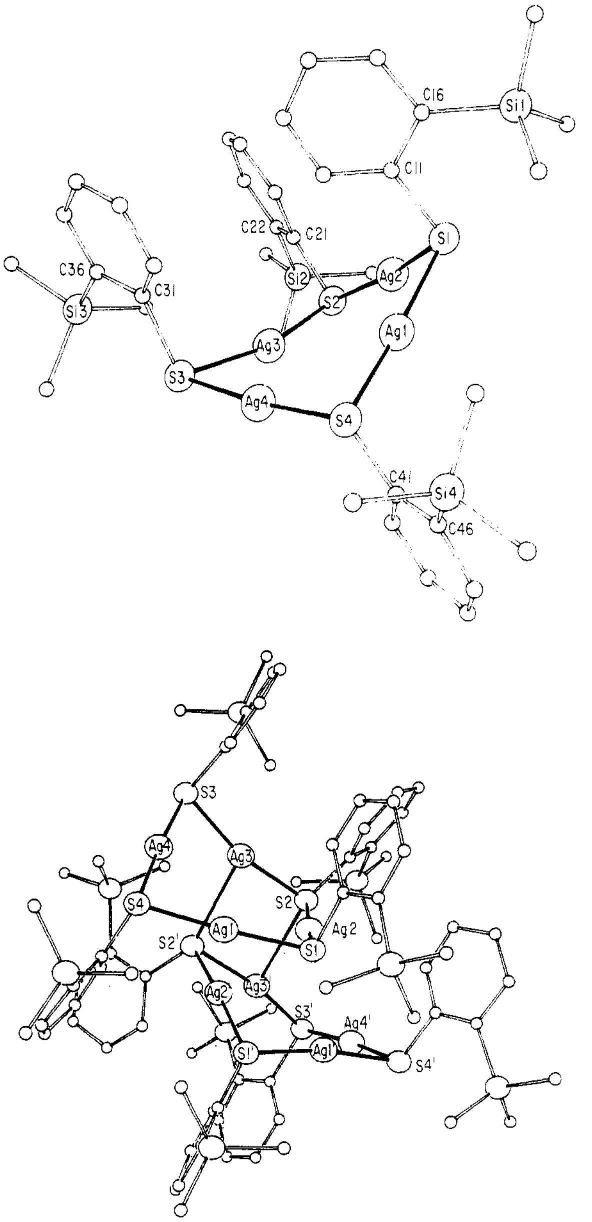

Figure 6. (a, top) Structure of the tetranuclear core $[Ag(SC_6H_4\text{-}o\text{-}SiMe_3)]_4$, showing the atom-labeling scheme. (b, bottom) Fusing of two tetranuclear units via Ag(3)–S(2′) secondary interactions giving the bis-cyclic structure of $\{[Ag(SC_6H_4\text{-}o\text{-}SiMe_3)]_4\}_2$.

ciation of silver thiolate complexes $[AgSR]_n$ is related to the chain branching at the thiolate. Thus, silver *tert*-alkanethiolates are octameric in solution while *sec*-alkanethiolate complexes are dodecameric. Of the structurally characterized [AgSR] complexes $[AgSCMeEt_2]_\infty$ contains a chain of two intertwined but unconnected $[Ag(\mu\text{-}SR)]_\infty$ strands, while $[AgSC_6H_{11}]_{12}$ displays a cyclic dodecameric structure.[32] In structures where there is considerable bulk associated with the substituents at the α-carbon, such as the series $[Ag(SR)]_n$ where $R = -CH_m(SiMe_3)_{3-m}$, n is clearly a function of steric bulk, decreasing with increasing m.[33] Thus, $[AgSC(SiPhMe_2)_3]_3$ consists of a cyclic trinuclear structure while $[AgSC(SiMe_3)_3]_4$ consists of a cyclic tetranuclear structure. In contrast, the less hindered ligand $-SCH(SiMe_3)_2$ is similar to $-SC_6H_4\text{-}o\text{-}SiMe_3$ in allowing formation of secondary Ag- - -S interactions to produce a bis-cyclic structure $[\{AgSCH(SiMe_3)_2\}_4]_2$. The consequences of further reduction in ligand bulk are dramatically illustrated by the polymeric structure of $[Ag_4\{SCH_2(SiMe_3)\}_3]_n(OCH_3)_n$.

The $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ structure is closely related to the bis-cyclic structure of $[\{AgSCH(SiMe_3)_2\}_4]_2$ with a number of significant differences. The tetranuclear Ag_4S_4 units of $[\{AgSCH(SiMe_3)_2\}_4]_2$ achieve a closer approach than that observed for $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$, as demonstrated by eight Ag- - -S interactions in the 3.17–3.38 Å range in contrast to only two close contacts at 3.05 Å for the title complex. As a consequence, all eight Ag centers of $[\{AgSCH(SiMe_3)_2\}_4]_2$ display "T"-type geometry. Furthermore, the Ag_4S_4 cycles of this structure deviate considerably from planarity, displaying a dihedral angle of 78.0° between least-squares planes through S(1)Ag(1)S(4)Ag(4)S(3) and S(3)Ag(3)S(2)Ag(2)S(1), as compared to an angle of 139.6° for $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$. The orientations of the thiolate substituents relative to the Ag_4S_4 cycle also display considerable differences for these structures. While all four substituents are directed to the same side of one face of the Ag_4S_4 cycle in $[\{AgSCH(SiMe_3)_2\}_4]_2$ to give an aaaa configuration, in $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ three substituents are directed to one side of the Ag_4S_4 cycle so as to minimize interactions with the second Ag_4S_4 cycle, while the fourth substitutent is disposed toward the opposite side, producing the aaab configuration. This contrasting orientation of substituents appears to be related to the relative steric bulk of the $-CH(SiMe_3)$ and $-C_6H_4\text{-}o\text{-}SiMe_3$ groups. Thus, this disposition of substituents and the overall decreased interaction of Ag_4S_4 units in $[\{Ag(SC_6H_4\text{-}o\text{-}SiMe_3)\}_4]_2$ relative to $[\{AgSCH(SiMe_3)_2\}_4]_2$ would suggest that $-SC_6H_4\text{-}o\text{-}SiMe_3$ displays an effectively greater steric influence than $-SCH(SiMe_3)_2$.

The cyclic structural unit $[Ag_4(\mu\text{-}SR)_4]$ appears as a recurring theme in the structural chemistry of $[Ag(SR)]_n$ species. A cyclic tetranuclear unit has been identified in the structures of $(Ph_3P)_2(AgSCMeEt_2)_8$[34] and of $[Ag_4(SCH_2SiMe_3)_3]_n$, in addition to those of $[AgSC(SiMe_3)_3]_4$ and the examples discussed above.

Although a number of anionic silver thiolate complexes of general type $[Ag_x(SR)_y]^{x-y}$ have been structurally characterized in recent years,[35-40] including one with a conventional type bulky thiolate ligand $[Ag(SC_6HMe_4)_2]^-$, we find no evidence under similar reaction conditions for anionic silver thiolate species with ligands of the $-SC_6H_{5-n}(SiMe_3)_n$ or $-SCH_{3-n}(SiMe_3)_n$ classes. Whether this observation is a consequence of the tendency of silver–thiolate interactions to form cyclic Ag_4S_4 units when bulky

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thiolate substituents effectively block further secondary interactions or of some more subtle steric or electronic effects remains problematical.

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Supplementary Material Available: Tables of bond lengths (Tables S1 and S10), bond angles, (Tables S2 and S11), anisotropic temperature factors (Tables S3 and S12), and calculated hydrogen atom positions (Tables S4 and S13) for I and III, tables of bond lengths (Table S6), bond angles (Table S7), and anisotropic temperature factors (Table S8) for II, and a summary of the experimental details for the X-ray diffraction studies of I–III (Table S15) (22 pages); tables of observed and calculated structure factors (Tables S5, S9, and S14) for I–III (65 pages). Ordering information is given on any current masthead page.

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Magneto–Structural Correlations and Metal–Metal Bonding in Exchange-Coupled $A_3Mo_2X_9$ (X = Cl, Br, I) Complexes

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The magneto–structural properties and the role of M–M bonding in $A_3Mo_2X_9$ (X = Cl, Br, I) complexes are examined. Structural and magnetic data are given for the new salts $A_3Mo_2X_9$ [A = Rb, NH_4, RNH_3 (R = Me, Et, Bu, Hex), R_2NH_2 (R = Me, Et), Me_3NH], $A_3Mo_2Br_9$ (A = Rb, Me_4N), and $A_3Mo_2I_9$ (A = Cs, $EtNH_3$). The structure of $(MeNH_3)_3Mo_2Cl_9$ was refined by Rietveld analysis of powder X-ray diffraction data. It has orthorhombic symmetry, space group *Cmcm* ($Z = 4$), with unit cell dimensions of $a = 7.187$ (1) Å, $b = 15.086$ (1) Å, and $c = 17.649$ (1) Å. The $MeNH_3$ group is oriented along the *b* axis, and the geometry of the $Mo_2Cl_9^{3-}$ anion is almost identical with that in $Cs_3Mo_2Cl_9$. The cation effect on the M_2X_9 structure is shown to result from a size increase along the *c* axis direction of the A(1) cation lying in the plane of the bridging halogens. For the strongly coupled $Mo_2X_9^{3-}$ anion, calculations show that the ground-pair levels no longer obey a Heisenberg (HDVV) coupling although the $S = 0, 1, 2$ pair spin levels still follow a Landé type interval separation. The ground exchange coupling is shown to be very sensitive to the single-ion electron repulsion parameters, and the weakly coupled limit applies only when the single-ion Coulombic exchange is at least 5 times greater than the largest pair-exchange parameter. The observed correlation between J_{ab} and the M–M separation in $A_3Mo_2Cl_9$ complexes is modeled by using a semiquantitative MO model based on the M–M σ-orbital overlap.

Introduction

The complex salts of stoichiometry $A_3M_2X_9$ represent an ideal series to study magneto–structural correlations in exchange-coupled systems since variation in A, M, or X can significantly alter the observed magnetic and spectroscopic properties of the $M_2X_9^{3-}$ binuclear unit. Studies on a number of such systems containing paramagnetic M^{3+} transition-metal ions have appeared previously in the literature.[1–38] Intermediate between the weakly coupled $Cr_2X_9^{3-}$ and metal–metal-bonded $W_2X_9^{3-}$ anions are the complex salts of $Mo_2X_9^{3-}$. Magnetic studies on this system[36–39] have shown the ground exchange coupling to be strongly antiferromagnetic and quite sensitive to the size of the univalent A cation.[36,37] An exponential relationship between the ground magnetic exchange constant J_{ab} and the M–M separation in the binuclear unit was obtained in the case of spherical A cations. The metal–metal distances used were derived from the *c* axis unit cell lengths on the assumption of a constant *z*/*c* fractional coordinate for the Mo atoms. However, we recently reported[35] structural refinements using the Rietveld method[40] on a number of alkali-metal and alkylammonium salts of $Mo_2X_9^{3-}$ (X = Cl, Br, I). The previous assumption of a constant *z*/*c* fractional coordinate for Mo was not observed, particularly for the alkylammonium salts. Furthermore, magnetic studies on a number of substituted pyridinium and piperidinium salts of $Mo_2X_9^{3-}$ (X = Cl, Br) have since been reported[38] and these salts deviate significantly from the above J_{ab} versus M–M separation curve. Finally, previous magnetic studies[36–39] have ignored the effects of M–M bonding on the ground exchange coupling, yet the electronic spectrum of $Cs_3Mo_2Cl_9$ has now been interpreted on the basis of a large M–M σ interaction and two weaker π interactions.[43]

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