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Layered Structure of Crystalline Compounds AgSR

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The insoluble silver thiolate compounds $AgS(CH_2)_2CH_3$ (**1**), $AgS(CH_2)_3CH_3$ (**2**), $AgS(CH_2)_5CH_3$ (**3**), $AgS(CH_2)_7CH_3$ (**4**), $AgSC_6H_5$ (**5**), $AgSC_6H_4$-4-F (**6**), $AgSC_6H_4$-4-Cl (**7**), $AgSC_6H_4$-4-Br (**8**), $AgSC_6H_4$-4-CH_3 (**9**) and $AgSC_6H_4$-4-OCH_3 (**10**) have not yielded crystals suitable for full diffraction analysis, but do reveal the essential features of their two-dimensionally nonmolecular structure in their powder diffraction patterns. For each compound, a strongly developed progression of axial reflections $\{0k0\}$ shows that there are ${}^{2}_{\infty}\{\mathrm{AgSR}\}$ layers in which substituents extend perpendicular to both sides of a central slab of Ag and S atoms. These data, together with the nonaxial reflections, allow assignment of an approximate monoclinic unit cell as $a \approx 8.7$ Å, b in proportion to the length of the substituent, $c \approx 4.35$ Å, and $\beta \approx 120°$. The thickness of the central Ag,S slab and the small degree of interpenetration of substituents at the interface between layers can be estimated. More sterically demanding substituents R do not permit this layer structure. All attempts to form intercalation compounds, with guests between the distal atoms of the substituents on adjacent layers, were unsuccessful.

Introduction

The solubilities of compounds of the type $(AgSR)_p$ correlate with the nature of R. When R is a tertiary or secondary alkyl, the compounds are soluble in inert solvents, and there is correlation of the molecular size in solution with the type of substituent: $p = 8$ for tertiary R; $p = 12$ for secondary R.[1-3] The crystal structure of ${}^{1}_{\infty}[\mathrm{AgSC(CH_3)_2CH_2CH_3}]$ has been determined, and related to the probable cyclic structure of its octameric molecule $(AgSR)_8$ in solution.[4] Cyclic molecules $[AgSR]_{12}$ occur in crystalline *cyclo*-(hexanethiolato)silver.[5] More sterically hindered secondary and tertiary thiolates yield cyclic $[AgSR]_4$ and $[AgSR]_3$ molecules, which may be associated in crystals.[6] Structural principles for these compounds have been enunciated.[7]

However, when the substituent is primary alkyl, or aryl, the solubility of AgSR is generally very low, hindering crystal growth and structure determination: nonmolecular structures probably exist in these compounds. The only crystallographic characterization of a compound of this type was achieved by introduction of a bulky substituent, in the weakly associated molecules of $[AgSC_6H_4\text{-}2\text{-}Si(CH_3)_3]_4$.[8] One approach to the structural chemistry of the nonmolecular compounds has been to derivatize them by incorporation of a minimum proportion of heteroligands, in order to excise a molecular fragment representative of the supposed nonmolecular structure. We have published such structures for $[Ag_6(SAr)_6(PPh_3)_5]$[9] and related copper compounds $[Cu_4(SC_6H_5)_4(PPh_3)_4]$[10] and $[Cu_3(SAr)_3(PPh_3)_4]$ (Ar = C_6H_5,[11] C_6H_4-4-Cl). This strategy has also been used to postulate nonmolecular structures for compounds CuSR.[12] The nonmolecular structure of ${}_{\infty}[\mathrm{Ag\{SCH_2Si(CH_3)_3\}_3(OCH_3)}]$ is known.[6]

We here report on the primary alkane thiolates $AgS(CH_2)_2CH_3$ (**1**), $AgS(CH_2)_3CH_3$ (**2**), $AgS(CH_2)_5CH_3$ (**3**), and $AgS(CH_2)_7CH_3$ (**4**) and the arenethiolates $AgSC_6H_5$ (**5**), $AgSC_6H_4$-4-F (**6**), $AgSC_6H_4$-4-Cl (**7**), $AgSC_6H_4$-4-Br (**8**), $AgSC_6H_4$-4-CH_3 (**9**), and $AgSC_6H_4$-4-OCH_3 (**10**). Although single crystals are unobtainable, the polycrystalline diffraction reveals the main features of the layered structures of **1**-**10**. These compounds are structurally analogous to monolayers of thiols on gold surfaces.[13-15]

Experimental Section

Preparation of Compounds. All compounds **1**-**10** were precipitated by addition of a solution of $AgNO_3$ in acetonitrile to a solution of the thiol plus equimolar triethylamine (as base) also in acetonitrile. The silver thiolates precipitated and after filtration were washed thoroughly with acetonitrile and dried in vacuum. All of the solids are colorless except **7**, which is yellow. **5** occurs as very thin flaky crystals, and **7** has been obtained as small needles. None of these compounds is soluble in inert solvents.

X-ray diffraction measurements were made with a Siemens D500 diffractometer, with Cu Kα radiation.

Results

Representative X-ray diffraction patterns of polycrystalline samples of the compounds **2**, **4**, **5**, and **10** are shown in Figures 1 and 2. All show a well-developed progression of intense reflections, which are successive orders of diffraction from a layer structure with a large d spacing. There are very few other large-d reflections in these patterns. Comparatively weak reflections occur in each pattern, but almost all of these have d spacings less than ca. 4.5 Å. It is clear that the diffraction patterns can be interpreted in terms of a crystal structure in which the Ag and S atoms occur in regularly stacked layers with a very large interlayer lattice dimension, and that the intralayer two-dimensional lattice possesses relatively small repeat distances. The presence of narrow intralayer reflections indicates that there is crystallographic registry of layers. For the analysis of these diffraction patterns, we define b as the axial direction normal to the layers, to be consistent with the monoclinic unit cell proposed below.

Details of the progressions of interlayer reflections $(0k0)$ are presented in Table I. For each compound, there is excellent agreement between the values of kd, that is the large interlayer repeat distance b, for reflections with k up to 5 in all compounds and as high as 10 in **10**. The large interlayer spacings are clearly related to the lengths of the substituents.

The model that fits this data is comprised of parallel slabs of connected Ag and S atoms, with the substituents on S inclined perpendicular (or close to perpendicular) to the slab and substituents extending from both sides of each slab. The stacking of the layers involves only van der Waals contact between the distal atoms of the thiolate substituents. A cross-sectional schematic diagram of the stacked slabs is given in Figure 3, which defines the parameters used in modeling the dimensions normal to the slab.

We first discuss the model in terms of the layer thickness parameters of Figure 3 relative to the observed interlayer separations and then consider possible bonding patterns and geometry for the Ag,S slab in relation to the slab thickness and the additional reflections of the diffraction patterns. The Ag and S atoms in

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Table I. Observed Interlayer Spacing (*kd* Values) from the Pronounced (0*k*0) Reflections

compound	interlayer spacing $b = kd$ values, Å									
	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$	$k = 8$	$k = 9$	$k = 10$
$AgS(CH_2)_2CH_3$ (**1**)	12.38	12.52	12.51	12.55	12.58					
$AgS(CH_2)_3CH_3$ (**2**)	15.45	15.47	15.42	15.42	15.49	15.66				
$AgS(CH_2)_5CH_3$ (**3**)	19.59	19.87	20.06	20.11	20.10					
$AgS(CH_2)_7CH_3$ (**4**)	24.8	24.0	24.76	24.81	24.95	25.00	24.96	24.98		
$AgSC_6H_5$ (**5**)	14.06	14.01	14.06	14.04	14.05	14.06	14.08	14.22		
$AgSC_6H_4$-4-F (**6**)	14.67	14.66	14.66	14.67	14.68	14.68	14.69	14.70		
$AgSC_6H_4$-4-Cl (**7**)	16.35	16.40	16.28	16.33	16.34	16.32	16.44			
$AgSC_6H_4$-4-Br (**8**)	16.88	16.93	16.89	16.87	16.86	16.84	16.67			
$AgSC_6H_4$-4-CH_3 (**9**)	16.38	16.43	16.37	16.36	16.38	16.38	16.49	16.39		
$AgSC_6H_4$-4-OCH_3 (**10**)	17.12	16.93	17.04	17.10	17.13	17.13	17.15	17.15	17.04	17.00

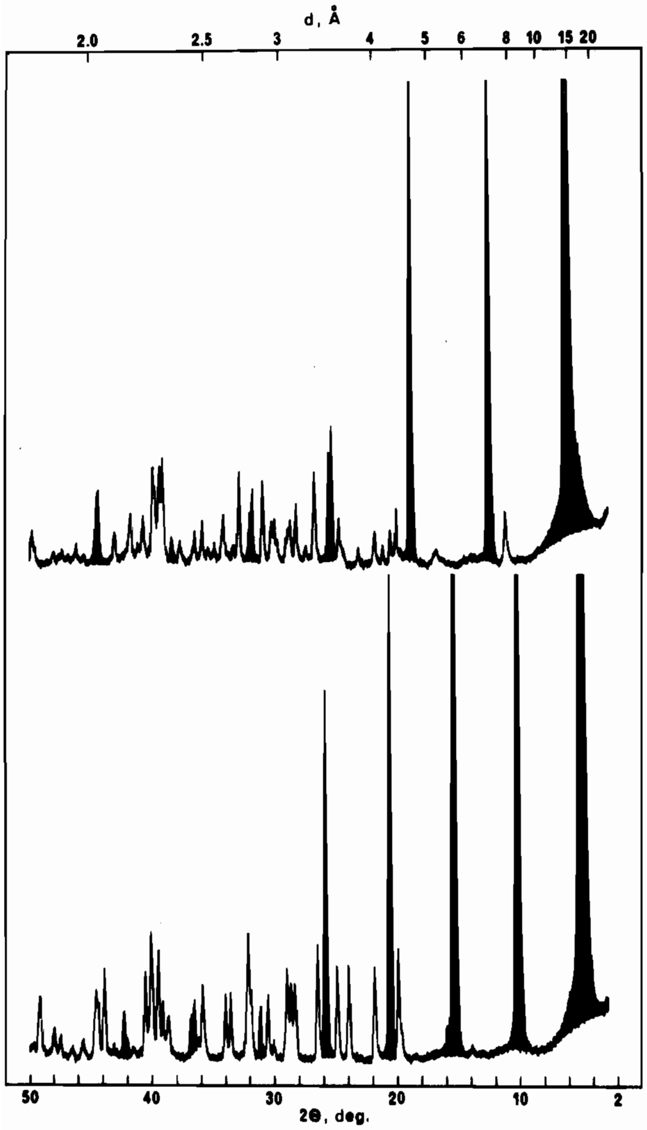

Figure 1. Polycrystalline diffraction patterns of **2** (upper) and **4** (lower). The interlayer reflections (0*k*0) are marked as filled lines.

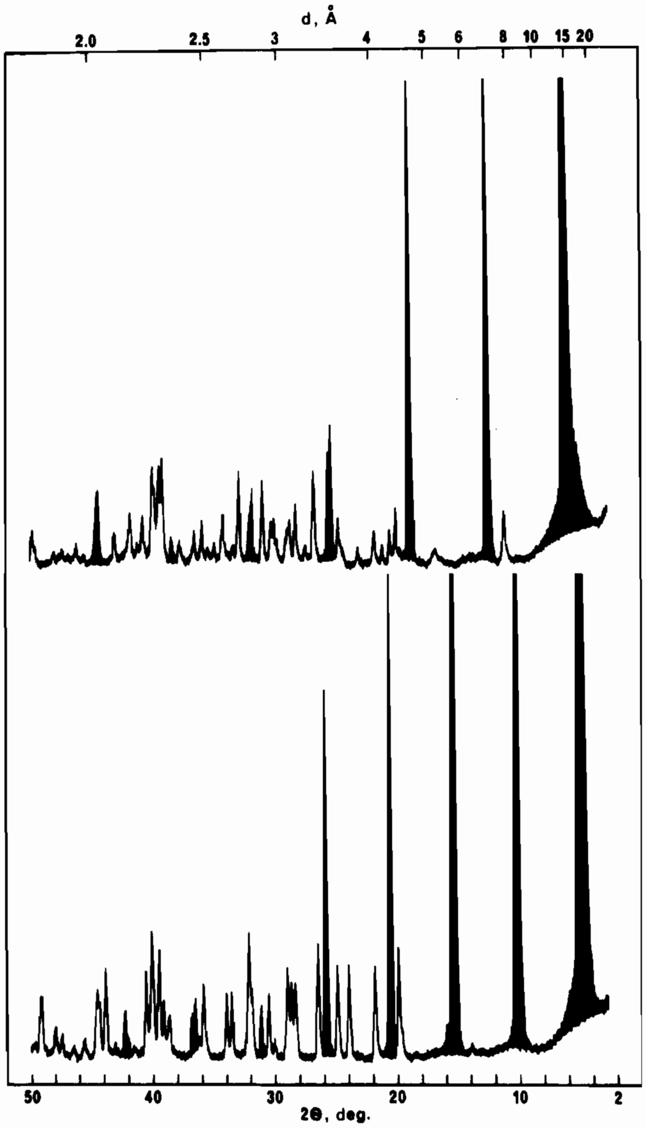

Figure 2. Polycrystalline diffraction patterns of **5** (upper) and **10** (lower). The interlayer reflections (0*k*0) are marked as filled lines.

the slab are not coplanar, but contribute a small thickness, $2t_1$, which is the perpendicular separation of the planes of S atoms. The principal thickness of the layer is due to the length L of the substituents, from S to the distal atom X. With $r_w(X)$ as the van der Waals radius of X, each substituent contributes $t_2 = L + r_w(X)$ to the thickness of the slab. We initially assume that ϕ, the inclination of the substituent with the slab, is 90°. The calculated thickness of the complete layer is then $(2t_1 + 2t_2)$.

The comparison of the calculated model and the observed layer thickness ($T_{obs} = b$) is made in Table II and is expressed as $T_{obs} - 2t_2$ (that is with initial assumption of $t_1 = 0$). It can be seen that this difference is small, relative to its components. The difference ($T_{obs} - 2t_2$) should be positive due to neglected $2t_1$, but may contain small negative contributions from the interpenetration of the undulating van der Waals surfaces of the layers at X (as illustrated in Figure 3) and positive contributions if the substituent is inclined at $\phi < 90°$. In the four compounds with *n*-alkyl substituents, a fully extended conformation of the chain has been assumed, and it is concluded that the slab thickness $2t_1$ is 1–1.5Å. This is consistent with the intraslab model proposed below. For the six compounds with aryl substituents, we conclude that $2t_1$ is also ca. 1 Å and that there is some substituent interpenetration at the van der Waals surface, up to ca. 1 Å. The scatter of the ($T_{obs} - 2t_2$) values is an indication of the precision of the model and the influences of different substituents on the undulations and interpenetrations at the van der Waals surface.

Table II

compound	L, Å	t_2,[a] Å	T_{obs},[b] Å	$T_{obs} - 2t_2$, Å
$AgS(CH_2)_2CH_3$ (**1**)	4.0[c-e]	5.7	12.5	1.1
$AgS(CH_2)_3CH_3$ (**2**)	5.2[c-e]	6.9	15.45	1.65
$AgS(CH_2)_5CH_3$ (**3**)	7.8[c,e]	9.5	20.0	1.0
$AgS(CH_2)_7CH_3$ (**4**)	10.2[c,e]	11.9	24.8	1.0
$AgSC_6H_5$ (**5**)	5.55[d]	6.55	14.06	0.96
$AgSC_6H_4$-4-F (**6**)	5.87[d]	7.34	14.67	0.0
$AgSC_6H_4$-4-Cl (**7**)	6.27[d]	8.03	16.37	0.31
$AgSC_6H_4$-4-Br (**8**)	6.42	8.24	16.88	0.40
$AgSC_6H_4$-4-CH_3 (**9**)	6.14[d,e]	7.83	16.38	0.72
$AgSC_6H_4$-4-OCH_3 (**10**)	6.8[d,e]	8.49	17.12	0.14

[a] van der Waals radii (Å): CH_3, 1.69; H, 1.00; F, 1.47; Cl, 1.76; Br, 1.85. [b] T_{obs} here is set equal to the observed interlayer dimension, that is with the assumption that there is no interpenetration of the layers at their boundaries. [c] Assuming a fully extended conformation of the *n*-alkyl chain. [d] Taken from crystal structure data on relevant compounds. [e] X is the C atom of the CH_3 group.

Intralayer Structure. Apart from the progressions of layer reflections, the diffraction patterns of all of the compounds show additional sharp reflections of medium to weak intensity. The *d* spacings and qualitative intensities of these additional reflections are listed in Table III. Generally the largest *d* spacing is about 4.5 Å, and there are prominent reflections in other common regions. There is no apparent dependence of *d* spacings on the variable interlayer separations, indicating that the additional reflections are mostly $\{h0l\}$ and that there is a common intralayer structure. The presence of these reflections indicates that there is registry and not disorder of the layers (again supporting the postulate of some interpenetration of the substituents at the layer boundaries), and it is evident that all compounds contain well-defined unit cells with *a* and *c* short and relatively invariant, in contrast to the long and variable *b*.

Expectation coordination geometries for silver with thiolate coordination are linear digonal (Ag–S = 2.37 Å) and planar trigonal (Ag–S = 2.55 Å). Digonal primary coordination with one long secondary connection (Ag–S of ca. 3 Å) is also known.[3,7] Thiolate ligands SR may be terminal, doubly bridging, or triply bridging. The stoichiometry AgSR requires that the coordination numbers (but not geometries) of Ag and SR be the same.

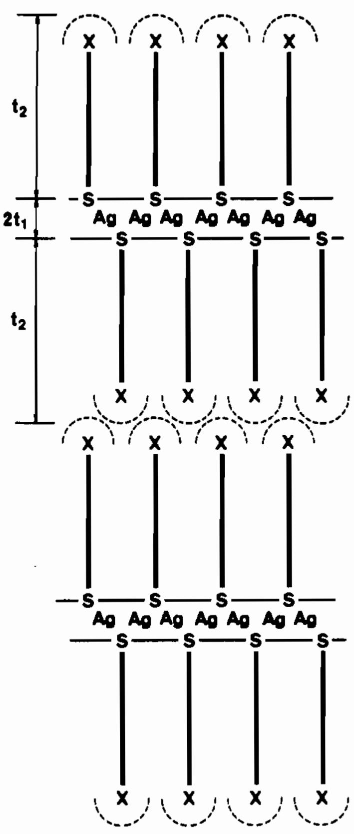

Figure 3. Cross-sectional schematic representation of the layered crystal structure. Horizontal lines define the thickness ($2t_1$) of the central Ag,S slab, drawn without Ag–S bonds. The vertical thick lines represent the substituent extending from sulfur to the distal atom X, with broken arcs outlining the van der Waals radii of the atoms X at which the layers are in contact. The total thickness of one layer is $2t_1 + 2t_2$. A small interpenetration of layers at their interface is shown.

Two-coordinate Ag and SR can form only chains, from which it is difficult to conceive of a central slab required to be rigid and

Table III. *d* Spacings (Å) for Reflections Other Than the $\{0k0\}$ Layer Progressions

1	2	3	4	5	6	7	8	9	10
				15.92 s[a]					
				7.49 m					
			4.50 ms		4.54 w			4.53 w	
	4.37 m	4.44 w		4.41 w	4.40 ms	4.41 wm	4.41 w	4.37 m	4.43 m
				4.33 w					
				4.20 w				4.23 w	
				4.06 w			4.02 m	4.00 m	4.05 m
	3.80 w		3.81 w	3.83 w					3.70 m
	3.54 w			3.60 w	3.58 w	3.61 m	3.60 m	3.61 s	3.56 m
3.41 m	3.45 m		3.34 m	3.35 m	3.38 s	3.36 w		3.37 s	3.35 m
	3.22 ms		3.19 wm	3.16 m				3.12 wm	3.13 m
				3.10 m					3.10 m
3.08 w					3.08 m	3.05 m	3.09 ms	3.06 s	3.07 m
			2.99 wm	2.98 m	3.01 w			3.00 ms	
	2.92 m							2.92 w	2.92 wm
2.87 w	2.86 m			2.89 m		2.87 wm	2.86 wm	2.87 m	
2.80 m	2.82 ms	2.82 vw	2.82 ms		2.78 w			2.82 w	2.80 w
	2.77 wm			2.73 m	2.74 m			2.75 s[a]	2.77 ms
	2.69 wm		2.70 w					2.67 w	2.66 wm
2.61 w			2.62 w	2.62 m	2.56 m			2.57 ms	2.63 wm
2.52 w				2.50 wm					2.50 m
				2.46 w	2.42 w		2.40 ms	2.45 ms	2.44 m
								2.38 w	2.32 w
2.31 w		2.34 vw		2.30 m	2.30 s	2.35 m		2.29 ms	2.30 w
				2.28 m			2.28 wm	2.27 m	2.28 ms
				2.26 m	2.25 m			2.23 m	2.24 ms
				2.21 m			2.23 m	2.20 m	2.22 m
				2.16 m					
2.13 w	2.09 m			2.10 m				2.11 w	2.06 m
1.99 w		2.02 vw			2.02 w			2.00 m	2.03 m

[a] Overlap with (010).

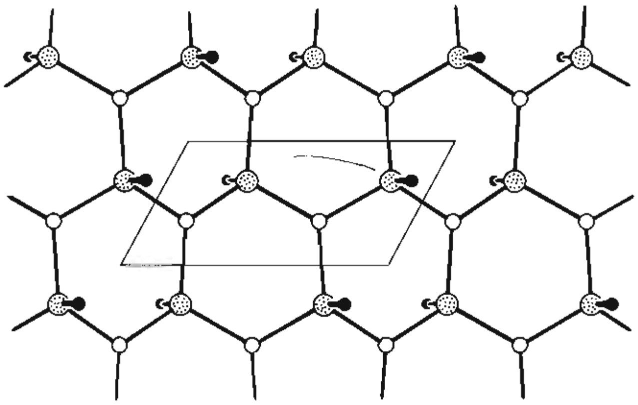

Figure 4. Quasi-hexagonal network proposed for the central slab of AgSR. Dotted circles are S, and the filled circles represent the substituents R. The view direction is off-normal, in order to show the directions of the substituents that are perpendicular above and below the slab. Each AgS_3 trigonal coordination plane is tilted between two S atoms on one side of the Ag plane and one on the other. The two-dimensional unit cell is outlined.

thin, so it is more likely that Ag and SR are three-coordinate.

A straightforward quasi-hexagonal network with trigonal-planar coordination of Ag by three SR moieties and RS coordinated by three Ag atoms in pseudotetrahedral geometry is shown in Figure 4. In this network the Ag atoms occur in a central plane, the S atoms occur in planes on either side, and the R groups extend perpendicular to the slab on both sides, as modeled in Figure 3. There are equal numbers of substituents on each side of the slab. Each AgS_3 trigonal coordination plane is tilted between two S atoms on one side of the Ag plane and one on the other. Entirely reasonable dimensions can be achieved with this slab structure: if Ag–S is 2.56 Å and the S planes are 0.5 Å either side of the Ag plane (i.e. $2t_1 = 1.0$ Å) as indicated by the $\{0k0\}$ reflections, S–Ag–S angles are 116.3 and 121.3° and Ag–S–Ag angles are 116.3°.

This model is supported by the observed $\{h0l\}$ reflections. The two-dimensional unit cell of Figure 4 has the dimensions $a = 8.70$ Å, $c = 4.35$ Å, and $\beta = 120°$, derived from the slab dimensions Ag–S = 2.56 and $2t_1 = 1.0$ Å. Translation of one layer by b allows the X groups from one layer to fit into gaps between the substituents in the contiguous layer. Therefore, the unit cell for the model is monoclinic with a, c, and β as above, and with b variable as determined in Table I. This cell is artificially symmetric, but it serves to index the main types of reflections. The largest d spacing for $\{h0l\}$ reflections is calculated as 7.53 Å for $\{100\}$, and is evident (at 7.49 Å, see Table III) for **5**. Next, the $(10\bar{1})$, $(\bar{1}01)$, $(30\bar{1})$, and $(\bar{3}01)$ reflections calculate as $d = 4.35$ Å, and there is a medium to strong reflection in the range 4.37–4.50 Å for all compounds except **9**. $\{001\}$, $\{200\}$, and $\{20\bar{1}\}$ reflections calculate as $d = 3.77$ Å, and there is a band of moderate-intensity reflections observed for all compounds in the range 3.54–3.83 Å which is due to these zones. Each compound shows a medium to strong reflection in the range 3.34–3.45 Å. The $\{101\}$ reflections calculate as 2.85 Å, and there is a band of medium to strong reflections in the range 2.74–2.92 Å. The $\{20\bar{2}\}$ reflections at 2.16–2.30 Å and the $\{10\bar{2}\}$ reflections at 2.09 Å are observed.

These regions of reflections in the diffraction patterns establish the general lattice geometry, but the multiplicity of reflections indicates that the assumptions $a = 2c$ and $\beta = 120°$ are artificially symmetric. The lowering of symmetry can be achieved by local variations of geometry, such as elongation of one Ag–S connection and concomitant opening of the opposite S–Ag–S angle toward 180°. Some $\{hkl\}$ reflections will occur in the same region as the $\{h0l\}$ reflections.

In the AgSAr compounds, rotation about the S–C bond is a conformational variable. A probable array for the Ar substituents of one layer is shown in Figure 5a, allowing adequate separation of adjacent rings and the rings of one layer to fit between the rings of the next layer. Figure 5b, presenting the space filling of part of the model for AgSPh (**5**), shows how the rings interpenetrate.

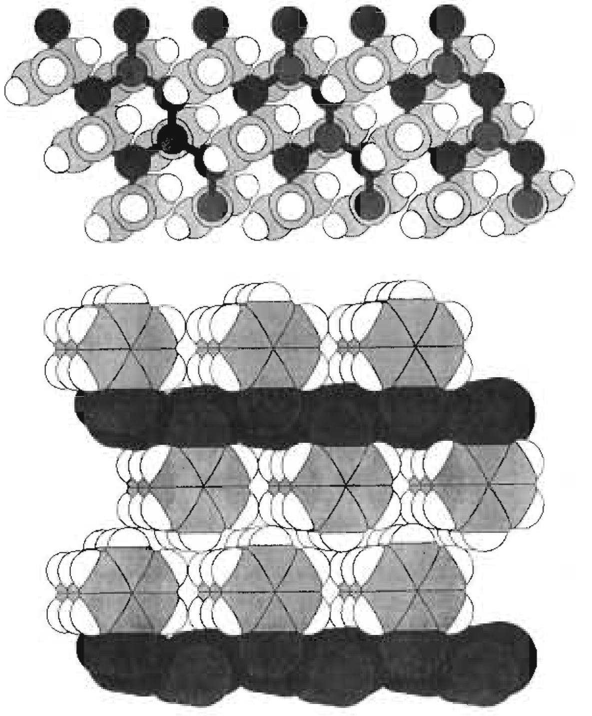

Figure 5. Representations of the model for **5**, with atom shading increasing with atomic number. (a) Top: View normal to part of one layer showing a probable orientation of the phenyl rings. Rings above the layer obscure sulfur atoms. Note that with superposition of layers, the rings on one side of one layer will be located midway between four rings of the next layer. (b) Bottom: Space-filling view normal to the layers of **5**, showing the interpenetration of the rings from adjacent layers.

There are some AgSR compounds with bulkier substituents that do not show the prominent pattern of strong $\{0k0\}$ reflections in their polycrystalline diffraction patterns: these are $AgSC(CH_3)_3$, $AgSC_6H_4$-2-Cl, $AgSC_6H_4$-2-CH_3, and $AgSC_6H_4$-4-$C(CH_3)_2CH_2CH_3$. Evidently, the pronounced layer structure is disrupted by steric crowding close to S or, in the last compound, increasing the cross-sectional area of the substituent beyond that which can be accommodated by the Ag,S network of the slab. It is probable that these compounds have one dimensionally nonmolecular chain structures with doubly bridging thiolate and two-coordinate Ag, analogous to that of $AgSC(CH_3)_2CH_2CH_3$. We have not observed the layer type diffraction pattern for any CuSR compounds.

In attempt to grow thicker plates of **5**, many slow diffusion experiments were undertaken. The $AgNO_3$ and C_6H_5SH were allowed to diffuse together slowly through gels, including aqueous silica gels and nonaqueous Sephadex LH-20 gels.[16] Although crystal size was increased, no crystal suitable for single-crystal diffractometry was obtained.

A characteristic property of layered structures is intercalation of guest molecules.[17-20] We have attempted to intercalate a variety of liquid guests into crystals of **5** and **7**. The potential guests included amines and common polar and nonpolar solvents. Diffraction patterns of **5** and **7** were measured while these compounds were soaked in these liquids, but there was no evidence of layer expansion. Among all of the layered hosts known to intercalate,[18,19] most present a polar face of M–O, M–OH, M–S, or M–Cl groups to the guest: the AgSR compounds are thus

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different in presenting a relatively nonpolar and, in some cases, hydrocarbon interface to potential guests.

Discussion

There is some geometrical analogy between the structure of crystalline AgSAr compounds and the monolayers of thiols that can be formed on clean gold surfaces.[13-15,21-23] In both cases, there is a two-dimensional lattice of coinage-metal atoms, with a layer of sulfur atoms and with substituents on the sulfur atoms arrayed orthogonally or at a steep angle to the layer. The substituents shield the metal. There are also significant chemical differences between the two systems. One is the Ag-SR bond contrasted with the Au-HSR adsorption. A second is that the Au-HSR monolayer presents an accessible interface with other media, allowing the investigations of physical, optical, and electrochemical properties of the interface. The AgSR compounds are bulk crystals, but **5** adopts a platy habit, which presumably presents the AgSR layer at the surface. A third difference is that the packing density of substituents is determined by the Ag,S lattice structure and not the cross section of the substituent as it is in the Au monolayers. Fourth, arenethiolate layers are known only for the Ag compounds.

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Mercury Polysulfide Complexes, $[Hg(S_x)(S_y)]^{2-}$: Syntheses, ^{199}Hg NMR Studies in Solution, and Crystal Structure of $(Ph_4P)_4[Hg(S_4)_2]Br_2$

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Mercury polysulfide complexes $[Hg(S_x)(S_y)]^{2-}$ have been prepared in DMF solution by the reaction $HgS + Na_2S + S_8$. The nominal compositions $[Hg(S_m)_n]$ of these solutions can be varied widely, with the average polysulfide chain length *m* ranging from 3 to 8 and the nominal ligand to metal ratio *n* ranging from 2 to 4. ^{119}Hg NMR spectroscopy reveals the existence of at least three distinct $[Hg(S_x)(S_y)]^{2-}$ complexes that are in equilibrium and undergo chemical exchange which is slow on the NMR time scale at room temperature. The three principal species are $[Hg(S_4)_2]^{2-}$, $[Hg(S_4)(S_5)]^{2-}$, and $[Hg(S_5)_2]^{2-}$, and there is evidence for $[Hg(S_5)(S_6)]^{2-}$. Addition of Ph_4Br to the $[Hg(S_4)_2]^{2-}$ solution causes crystallization of the new complex $(Ph_4P)_4[Hg(S_4)_2]Br_2$ (**1**), which contains well-separated tetrahedral $[Hg(S_4)_2]^{2-}$, Ph_4P^+, and Br^- ions, with no secondary bonding. Crystal data for **1**: space group $I\bar{4}$, $a = 19.563$ (4) Å, $c = 11.531$ (2) Å, $V = 4413$ (1) Å^3, $Z = 2$ ($[Hg(S_4)_2](PPh_4)_4Br_2$), 1661 independent observed reflections (Mo Kα, $I/\sigma(I) > 3$), $R = 0.024$.

Introduction

Homoleptic metallapolysulfane complexes $[M(S_x)_w]^z$ containing polysulfide chains as chelating ligands have been known for a very long time.[1,2] The chemistry of these compounds has been revived recently[3-6] by the deployment of nonaqueous media, which increase the thermodynamic activities of polysulfide ions in solution and therefore expand the range of complexes that can exist in solution equilibria. The principal method for the formation of nonaqueous $(S_x)^{2-}$ has been the direct analogue of the aqueous method,[7] namely

$$\text{solvent} + S_8 + NH_3(g) + H_2S(g) \rightarrow (NH_4)_2S_x(\text{solv})$$

applied by Müller et al.[8-11] The use of gaseous reagents in this preparation has led to variability of composition of the $(NH_4)_2S_x$ solutions and can introduce difficulties in attaining reproducible metallapolysulfane stoichiometry.

We have used alternative methods for the controlled generation of active nonaqueous solutions of $(S_x)^{2-}$, for reaction with suitable transition- or post-transition-metal precursors. These methods include the use of salts such as $(Bu_4N)_2S_6$[12] and $(Ph_4P)_2S_6$,[13] which are soluble in aprotic solvents of interest, and the in situ formation of Na_2S_x in DMF by the reactions of Na or Na_2S with S_8. We also use sulfides of the post transition metals in reactions with the polysulfide solutions, in order to avoid the introduction of anions that could compete with the polysulfide ligands.

Although an astonishing variety of molecular structures has been revealed in the crystal structures of metal polysulfides, it is recognized that such structures need not be representative of the complexes existing in solution, and the crystal structures do not provide information about the species, reactions, and equilibria that occur in solution, information which could be used to support rational syntheses and applications. Therefore, we have used ^{199}Hg NMR spectroscopy to probe solutions of mercury polysulfides.

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