Insertion of CS_2 into Ag–S Bonds. Preparations and Crystal Structures of $[\{[Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)]_4\cdot CHCl_3\}_n]$ and Its Insertion Product with CS_2, $[\{Ag(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]\cdot 8CHCl_3$†

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By the use of a sterically hindered arenethiolate ligand, 2,4,6-$Pr^i{}_3C_6H_2SH$ the colourless silver thiolate complex $[\{[Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)]_4\cdot CHCl_3\}_n]$ (**1**) has been synthesized and structurally characterized. The structure of (**1**) consists of a one-dimensional double $(Ag\text{–}SR)_n$ strand belt polymer. The strand $(Ag\text{–}SR)_n$ is formed by alternating silver and sulphur atoms of the ligands. Complex (**1**) reacts with a small amount of CS_2 to give a pale yellow product $[\{Ag(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]\cdot 8CHCl_3$ (**2**), and CS_2 is inserted into a quarter of the Ag–S bonds of complex (**1**). The unusual structure of complex (**2**) consists of eight coplanar silver atoms linked through arenethiolate (RS) and aryl thiocarbonate ($RSCS_2$) ligands, exhibiting a number of interesting features. A novel structural type of insertion of CS_2 into M–S bonds has been found. Crystal data: (**1**), triclinic, space group $P\bar{1}$, a = 14.443(7), b = 16.201(12), c = 16.586(14) Å, α = 68.27(6), β = 80.84(6), γ = 75.73(5)°, for Z = 2, R = 0.074, for 2 065 observed reflections; (**2**), monoclinic, space group $P2_1/n$, a = 17.897(7), b = 27.131(18), c = 19.111(9) Å, β = 113.59(3)°, for Z = 2, R = 0.084, for 3 930 observed reflections.

Uncharged silver(I) or copper(I) thiolate complexes $[\{M(SR)\}_n]$, in which R is not bulky, are frequently insoluble in inert solvents, forming non-molecular aggregates. The degree of aggregation depends intimately on both the reaction conditions and the nature of the thiolate ligands. By the use of a novel series of sterically hindered polysilylated thiol ligands, $(RR'R''Si)_nCH_{3-n}SH$ (R,R′,R″ = Me or Ph), a number of silver(I) or copper(I) thiolate complexes have been synthesized and structurally characterized by us.[1–4] In a previous paper we reported the synthesis and structure of an octanuclear copper cluster complex $[\{Cu(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_8]$ with a sterically hindered arenethiolate ligand.[5] In this paper we present the synthesis and crystal structure of the silver complex with the same ligand $[\{[Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)]_4\cdot CHCl_3\}_n]$ (**1**), which is a polymeric belt complex.

The insertion of CS_2 into an M–X bond (M = transition metal; X = H, N, O, S, halide, alkyl, amine, alkoxide, *etc.*) has been widely studied.[6] Carbon disulphide can be inserted into Cu–S bonds in some copper thiolate complexes [Cu(SR)] to give copper alkyl (or phenyl) trithiocarbonate complexes.[7–10] However, very few reports on the insertion of CS_2 into Ag–S bonds have been made. In a systematic investigation on the insertion of CS_2 into Ag–S bonds we have found silver thiolate complexes $[\{Ag(SR)\}_n]$ with less bulky substituents difficult to react with CS_2, *e.g.* R = Bu^t, Ph, or $C_6H_2Me_3$-2,4,6. However, the complex with R = Bu^t readily reacted with CS_2 to give an insertion product $[Ag(S_2CSBu^t)(PPh_3)_2]$.[11] By a change of the substituents of the ligand to the larger R = $C_6H_2Pr^i{}_3$-2,4,6 the reaction with CS_2 proceeded more readily to give a peculiar product $[\{Ag(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]\cdot 8CHCl_3$ (**2**) involving insertion of CS_2 into a quarter of the Ag–S bonds of complex (**1**).

Experimental

Reagent grade chemicals were used throughout without further purification. Infrared spectra were recorded from KBr pellets with a Perkin-Elmer 983G spectrometer.

Preparation of Complex (**1**).—A solution of $AgNO_3$ (400 mg, 2.4 mmol) in acetonitrile (20 cm^3) was added dropwise to a solution of 2,4,6-tri-isopropylthiophenol[12] (560 mg, 2.37 mmol) and NEt_3 (0.5 cm^3) in acetonitrile (10 cm^3) at room temperature during 5 min. The mixture was stirred for 1 h. The white precipitate was collected by filtration, washed with ethanol, and dried *in vacuo*. The crude product was dissolved in chloroform, and colourless needle crystals were obtained by slow diffusion of ethanol into the chloroform solution over 10 d. The crystals effloresced and turned into a white powder in the air. The white powder decomposed at about 200 °C. I.r. (KBr): 3 042w, 2 956vs, 2 868m, 1 758w, 1 598w, 1 559w, 1 458s, 1 423m, 1 028m, 934w, 921w, 875s, 752w, 646w, 635w, 522m, 424vw, and 339w cm^{-1}.

Preparation of Complex (**2**).—Three drops of carbon disulphide were added to a solution of complex (**1**) (200 mg) in chloroform (5 cm^3), and the colourless solution turned yellow in several minutes. The yellow solution was evaporated slowly at room temperature for 2 d, whereupon pale yellow prismatic crystals were obtained. The crystals effloresced in the air into an opaque solid which turned into a white powder when heated to 100 °C. I.r. (KBr): 3 043w, 2 968vs, 2 865vs, 1 759w, 1 597m, 1 560m, 1 516w, 1 457vs, 1 423s, 1 381s, 1 360s, 1 309m, 1 166m, 1 101m, 1 056s, 1 027s, 1 000s, 936m, 921w, 875s, 844m, 751m, 646m, 633m, 522w, 404w, and 322w cm^{-1}.

X-*Ray Crystal Structural Determination of Complexes* (**1**) *and* (**2**).—The crystal data for complexes (**1**) and (**2**) are summarized in Table 1 together with some experimental details. The diffraction intensities were collected at room temperature on a Nicolet R3 diffractometer with Mo-K_α radiation (λ = 0.710 73 Å). Both crystals were sealed in glass capillaries. The structures were solved by a combination of direct and Patterson methods with the SHELXTL program.[13] All calculations were

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† *Supplementary date available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

completed on an Eclipse 230 computer. Full-matrix block least-squares refinement of all positional parameters, anisotropic thermal parameters for the silver and sulphur atoms, and individual isotropic thermal parameters for the carbon and chloride atoms was applied. The hydrogen atoms were located in calculated positions and each was assigned an isotropic thermal parameter 1.2 times that of the carbon to which it was attached. Atoms of the chloroform molecules are disordered and were fixed as a rigid group during refinement. A weighting scheme of the form $w = [\sigma^2(F) + 0.0001\ F^2]^{-1}$ was applied. The atomic co-ordinates for the non-hydrogen atoms of complexes (**1**) and (**2**) are reported in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Structure of Complex (**1**).—The structure determination shows that (**1**) is a polymeric complex. The structure may be described in terms of a one-dimensional double $(Ag{-}SR)_n$ strand belt as shown in Figure 1. The atom labelling scheme is given in Figure 2. The strand $(Ag{-}SR)_n$ is formed by alternating silver and sulphur atoms of the arenethiolate ligands. Each belt contains two strands of $(Ag{-}SR)_n$ connected by Ag–Ag links between the Ag atoms of the two strands. All Ag atoms participate in the formation of Ag–Ag links. The centres of symmetry in the triclinic cell are located at the midpoints of Ag(a)–Ag(a′) and Ag(c)–Ag(c″) respectively. This structure of

Table 1. Summary of crystal data and experimental details for complexes (**1**) and (**2**)

	(**1**)	(**2**)
Formula	$C_{60}H_{92}Ag_4S_4{\cdot}CHCl_3$	$C_{122}H_{184}Ag_8S_{12}{\cdot}8CHCl_3$
M	1 492.6	3 853.7
Colour/habit	Colourless needle	Pale yellow block
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	14.443(7)	17.897(7)
b/Å	16.201(12)	27.131(18)
c/Å	16.586(14)	19.111(9)
α/°	68.27(6)	
β/°	80.84(6)	113.59(3)
γ/°	75.73(5)	
U/Å^3	3 484(4)	8 504(7)
Z	2	2
D_c/g cm^{-3}	1.42	1.50
μ(Mo-K_α)/cm^{-1}	13.4	14.3
F(000)	1 524	3 896
Crystal dimensions/mm^3	0.25 × 0.25 × 0.30	0.20 × 0.20 × 0.25
Scan mode	ω	θ—2θ
Scan rate/° min^{-1}	4—29.3	4—29.3
Scan range/°	$3.5 \leqslant 2\theta \leqslant 45$	$3.5 \leqslant 2\theta \leqslant 45$
No. of reflections measured	6 369	6 243
No. observed $[I \geqslant 3\sigma(I)]$	2 065	3 930
R	0.074	0.084
R'	0.065	0.077

Table 2. Atom co-ordinates (× 10^4) of non-hydrogen atoms for complex (**1**)

Atom	*x*	*y*	*z*
Ag(a)	378(2)	4 706(2)	−880(2)
Ag(b)	2 864(2)	3 592(2)	259(2)
Ag(c)	4 588(2)	6 057(2)	26(2)
Ag(d)	2 254(2)	4 914(2)	1 195(2)
S(a)	1 737(7)	3 497(5)	−572(5)
S(b)	4 162(7)	3 545(6)	1 008(5)
S(c)	3 392(7)	5 774(6)	1 164(6)
S(d)	978(7)	4 166(6)	1 381(5)
C(1)	2 310(21)	3 636(17)	−1 633(17)
C(2)	2 642(22)	4 457(17)	−2 191(17)
C(3)	3 070(24)	4 518(20)	−2 998(19)
C(4)	3 061(23)	3 844(19)	−3 302(18)
C(5)	2 829(22)	3 005(19)	−2 782(18)
C(6)	2 414(23)	2 920(18)	−1 930(19)
C(21)	4 463(23)	2 371(20)	1 702(20)
C(22)	4 394(25)	2 254(21)	2 594(21)
C(23)	4 591(28)	1 339(24)	3 212(25)
C(24)	4 863(1)	654(1)	2 879(2)
C(25)	4 932(24)	770(21)	1 983(20)
C(26)	4 787(24)	1 653(22)	1 383(20)
C(41)	2 706(25)	6 875(21)	1 144(19)
C(42)	2 155(24)	7 434(21)	463(19)
C(43)	1 614(23)	8 323(20)	419(19)
C(44)	1 702(23)	8 575(18)	1 087(18)
C(45)	2 294(23)	8 086(20)	1 769(20)
C(46)	2 812(23)	7 180(19)	1 777(18)
C(61)	769(22)	3 644(18)	2 565(18)
C(62)	615(23)	4 113(20)	3 128(19)
C(63)	502(22)	3 673(19)	4 015(18)
C(64)	564(25)	2 748(20)	4 372(19)
C(65)	766(25)	2 245(23)	3 795(21)
C(66)	855(23)	2 705(19)	2 869(18)
C(11)	2 513(23)	5 192(20)	−1 834(20)
C(12)	2 041(24)	6 082(20)	−2 461(20)
C(13)	3 494(24)	5 299(22)	−1 739(22)
C(14)	3 440(15)	3 850(19)	−4 226(3)
C(15)	2 776(27)	456 1(24)	−4 911(23)
C(16)	4 497(23)	3 914(33)	−4 500(32)
C(17)	2 080(29)	2 018(22)	−1 412(23)
C(18)	1 044(29)	2 125(24)	−1 486(23)
C(19)	2 663(26)	1 194(23)	−1 588(22)
C(31)	4 132(29)	3 070(26)	2 950(25)
C(32)	3 287(33)	2 891(29)	3 545(28)
C(33)	4 943(37)	3 126(34)	3 336(33)
C(34)	5 095(20)	−349(13)	3 275(14)
C(35)	5 827(27)	−623(24)	3 908(28)
C(36)	4 217(30)	−680(25)	3 729(32)
C(37)	4 814(23)	1 762(21)	446(19)
C(38)	5 790(24)	1 283(21)	189(20)
C(39)	4 064(25)	1 416(22)	235(22)
C(51)	1 977(29)	7 166(24)	−305(21)
C(52)	974(27)	7 094(22)	−349(22)
C(53)	2 360(28)	7 837(24)	−1 172(23)
C(54)	1 158(1)	9 551(5)	977(22)
C(55)	1 782(24)	10 247(21)	831(22)
C(56)	397(26)	9 497(25)	1 749(19)
C(57)	3 530(29)	6 628(26)	2 473(23)
C(58)	3 148(27)	6 751(23)	3 325(22)
C(59)	4 476(27)	6 890(24)	2 167(23)
C(71)	474(22)	5 147(20)	2 828(20)
C(72)	−479(23)	5 542(20)	3 239(19)
C(73)	1 282(24)	5 413(21)	3 085(20)
C(74)	492(33)	2 227(30)	5 397(27)
C(75)	1 398(36)	2 000(35)	5 703(33)
C(76)	−411(37)	2 675(33)	5 768(33)
C(77)	1 136(27)	2 126(22)	2 241(22)
C(78)	344(29)	1 530(25)	2 483(25)
C(79)	2 069(32)	1 582(29)	2 376(27)
C(81)	8 240(49)	1 593(29)	4 242(36)
Cl(1)	7 536(19)	1 200(19)	3 733(18)
Cl(2)	7 404(19)	2 211(19)	4 824(18)
Cl(3)	8 625(22)	583(15)	5 116(16)

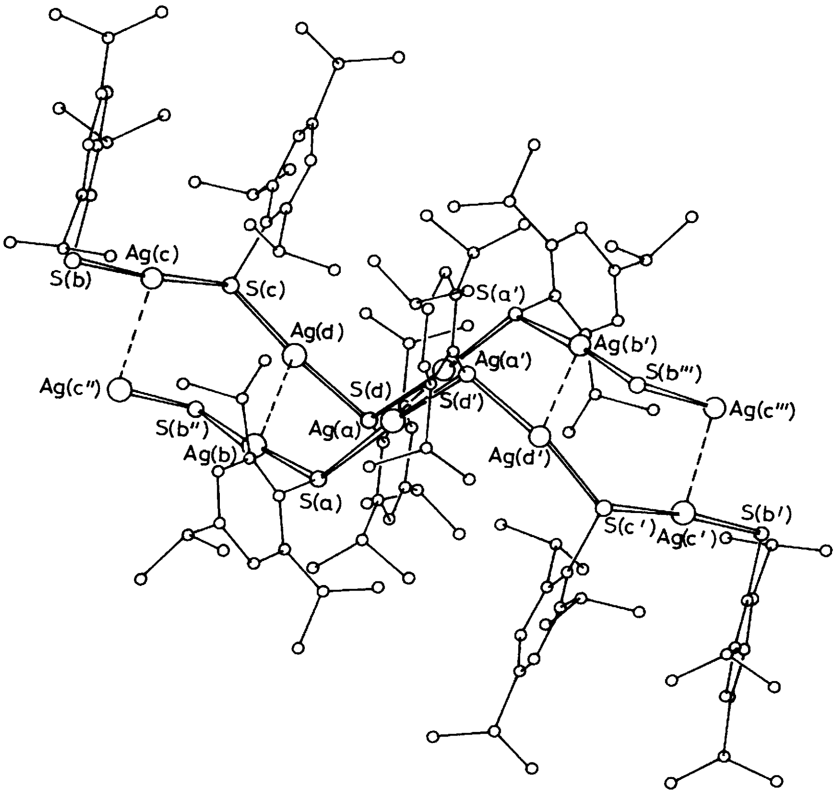


Figure 1. View of the polymeric structure of [{Ag(SC$_6$H$_2$Pr$^i_3$-2,4,6)}$_n$]

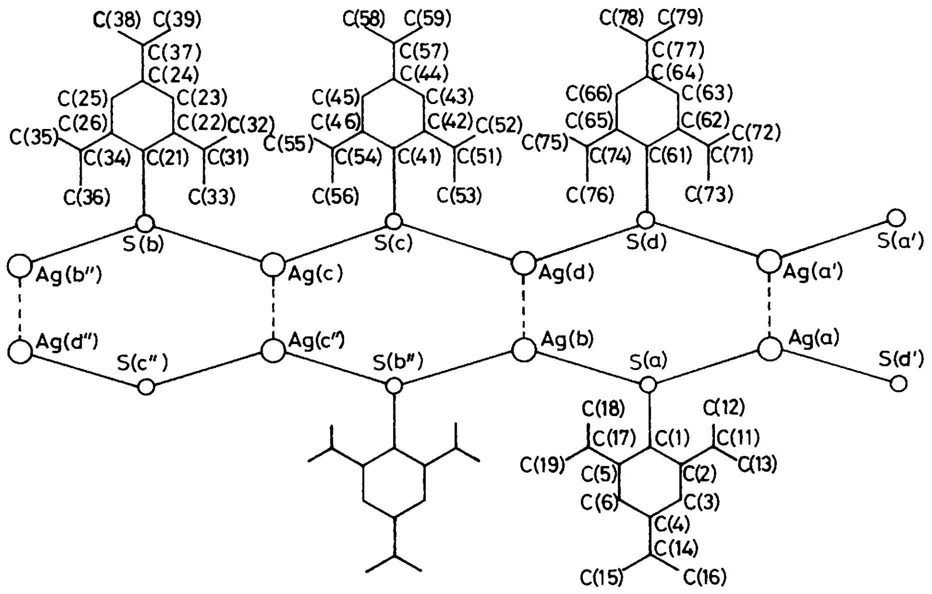


Figure 2. The atom labelling scheme for [{Ag(SC$_6$H$_2$Pr$^i_3$-2,4,6)}$_n$]

complex (1) is somewhat similar to that of [{Ag(SCMeEt$_2$)}$_n$] which contains a chain of two intertwined but totally unconnected (Ag–SR)$_n$ strands.[14] All S–Ag–S segments are almost linear. The average bond angle of S–Ag–S is 171.3° (170.6—172.0°), and the average distance Ag–S is 2.358 Å (2.320—2.387 Å). The Ag–Ag bond distances between two strands fall into two categories: Ag(b)–Ag(d) without riding on a symmetry centre gives the shortest distance (2.978 Å), slightly longer than Ag–Ag 2.886 Å in silver metal;[15] Ag(a)–Ag(a') and Ag(c)–Ag(c'') both riding on a symmetry centre are respectively 3.339 and 3.367 Å, shorter than the van der Waals diameter of silver 3.40 Å.[16] However, there is no Ag···S interaction between two linked strands. The hindrance of the arenethiolate ligand with bulky substituents, $^-$SC$_6$H$_2$Pr$^i_3$-2,4,6, prevents the neighbouring belts from close approach and precludes concomitant Ag··· Ag interactions to form further layers. The use of the less bulky ligand HSC$_6$H$_2$Me$_3$-2,4,6 gives an insoluble white solid.[17] The less bulky the ligand is the more tightly the strands are linked by Ag··· Ag interactions. Solvent molecules then would penetrate with difficulty into the solid phase of

Table 3. Atom co-ordinates (× 10^4) of non-hydrogen atoms for complex (**2**)

Atom	*x*	*y*	*z*
Ag(1)	7 345(1)	492(1)	10 884(1)
Ag(2)	5 788(1)	21(1)	10 563(1)
Ag(3)	6 949(1)	−316(1)	12 147(1)
Ag(4)	5 309(1)	667(1)	8 947(1)
S(1)	6 752(4)	596(3)	9 549(4)
S(2)	5 444(4)	716(3)	11 137(4)
S(3)	4 047(4)	931(3)	8 003(4)
S(4)	7 786(4)	368(3)	12 206(4)
S(5)	4 327(4)	1 454(3)	11 053(4)
S(6)	3 744(4)	693(3)	9 868(4)
C(1)	−100(21)	884(15)	1 480(21)
C(2)	2 157(23)	1 215(14)	6 170(21)
C(3)	5 980(28)	1 747(18)	2 774(27)
C(4)	8 592(32)	2 258(19)	7 011(27)
C(5)	4 480(14)	928(9)	10 627(13)
Cl(1)	248(7)	546(5)	958(7)
Cl(2)	−1 071(7)	1 135(4)	843(6)
Cl(3)	494(7)	1 368(5)	1 957(7)
Cl(4)	1 513(7)	695(5)	6 171(7)
Cl(5)	2 164(10)	1 204(7)	5 336(10)
Cl(6)	1 545(11)	1 697(7)	6 153(10)
Cl(7)	5 977(8)	2 335(5)	2 452(7)
Cl(8)	5 493(10)	1 689(6)	3 341(9)
Cl(9)	6 988(11)	1 603(7)	3 268(10)
Cl(10)	7 775(11)	1 634(7)	5 899(11)
Cl(11)	7 316(16)	2 172(9)	6 735(14)
Cl(12)	8 973(24)	1 950(17)	6 884(25)
C(11)	7 046(15)	1 217(10)	9 381(14)
C(12)	7 397(17)	1 245(12)	8 866(16)
C(13)	7 611(16)	1 694(11)	8 727(15)
C(14)	7 534(17)	2 128(12)	9 087(17)
C(15)	7 182(16)	2 072(11)	9 603(15)
C(16)	6 919(15)	1 620(10)	9 764(14)
C(121)	7 542(17)	800(11)	8 423(15)
C(122)	6 894(17)	804(12)	7 609(16)
C(123)	8 402(19)	787(13)	8 481(19)
C(141)	7 810(21)	2 655(13)	8 894(20)
C(142)	6 999(21)	2 938(13)	8 508(19)
C(143)	8 499(26)	2 846(18)	9 430(26)
C(161)	6 541(14)	1 609(10)	10 321(14)
C(162)	7 092(17)	1 789(11)	11 107(15)
C(163)	5 750(16)	1 932(11)	9 998(16)
C(31)	4 305(14)	928(9)	7 205(12)
C(32)	4 405(13)	522(9)	6 814(12)
C(33)	4 597(14)	563(10)	6 207(14)
C(34)	4 669(15)	1 020(11)	5 910(14)
C(35)	4 613(15)	1 433(11)	6 286(14)
C(36)	4 461(14)	1 414(6)	6 972(12)
C(321)	4 305(14)	−7(10)	7 054(14)
C(322)	5 112(14)	−276(10)	7 273(14)
C(323)	3 624(15)	−273(10)	6 452(15)
C(341)	4 903(17)	1 067(11)	5 204(15)
C(342)	4 325(17)	822(11)	4 530(16)
C(343)	5 732(18)	889(12)	5 408(18)
C(361)	4 437(7)	1 889(2)	7 387(11)
C(362)	5 301(11)	2 071(12)	7 847(16)
C(363)	3 914(17)	2 279(10)	6 835(16)
C(41)	8 858(14)	190(9)	12 576(14)
C(42)	9 384(19)	497(12)	13 167(17)
C(43)	10 230(19)	386(11)	13 443(16)
C(44)	10 494(17)	13(12)	13 192(15)
C(45)	9 996(16)	−282(11)	12 621(15)
C(46)	9 162(15)	−180(9)	12 286(13)
C(421)	9 044(21)	941(14)	13 514(20)
C(422)	9 493(26)	1 393(16)	13 495(24)
C(423)	9 223(25)	854(16)	14 256(23)
C(441)	11 438(20)	−124(13)	13 492(18)
C(442)	11 883(19)	279(12)	13 342(18)
C(443)	11 712(22)	−281(14)	14 287(22)
C(461)	8 609(18)	−538(11)	11 624(16)
C(462)	8 753(18)	−1 050(11)	11 892(17)
C(463)	8 750(17)	−467(11)	10 941(16)
C(51)	3 255(14)	1 603(9)	10 586(13)
C(52)	2 800(16)	1 424(9)	10 915(14)
C(53)	1 984(15)	1 597(9)	10 613(13)
C(54)	1 682(17)	1 920(11)	10 015(16)
C(55)	2 231(16)	2 057(9)	9 705(14)
C(56)	3 042(15)	1 911(9)	9 971(14)
C(521)	3 041(18)	1 069(6)	11 569(13)
C(522)	2 574(16)	595(6)	11 384(17)
C(523)	2 933(19)	1 252(12)	12 263(17)
C(541)	820(16)	2 099(13)	9 605(21)
C(542)	146(22)	1 724(14)	9 361(22)
C(543)	631(25)	2 440(15)	10 134(23)
C(561)	3 574(14)	2 084(7)	9 608(11)
C(562)	3 196(16)	2 081(11)	8 773(13)
C(563)	3 873(16)	2 578(4)	9 889(15)

Table 4. Selected bond lengths (Å) and angles (°) for complex (**1**)

Ag(a)–Ag(a′)	3.339(6)	Ag(b)–Ag(d)	2.978(4)
Ag(c)–Ag(c″)	3.367(6)	Ag(a)–S(a)	2.374(9)
Ag(a)–S(d′)	2.343(9)	Ag(b)–S(a)	2.360(12)
Ag(b)–S(b″)	2.381(11)	Ag(c)–S(c)	2.338(10)
Ag(c)–S(b)	2.320(9)	Ag(d)–S(c)	2.387(12)
Ag(d)–S(d)	2.367(11)	S(a)–C(1)	1.779(28)
S(b)–C(21)	1.806(27)	S(c)–C(41)	1.805(34)
S(d)–C(61)	1.836(27)		
S(a)–Ag(a)–Ag(a′)	109.5(3)	S(a)–Ag(a)–S(d′)	170.6(4)
Ag(a′)–Ag(a)–S(d′)	79.6(3)	Ag(d)–Ag(b)–S(a)	117.6(2)
Ag(d)–Ag(b)–S(b″)	70.6(2)	S(a)–Ag(b)–S(b″)	171.7(3)
Ag(c″)–Ag(c)–S(b)	85.9(3)	Ag(b)–Ag(d)–S(c)	116.7(3)
Ag(b)–Ag(d)–S(d)	72.2(3)	S(c)–Ag(d)–S(d)	171.0(4)
Ag(a)–S(a)–Ag(b)	116.3(4)	Ag(a)–S(a)–C(1)	101.3(8)
Ag(b)–S(a)–C(1)	106.3(12)	Ag(b″)–S(b)–C(21)	103.8(13)
Ag(b″)–S(b)–Ag(c)	107.5(4)	C(21)–S(b)–Ag(c)	110.9(11)
Ag(c)–S(c)–Ag(d)	120.8(5)	Ag(c)–S(c)–C(41)	105.8(11)
Ag(d)–S(c)–C(41)	106.0(14)	Ag(d)–S(d)–C(61)	104.6(12)
Ag(d)–S(d)–Ag(a′)	107.0(3)	C(61)–S(d)–Ag(a′)	107.6(9)

polymeric complexes. That might account for the fact that $[\{Ag(SR)\}_n]$ complexes are usually insoluble when the group R is small enough. This result is consistent with our studies on silver complexes with (triorganosilyl)methanethiolate ligands[1] and aromatic dithiocarboxylate ligands.[18]

Compared with the copper complex with the same ligand $[\{Cu(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_8]$,[5] the structure of which consists of a discrete twisted 16-membered ring of alternating copper and sulphur atoms, the silver complex (**1**) forms a polymer. This indicates once more that silver complexes usually have a higher degree of aggregation than copper complexes with the same ligand.[3,4,18]

Structure of Complex (**2**).—The molecular structure of complex (**2**) consists of eight coplanar silver atoms linked through arenethiolate (RS) and aryl trithiocarbonate ($RSCS_2$) ligands. Figures 3 and 4 give the molecular configuration and atom labelling scheme respectively. There are a number of interesting features to this unusual structure.

The eight silver atoms are all in one plane, the maximum deviation from the plane (1) being only 0.01 Å. There is a symmetry centre at the midpoint of Ag(2)–Ag(2′). The structure

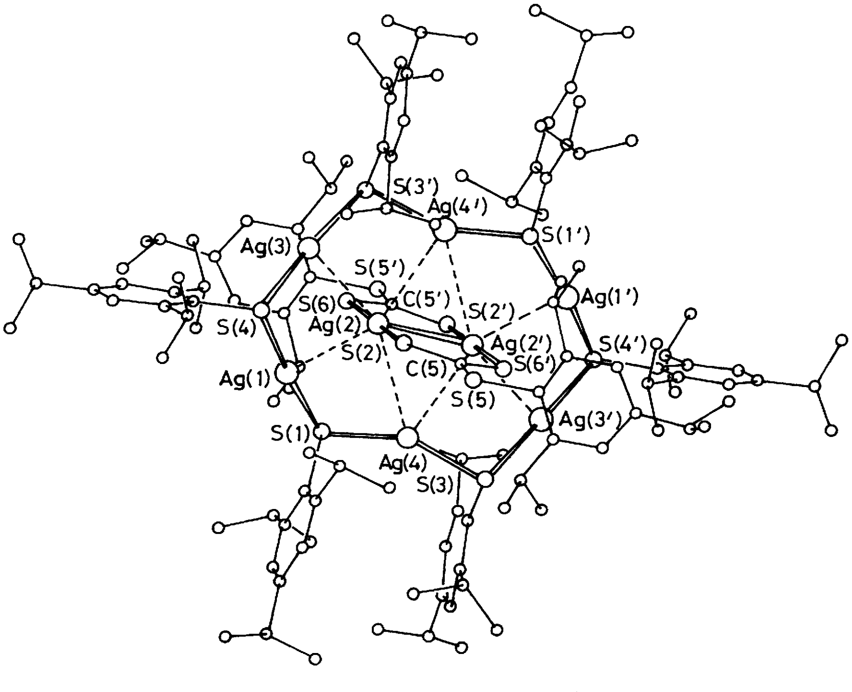


Figure 3. Perspective view of the structure of $[\{Ag(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]$

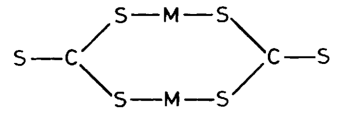
Table 5. Selected bond lengths (Å) and angles (°) for complex (**2**)

Ag(2)–Ag(1)	2.899(3)	Ag(2)–Ag(3)	3.047(3)
Ag(2)–Ag(4)	3.350(3)	Ag(2)–Ag(2′)	2.782(3)
Ag(2)–Ag(4′)	3.113(4)	Ag(1)–S(1)	2.354(7)
Ag(1)–S(4)	2.352(8)	Ag(2)–S(2)	2.381(9)
Ag(2)–S(6′)	2.387(8)	Ag(3)–S(4)	2.360(9)
Ag(3)–S(3′)	2.372(8)	Ag(4)–S(1)	2.376(7)
Ag(4)–S(3)	2.368(3)	S(1)–C(11)	1.831(28)
S(3)–C(31)	1.763(29)	S(4)–C(41)	1.824(25)
S(5)–C(51)	1.807(23)	S(2)–C(5)	1.706(23)
S(5)–C(5)	1.720(28)	S(6)–C(5)	1.648(21)
Ag(1)–Ag(2)–Ag(3)	73.0(1)	Ag(1)–Ag(2)–Ag(4)	80.4(1)
Ag(3)–Ag(2)–Ag(4)	153.4(1)	Ag(1)–Ag(2)–Ag(2′)	140.6(1)
Ag(3)–Ag(2)–Ag(2′)	146.4(2)	Ag(4)–Ag(2)–Ag(2′)	60.2(1)
Ag(1)–Ag(2)–Ag(4′)	150.4(1)	Ag(3)–Ag(2)–Ag(4′)	77.4(1)
Ag(4)–Ag(2)–Ag(4′)	129.2(1)	Ag(2′)–Ag(2)–Ag(4′)	69.0(1)
Ag(2)–Ag(4)–Ag(2′)	50.8(1)	S(2)–Ag(2)–Ag(2′)	91.2(2)
S(6)–Ag(2)–Ag(2′)	94.9(2)	S(1)–Ag(1)–S(4)	173.5(3)
S(2)–Ag(2)–S(6)	173.3(2)	S(4)–Ag(3)–S(3′)	172.1(3)
S(1)–Ag(4)–S(3)	156.0(3)	Ag(1)–S(1)–Ag(4)	117.7(4)
Ag(4)–S(3)–Ag(3′)	108.8(3)	Ag(1)–S(4)–Ag(3)	97.3(3)
Ag(2)–S(2)–C(5)	113.1(9)	C(5)–S(6)–Ag(2′)	110.5(10)
C(5)–S(5)–C(51)	106.9(11)	Ag(1)–S(1)–C(11)	105.3(8)
Ag(4)–S(1)–C(11)	100.0(8)	Ag(4)–S(3)–C(31)	99.0(8)
C(31)–S(3)–Ag(3′)	109.7(8)	Ag(1)–S(4)–C(41)	107.6(10)
Ag(3)–S(4)–C(41)	111.1(9)	S(2)–C(5)–S(5)	109.0(12)
S(2)–C(5)–S(6′)	130.0(17)	S(5)–C(5)–S(6′)	121.0(14)

can be divided into two parts: one consists of Ag(2) and Ag(2′) at the middle of the core, held together by two aryl trithiocarbonate ligands formed by insertion of CS_2 into Ag–S bonds. The second part is a 12-membered ring of alternating silver and sulphur atoms of the thiolate ligand around the core.

In the first part, Ag(2), Ag(2′), and the atoms of two CS_3 segments in aryl trithiocarbonate ligands are all in another plane [plane (2)]. This plane is approximately perpendicular to the plane (1) of eight silver atoms. The angle between the two planes is 94.0°. The distance between Ag(2) and Ag(2′) is only 2.782 Å, even shorter than Ag–Ag 2.886 Å in metallic silver.[15] This is a seldom occurrence in silver complexes.[19] The atoms Ag(2) and Ag(2′) are surrounded by six silver atoms doubly bridged by six sulphur atoms of the arenethiolate ligands. The distances between Ag(2) and surrounding silver atoms are all longer than the interatomic distance 2.886 Å in metallic silver and shorter than the van der Waals diameter of silver 3.40 Å.[16] Each Ag(2) and Ag(2′) atom interacts with five silver atoms in the same plane and is co-ordinated by two sulphur atoms, forming a somewhat distorted pentagonal bipyramid. Other silver atoms except Ag(4) and Ag(4′) are two-co-ordinated and have an approximately linear configuration, namely S–Ag–S(av.) is 173.0° (172.1—173.5°). However, S(1)–Ag(4)–S(3) is 156°, and bends towards the centre of the core. This indicates the stronger attraction due to the fact that Ag(4) and Ag(4′) interact with two core silver atoms. There is no secondary Ag···S interaction between the two parts of the structure. The Ag···Ag interactions make the structure stable.

Another interesting feature of complex (**2**) is that only a quarter of the Ag(SR) units of the complex (**1**) starting material react with CS_2, forming a novel type of structure involving insertion of CS_2 into M–S bonds.



The C–S distances of the resulting CS_3 group average 1.691 Å (1.648—1.720 Å), shorter than the length of a C–S single bond 1.812 Å and longer than that of a C=S double bond 1.607 Å,[20] and close to the mean C–S distance 1.702 Å observed in the CS_3 group of the complex $[Ag(S_2CSBu^t)(PPh_3)]$.[11]

The i.r. spectrum of complex (**2**), compared with that of (**1**), exhibits two extra peaks at 1 000s and 844m cm^{-1}, which are characteristic of the CS_3 group.

The crystalline compound (**1**) is colourless while (**2**) is pale

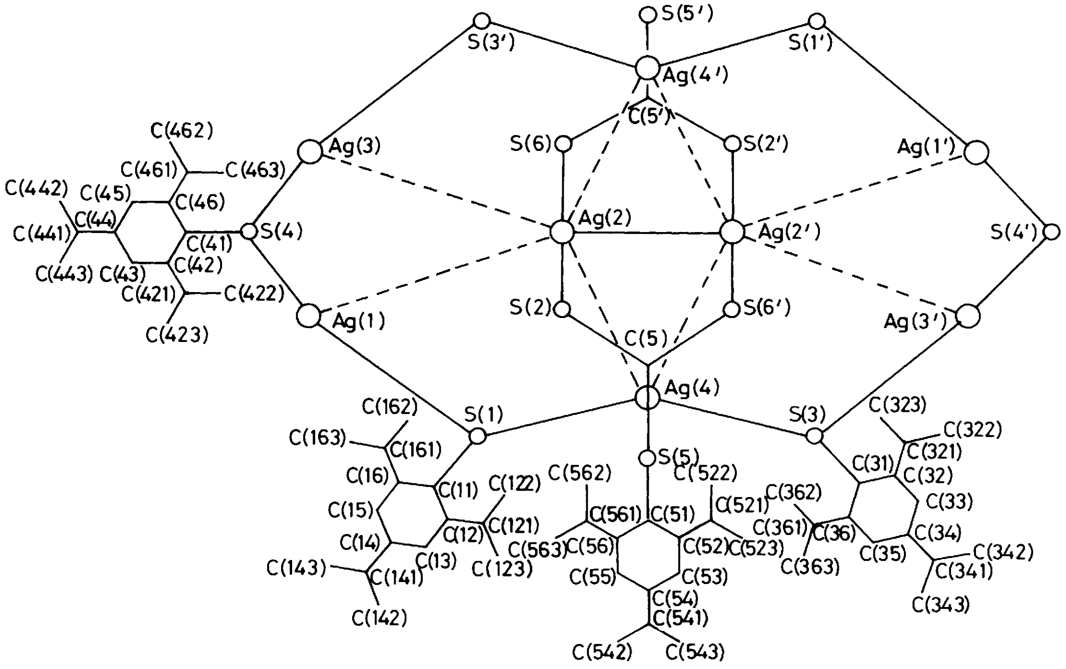


Figure 4. The atom labelling scheme for $[\{Ag(S_2CSC_6H_2Pr^i_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i_3\text{-}2,4,6)\}_6]$

yellow due to the CS_3 group. When heated to 100 °C, complex (**2**) lost CS_2 and turned into the white powder (**1**). The insertion of CS_2 into the Ag–S bond is reversible as we have observed in $[Ag(S_2CSBu^t)(PPh_3)_2]$.[11]

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