The Crystal and Molecular Structure of Silver(I) *N,N*-Diethyldithiocarbamate

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The crystal structure of silver(I) *N,N*-diethyldithiocarbamate was determined by the X-ray diffraction method. The crystals are monoclinic, with the space group $P2_1/c$, and with two hexameric molecules in a unit cell with dimensions of $a=10.90\pm0.02$, $b=24.72\pm0.01$, $c=11.51\pm0.02$ Å, and $\beta=125.8\pm0.1°$. The structure was solved by a heavy-atom method and was refined by block-diagonal least-squares methods to a final *R*-value of 0.029 for 2108 observed reflections. The structure consists of hexameric molecules, $[AgS_2CN(C_2H_5)_2]_6$. The hexameric structure was essentially consistent with Hesse's preliminary result (1960). The terminal silver atom in one molecule is bridged by a sulfur atom to that in the adjacent hexamer, forming a chain structure along the a axis. All the silver atoms are connected to five atoms (either 1Ag and 4S or 2Ag and 3S). The dithiocarbamate ligands are classified into three types: bidentate, intra-, and inter-molecule tetradentate.

The use of silver(I) *N,N*-diethyldithiocarbamate (Ag-EtDC) in the microdetermination of arsenic has been widely accepted in the last ten years,[1] and the mechanism of color development has been investigated in some detail.[2] The crystal and molecular structure of this interesting reagent was studied by Hesse. He reported that the molar ratio of metal and ligand contents was 1:1,[3] and that the six silver atoms of a hexameric molecule formed a doubly bent chain in the crystal,[4] although the detailed structure was left undetermined. Hitherto, the crystal structures of many other metal-EtDC complexes have also been studied; among them, the structure of Ag-PrDC[5] (silver dipropyldithiocarbamate) was reported by Hesse in detail.

Our precise determination of the crystal and molecular structure of Ag-EtDC was carried out in an attempt to reveal the relations between the arrangement of the silver atoms and the terminal alkyl group, and between the solubility and the molecular structure.

Experimental

Ag-EtDC (Dotite Arsemate of Dojindo Labs.) was recrystallized from pyridine. The crystals were light-yellow transparent prisms. The lattice parameters were determined using 15 reflections measured by a Syntex automated diffractometer ($P\bar{1}$) using Mo$K\alpha$ radiation monochromated with a graphite crystal (taken as 0.71069 Å). The density was measured by flotation in a mixed solution of methyl iodide and ethyl alcohol.

TABLE 1. THE CRYSTAL DATA

Silver (I) *N,N*-Diethyldithiocarbamate
Formula: $Ag_6[S_2CN(C_2H_5)_2]_6$
Crystal Class: Monoclinic prismatic
Space Group: $P2_1/c$
Cell Parameters:
$a=10.90\pm0.02$ Å
$b=24.72\pm0.01$ Å
$c=11.51\pm0.02$ Å
$\beta=125.8\pm0.1°$
Volume of Unit Cell: $V=2514.4\pm5.7$ Å^3
Density: $D_m=2.048$ g cm^{-3}
$D_x=2.082$ g cm^{-3}
Number of Formula per Unit Cell: $Z=2$
μ for Mo$K\alpha$: $\mu=31.3$ cm^{-1}

The crystal data are summarized in Table 1. A single crystal was ground by Bond's method[6] to make it a sphere with a diameter of 0.348 mm ($\mu r=0.545$ for Mo$K\alpha$ radiation); this sphere was then used for the intensity measurement. The intensity data were collected by the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min on a Syntex ($P\bar{1}$) four-circle diffractometer, using Mo$K\alpha$ radiation monochromated by a graphite crystal. The intensities were corrected for the Lorentz, polarization, and absorption effects. A total of 2108 observed reflections whose intensity was larger than three times their standard deviations was obtained within a range of $2\theta<40°$.

Structure Analysis

The positions of three unique silver atoms were deduced from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located by successive Fourier syntheses. Six cycles of block-diagonal least-squares refinement led an *R* value (defined as $\sum||F_o|-|F_c||/\sum|F_o|$) of 0.095 for the observed reflections. Subsequently, six further cycles of least-squares refinements with anisotropic thermal factors reduced the *R* value to 0.047. At this point, a difference Fourier synthesis was computed; all hydrogen atoms could be allocated with peak heights varying from 0.2 to 0.3 eÅ^{-3}. Introducing the hydrogen atoms with isotropic temperature factors brought the *R* value down to 0.032. Refinement was terminated when the shifts of the parameters for the non-hydrogen atoms were less than one-tenth of their estimated standard deviations. The final *R* value was 0.029. A final difference Fourier synthesis showed no significant features of the undulations, with ranged from −0.2 to 0.1 eÅ^{-3}. The atomic scattering factors for Ag^+, S, N, C, and H were taken from the International Tables for X-ray Crystallography.[7] The anomalous dispersion correction was not taken into account. In the least-squares procedure, the quantity minimized was $\sum w(k|F_o|-|F_c|)^2$, where *k* was a scale factor and $w=1$ for all the observed reflections. The final atomic coordinates and thermal parameters are given in Tables 2 and 3, along with their estimated standard deviations. The

TABLE 2. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS WITH THEIR STANDARD DEVIATIONS
(Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the least significant digits.)

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	0.2828(1)	0.0278(0)	0.3660(1)	126(1)	14(0)	137(1)	6(1)	188(2)	3(1)
Ag(2)	0.1421(1)	0.1065(0)	0.1442(1)	160(1)	20(0)	88(1)	24(1)	126(2)	−6(1)
Ag(3)	0.1100(1)	0.0110(0)	−0.0288(1)	110(1)	18(0)	103(1)	19(1)	139(2)	15(1)
S(1A)	0.1220(3)	0.0878(1)	0.3964(3)	130(4)	11(0)	125(4)	3(2)	193(7)	0(2)
S(1B)	0.2209(3)	0.1844(1)	0.3126(3)	156(4)	12(0)	93(3)	−6(2)	173(7)	−3(2)
S(2A)	0.4825(2)	0.0071(1)	0.3320(2)	70(3)	13(0)	68(3)	−2(2)	85(5)	5(2)
S(2B)	0.3165(3)	0.0826(1)	0.0757(3)	82(3)	18(1)	83(3)	10(2)	90(6)	24(2)
S(3A)	0.1420(3)	−0.0874(1)	0.0214(2)	116(4)	14(1)	75(3)	7(2)	131(6)	3(2)
S(3B)	0.1006(2)	−0.0609(1)	0.2534(2)	72(3)	11(0)	61(3)	1(2)	83(5)	−1(2)
N(1)	0.1496(9)	0.1876(3)	0.4957(8)	151(13)	13(2)	104(11)	21(7)	184(21)	0(7)
N(2)	0.6071(7)	0.0623(3)	0.2264(7)	85(11)	15(2)	78(10)	3(7)	105(18)	8(6)
N(3)	0.3225(8)	−0.1210(3)	0.2898(7)	87(11)	9(1)	80(10)	11(6)	49(18)	−5(6)
C(11)	0.1645(9)	0.1571(3)	0.4098(8)	53(12)	13(2)	52(11)	2(7)	35(19)	−2(7)
C(12)	0.0970(12)	0.1664(4)	0.5819(11)	198(20)	20(2)	151(17)	12(11)	262(36)	6(10)
C(13)	0.2233(14)	0.1579(5)	0.7353(13)	230(23)	25(3)	159(18)	−4(13)	260(36)	5(12)
C(14)	0.1767(12)	0.2464(4)	0.5039(11)	212(20)	9(2)	128(15)	33(10)	183(31)	−5(9)
C(15)	0.0309(17)	0.2744(5)	0.3923(16)	321(32)	17(3)	286(28)	22(15)	334(52)	−12(14)
C(21)	0.4815(9)	0.0516(3)	0.2156(8)	69(12)	12(2)	57(11)	−13(7)	71(20)	−11(7)
C(22)	0.6108(11)	0.0965(4)	0.1233(10)	126(16)	27(3)	111(14)	6(11)	176(27)	30(10)
C(23)	0.6406(18)	0.1554(5)	0.1665(16)	402(35)	20(3)	261(26)	−31(16)	478(54)	22(14)
C(24)	0.7560(10)	0.0388(4)	0.3401(10)	78(14)	22(2)	111(14)	−2(9)	111(24)	5(9)
C(25)	0.7857(14)	−0.0105(5)	0.2860(13)	233(23)	27(3)	195(21)	57(14)	305(39)	23(13)
C(31)	0.2012(9)	−0.0920(3)	0.1999(9)	76(13)	8(2)	68(11)	−18(7)	52(20)	−6(7)
C(32)	0.4211(11)	−0.1432(4)	0.2541(11)	133(16)	15(2)	175(17)	26(9)	212(29)	8(10)
C(33)	0.3875(17)	−0.1993(5)	0.2012(16)	324(30)	19(3)	329(29)	−23(15)	503(53)	−60(14)
C(34)	0.3775(11)	−0.1289(4)	0.4427(10)	141(17)	14(2)	87(13)	45(9)	68(25)	9(8)
C(35)	0.3160(17)	−0.1789(5)	0.4647(13)	357(32)	28(3)	152(19)	−32(16)	33(43)	4(13)

β_{ij} as given here are defined by: $T=\exp(-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23}))$

TABLE 3. COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR HYDROGEN ATOMS

Atom	x/a	y/b	z/c	B(Å^2)	Atom	x/a	y/b	z/c	B(Å^2)
H(11)	0.057(10)	0.129(4)	0.544(10)	2.69	H(26)	0.752(10)	0.027(4)	0.419(9)	2.63
H(12)	0.005(10)	0.184(4)	0.559(10)	2.89	H(27)	0.838(10)	0.068(5)	0.373(10)	3.05
H(13)	0.294(12)	0.133(4)	0.730(11)	4.85	H(28)	0.873(11)	−0.020(5)	0.352(11)	4.21
H(14)	0.160(9)	0.141(3)	0.768(8)	0.99	H(29)	0.720(11)	−0.033(5)	0.238(10)	4.07
H(15)	0.300(11)	0.186(4)	0.776(11)	4.46	H(210)	0.819(11)	0.000(5)	0.218(11)	5.13
H(16)	0.275(10)	0.255(4)	0.521(9)	2.33	H(31)	0.444(11)	−0.119(5)	0.233(10)	4.17
H(17)	0.197(11)	0.258(4)	0.594(11)	3.95	H(32)	0.447(13)	−0.158(6)	0.306(12)	7.26
H(18)	0.038(11)	0.300(4)	0.393(10)	4.09	H(33)	0.337(13)	−0.226(6)	0.205(12)	6.45
H(19)	−0.049(12)	0.263(4)	0.413(11)	5.46	H(34)	0.463(12)	−0.207(4)	0.173(11)	5.21
H(110)	−0.024(15)	0.259(5)	0.273(15)	8.98	H(35)	0.275(12)	−0.197(4)	0.108(11)	4.67
H(21)	0.518(12)	0.094(4)	0.038(11)	4.60	H(36)	0.341(8)	−0.102(3)	0.465(8)	0.87
H(22)	0.672(10)	0.081(4)	0.109(10)	3.23	H(37)	0.447(14)	−0.172(5)	0.479(13)	9.42
H(23)	0.562(13)	0.166(5)	0.177(12)	6.11	H(38)	0.380(12)	−0.182(5)	0.587(12)	5.64
H(24)	0.754(15)	0.143(5)	0.248(14)	9.46	H(39)	0.215(11)	−0.165(4)	0.419(10)	3.80
H(25)	0.659(11)	0.168(4)	0.104(11)	4.79	H(310)	0.347(12)	−0.201(4)	0.433(11)	5.25

calculated and observed structure factors are listed in Table 4.**

Results and Discussion

The Crystal Structure. The crystal structure of Ag-EtDC (except hydrogen atoms), projected along the c axis, is shown in Fig. 1. The crystal is composed of hexameric molecules, $[AgS_2CN(C_2H_5)_2]_6$. Each molecule has a center of symmetry. The molecular structure was essentially consistent with Hesse's preliminary result.[4] As is shown in Table 6, the distance between Ag(1) and S(2A″) in the neighboring molecule is 2.994 Å. The distance is longer than any other inner-hexameric bond, but it is nearly the same as that, 2.965 Å, of Hg–S in the β form of Hg-$(EtDC)_2$.[8] Since

** Table 4 is deposited as Document No. 7616 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

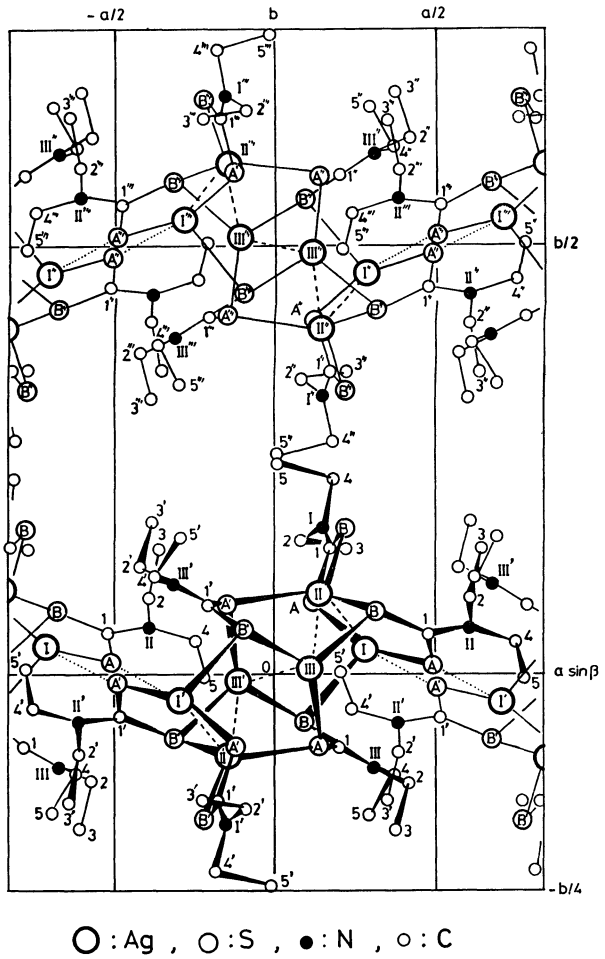

Fig. 1. The crystal structure of Ag-EtDC projected along the c axis.

the sum of the ionic radii of Ag and S (3.10 Å) is larger than the distance of Ag(1)–S(2A″) (2.994 Å), it is concluded that the terminal silver atom is bridged by a sulfur atom to the silver atom of the adjacent hexameric molecule and that the hexameric molecules form a chain polymer along the a axis. In the crystal, these chains sparsely contact with each other by van der Waals interaction. The inter-molecular distances are listed in Table 5; the limit of 0.3 Å is greater than the sum of the relevant van der Waals radii cited by Pauling.[9]

The Molecular Structure. A schematic drawing of the hexameric molecule of Ag-EtDC, which is a part of the chain polymer, is shown in Fig. 2. The hexamer contains three types of diethyldithiocarbamate ligands-1, 2, and 3. The atomic arrangement of the three types of ligands is shown in Fig. 3. The bond distances and angles are listed in Tables 6 and 7.

In the case of hexamers of univalent metal carbamates,[5,12,13] the geometrical arrangement of the metal atoms is usually octahedral, as is shown in Table 8. However, in the Ag-EtDC hexamer, the metal atoms do not form an octahedron, but instead form a doubly bent chain, as may be seen in Fig. 2. The silver-silver distances, Ag(1)–Ag(2), Ag(2)–Ag(3), and Ag(3)–Ag(3′) (2.841, 2.974, and 2.890 Å respectively), are similar to that of the metallic Ag–Ag bond (2.889 Å at

Table 5. Van der Waals contacts between molecules (Å)

Ag(1)···Ag(1′)	4.091(1)	S(1A)···H(26′)	3.31(9)
Ag(1)···C(24′)	4.000(13)	S(1A)···H(27)	2.99(13)
Ag(1)···C(34′)	3.906(10)	S(1A)···H(28′)	3.31(13)
Ag(2)···C(14″)	4.083(11)	S(1B)···H(37′)	2.96(11)
Ag(2)···C(15″)	3.798(15)	S(1B)···H(17″)	2.78(13)
Ag(3)···C(25′)	3.742(19)	S(2A)···H(36′)	3.07(7)
		S(3A)···H(22′)	3.15(14)
S(2A)···S(2A′)	3.674(4)	S(3B)···H(210)	3.24(13)
S(1A)···C(24)	3.845(12)	S(3B)···H(26′)	3.22(10)
S(1A)···C(25′)	3.703(15)	C(13)···H(29′)	3.12(10)
S(1B)···C(14″)	3.711(14)	C(13)···H(34′)	3.18(13)
S(1B)···C(34′)	3.814(10)	C(23)···H(38′)	3.04(16)
S(2A)···C(34′)	3.671(10)	C(25)···H(13′)	3.13(11)
S(3B)···C(25)	3.872(18)	C(32)···H(13′)	3.02(15)
		C(33)···H(38″)	3.20(12)
C(13)···C(25′)	3.648(18)	C(35)···H(110‴)	3.12(12)
C(15)···C(35‴)	3.784(16)	H(11)···H(27)	2.52(15)
C(21)···C(34′)	3.795(14)	H(13)···H(29′)	2.52(11)
		H(13)···H(31′)	2.66(19)
Ag(1)···H(26′)	3.02 (12)	H(15)···H(34′)	2.35(19)
Ag(2)···H(17″)	3.52 (10)	H(19)···H(33‴)	2.61(18)
Ag(2)···H(18″)	3.34 (11)	H(19)···H(35‴)	2.54(20)
Ag(3)···H(210′)	2.73 (15)	H(23)···H(38′)	2.43(20)

unprimed; (x, y, z), single-primed; $(a-x, -y, -z)$, double-primed; $(x, b/2-y, c/2+z)$, triple-primed; $(-x, b/2+y, c/2-z)$

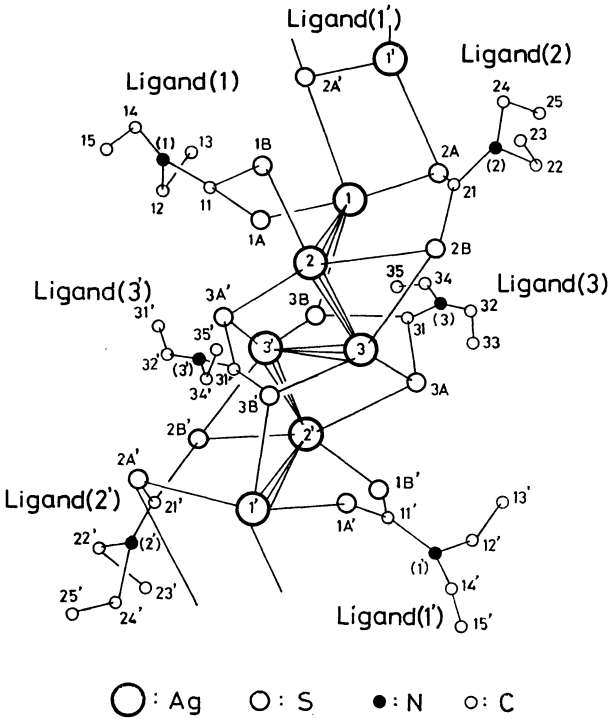

Fig. 2. Schematic drawing of Ag-EtDC hexamer.

20 °C);[14] they are slightly shorter than those of octahedrons, such as Ag-PrDC[5] and Ag-PrMC (silver dipropylmonothiocarbamate).[13] The Ag(1)···Ag(3), Ag(1)···Ag(3′), Ag(2)···Ag(3′), and Ag(1)···Ag(2′) distances

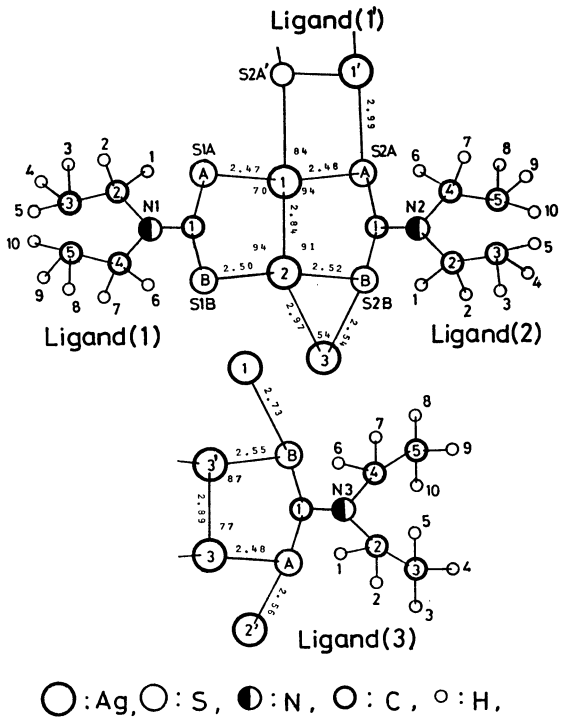

Fig. 3. Main bond distances (Å) and angles (°) of ligand 1, 2, and 3 in Ag-EtDC hexamer.

(3.786, 3.855, 3.673, and 5.928 Å respectively) are considerably longer than those of the octahedral conformation (3.20—3.28 Å). It seems that the unusual arrangement of the metal atoms causes the formation of a chain polymer and also a complicated coordination of the six ligands to the metal atoms, as will be discussed later. The thermal ellipsoids of atoms projected along the b axis are shown in Fig. 4. The atoms in the outer part of the molecule vibrate more than those of the inner part. The thermal vibrations of the terminal methyl carbons are the largest, as was expected.

The Coordination. All diethyldithiocarbamate

TABLE 6. BOND DISTANCES WITH THEIR e.s.d.'s (Å)

Ag(1)–Ag(2)	2.841(1)	Ag(2)–S(1B)	2.500(3)
Ag(2)–Ag(3)	2.974(1)	Ag(2)–S(2B)	2.519(4)
Ag(3)–Ag(3′)	2.890(2)	Ag(2)–S(3A′)	2.557(2)
Ag(1)–S(1A)	2.471(3)	Ag(3)–S(2B)	2.544(3)
Ag(1)–S(2A)	2.481(3)	Ag(3)–S(3A)	2.478(3)
Ag(1)–S(3B)	2.725(2)	Ag(3)–S(3B′)	2.554(2)
Ag(1)–S(2A″)	2.994(2)		

	Ligand 1	Ligand 2	Ligand 3
S(A)–C(1)	1.734(9)	1.727(10)	1.760(10)
S(B)–C(1)	1.710(2)	1.738(7)	1.721(12)
N( )–C(1)	1.340(14)	1.328(14)	1.315(9)
N( )–C(2)	1.501(19)	1.471(16)	1.465(18)
N( )–C(4)	1.476(12)	1.482(10)	1.503(14)
C(2)–C(3)	1.487(14)	1.521(17)	1.473(16)
C(4)–C(5)	1.504(16)	1.488(19)	1.497(20)

single-primed ($-x$, $-y$, $-z$); double-primed ($a-x$, $-y$, $-z$)

TABLE 7. BOND ANGLES WITH THEIR e.s.d.'s (degrees)

Ag(1)–Ag(2)–Ag(3)	81.23(3)	Ag(2)–Ag(1)–S(1A)	70.24(7)
Ag(2)–Ag(3)–Ag(3′)	77.57(4)	Ag(2)–Ag(1)–S(2A)	93.52(7)
		Ag(2)–Ag(1)–S(3B)	105.34(5)
Ag(2)–S(2B)–Ag(3)	71.94(9)	Ag(1)–Ag(2)–S(1B)	94.08(6)
Ag(2′)–S(3A)–Ag(3)	93.69(7)	Ag(1)–Ag(2)–S(2B)	90.62(6)
Ag(1)–S(3B)–Ag(3′)	93.76(8)	Ag(1)–Ag(2)–S(3A′)	108.90(7)
Ag(1)–S(2A)–Ag(1″)	96.25(5)	Ag(3)–Ag(2)–S(1B)	169.31(8)
		Ag(3)–Ag(2)–S(2B)	54.42(6)
S(1A)–Ag(1)–S(2A)	155.03(9)	Ag(3)–Ag(2)–S(3A′)	74.78(7)
S(1A)–Ag(1)–S(3B)	99.80(9)	Ag(2)–Ag(3)–S(2B)	53.64(8)
S(2A)–Ag(1)–S(3B)	102.83(9)	Ag(2)–Ag(3)–S(3A)	132.70(8)
S(1B)–Ag(2)–S(2B)	116.39(10)	Ag(2)–Ag(3)–S(3B′)	88.73(6)
S(1B)–Ag(2)–S(3A′)	115.90(10)	Ag(3′)–Ag(3)–S(2B)	130.30(9)
S(2B)–Ag(2)–S(3A′)	122.00(9)	Ag(3′)–Ag(3)–S(3A)	77.49(8)
S(2B)–Ag(3)–S(3A)	127.42(7)	Ag(3′)–Ag(3)–S(3B′)	87.03(7)
S(2B)–Ag(3)–S(3B′)	99.49(8)		
S(3A)–Ag(3)–S(3B′)	129.09(7)	Ag(2)–S(1B)–C(11)	95.74(30)
S(2A)–Ag(1)–S(2A″)	83.74(5)	Ag(2)–S(2B)–C(21)	112.00(42)
		Ag(2)–S(3A′)–C(31′)	108.35(34)
Ag(1)–S(1A)–C(11)	114.97(41)	Ag(3)–S(2B)–C(21)	106.31(31)
Ag(1)–S(2A)–C(21)	112.53(35)	Ag(3)–S(3A)–C(31)	103.96(29)
Ag(1)–S(3B)–C(31)	95.13(29)	Ag(3)–S(3B′)–C(31′)	103.72(28)

	Ligand 1	Ligand 2	Ligand 3		Ligand 1	Ligand 2	Ligand 3
S(A)–C(1)–S(B)	121.34(63)	122.16(63)	120.88(42)	C(1)–N( )–C(4)	120.92(95)	122.77(86)	121.33(98)
S(A)–C(1)–N( )	119.35(84)	121.04(54)	117.79(88)	C(2)–N( )–C(4)	116.08(99)	113.73(89)	115.13(71)
S(B)–C(1)–N( )	119.30(69)	116.76(71)	121.31(81)	N( )–C(2)–C(3)	112.80(109)	112.68(116)	115.02(122)
C(1)–N( )–C(2)	122.91(81)	123.43(66)	123.28(91)	N( )–C(4)–C(5)	109.02(82)	110.23(75)	113.21(78)

single-primed ($-x$, $-y$, $-z$); double-primed ($a-x$, $-y$, $-z$)

TABLE 8. BOND DISTANCES IN SOME COINAGE METALS DITHIOCARBAMATES AND MONOTHIOCARBAMATES

Compound	Metal arrangement	Bond distances (Å)					Ref.
		Metal–Metal	Metal–S	S–C	C–N	N–C(Et)	
$[Ag\text{-}EtDC]_6$	doubly bent chain	2.84—2.97	2.471—2.994	1.71—1.76	1.32—1.34	1.47—1.50	this work
$[Au\text{-}PrDC]_2$	pair	2.76	2.28	1.70	1.32	1.50	10
$[Cu\text{-}EtDC]_4$	tetrahedron	2.66—2.76	2.25—2.29	1.71	1.41	1.48	11
$[Cu\text{-}PrMC]_6$	octahedron	2.70—3.06	2.20—2.25	1.78	1.37	1.50	12
$[Ag\text{-}PrMC]_6$	octahedron	2.94—3.28	2.44—2.49				13
$[Ag\text{-}PrDC]_6$	octahedron	2.90—3.20	2.48—2.58	1.71	1.38	1.50	5

A comparison of bond distances in various Metal-EtDC complexes

Metal–EtDC	Metal–S	S–C	C–N	N–C(Et)	Ref.
$Ni\text{-}(EtDC)_2$	2.195—2.207	1.707	1.330	1.485	15
$[Cu(II)\text{-}(EtDC)_2]_2$	2.297—2.339	1.717	1.330	1.470	16
$[Zn\text{-}(EtDC)_2]_2$	2.331—2.815	1.727	1.325	1.473	17
$Co\text{-}(EtDC)_3$	2.258—2.260	1.704	1.319	1.496	18
$Na\text{-}EtDC\cdot 3H_2O$	—	1.726	1.344	1.417	19
$\alpha\ Hg_2\text{-}(EtDC)_4$	2.418—2.698	1.728	1.33	1.495	8
β Hg-$(EtDC)_2$	2.398—2.965	1.737	1.29	1.485	8
$[Ag\text{-}EtDC]_6$	2.471—2.994	1.732	1.328	1.483	this work

ligands are bidentate to the bivalent metals[8,15–17] and are bidentate[10] or tridentate[5,11–13] to the univalent metals. All six ligands in the hexamer, Cu(I)-PrMC,[12] Ag-PrDC,[5] and Ag-PrMC,[13] are tridentate. On the other hand, in the case of Ag-EtDC, there are three types of ligands in the hexameric molecules (i) Both sulfur atoms [S(1A), S(1B)] of the ligand-1 are monodentate (coordination number of the ligand-1, $p_1=2$). (ii) In the ligand-2, one [S(2A)] is mono- and the other [S(2B)] is bidentate. In addition, the sulfur atom [S(2A)] of the ligand-2 coordinates to another silver atom [Ag(1′)] of the adjacent hexameric molecule ($p_2=3+1$). (iii) The two sulfur atoms [S(3A), S(3B)] of the ligand-3 are bidentate ($p_3=4$), as is shown in Figs. 2 and 3. Consequently, each silver atom in a hexamer has five combined atoms (one silver and four sulfur atoms, or two silver and three sulfur atoms). It seems that the greater coordination number tends to give the shorter distance of C–N, and the longer distance of C–S, as is shown in Table 6. It may be considered that these three types of coordinations have influence on the different electron transfer from the nitrogen through carbon to the sulfur atoms.

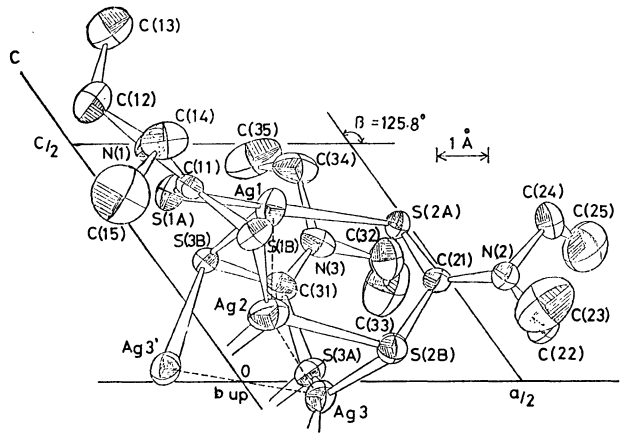

Fig. 4. Atomic arrangements of Ag-EtDC in an asymmetric unit (b axis projection).

The Ligand Structure. A comparison of the bond distances in various univalent metal-EtDC complexes is shown[8,15–19] in Table 8. The bond distances of S–C and C–N obtained in the present work are nearly the same as those of the other compounds. The bond distance of Ag–S in Ag-EtDC is, however, slightly longer than in the other Ag-complexes. This may be attributable to the doubly bent chain of the silver atom and to the formation of the chain polymer in the Ag-EtDC crystal. The distances between carbon and nitrogen show a double-bond character. All the ligands of the hexamer are planar except for the terminal alkyl groups, as is shown in Fig. 1. The terminal methyl groups of the ligands-1 and 2 take a *trans*-configuration, whereas those of the ligand-3 take a *cis*-configuration. This is the first example of an alkyldithiocarbamate complex in which the ligand molecules have both *trans*- and *cis*-type methyl groups. It may be caused by complicated packing among the hexameric molecules.

The C–H bond distances are around 0.96 Å, varying from 0.61 to 1.23 Å.

It seems that the solubility of a crystal depends on the polymerity of the molecule in the crystal. Whereas Ag-PrDC is a simple hexamer, in the case of Ag-EtDC the hexameric molecules form a chain polymer along the a axis. This agrees with the fact that Ag-PrDC is readily soluble, while Ag-EtDC is hardly soluble, in an organic solvent.

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