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Dimeric Iodo[bis(diphenylphosphinoethyl)sulphido]silver*

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Abstract. $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$, triclinic, $P\bar{1}$, $a = 11.796$ (2), $b = 10.108$ (2), $c = 12.332$ (3) Å, $\alpha = 96.45$ (2), $\beta = 102.95$ (3), $\gamma = 94.84$ (2)°, $V = 1415$ Å³, $Z = 1$, $D_{\text{calc}} = 1.62$, $D_{\text{obs}} = 1.61$ g cm⁻³. Bis(diphenylphosphinoethyl) sulphide, $[(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_4]_2\text{S}$, acts as a bidentate bridging ligand with the two P atoms coordinating different Ag atoms. The S to Ag distances imply no coordination between these atoms. The ligands are connected two-and-two by P–Ag–P bonds. The Ag atoms are also joined by a double I bridge. The crystal structure is thus built up by discrete dimeric molecules, $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$. A comparison is made between the structures of the isotopic compounds $(\text{AgXP}_2\text{SC}_{28}\text{H}_{28})_2$, X = I and Cl.

Introduction. Crystals of $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$ prepared according to Degischer (1968) were kindly provided by Professor G. Schwarzenbach, Zürich.

The compounds $(\text{AgXP}_2\text{SC}_{28}\text{H}_{28})_2$, X = Cl, Br and I, are isotopic (Degischer, 1968). Their cell dimensions and the structure of the Cl compound have been published (Aurivillius, Cassel & Fälth, 1974). A refinement of the cell parameters of the I complex revealed the values given above.

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A single crystal of the I compound of approximate dimensions $0.14 \times 0.15 \times 0.12$ mm along **a**, **b** and **c** respectively was used for the intensity measurements on a computer-controlled four-circle diffractometer (CAD-4) equipped with a graphite monochromator (Cu $K\alpha$ radiation). The ω - 2θ scan technique, with a scan interval of $(0.80 + 0.50 \tan \theta)^\circ$, was employed. At each end of the interval the background was measured for one fourth of the scan time. In the range $5^\circ < \theta < 70^\circ$, 5340 independent reflexions were recorded. Of these, 3659 were considered significantly above background with $I > 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics. The intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects [$\mu(\text{Cu } K\alpha) = 164.5$ cm⁻¹], as well as for fluctuations in two standard reflexions.

The positional and thermal parameters of the Cl compound were used as preliminary parameters for the calculations. Scattering factors for the neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964). Least-squares refinement with anisotropic thermal parameters for Ag, I, P and S reduced $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ to 0.052 and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ to 0.068. An anomalous dispersion correction of Ag and I (*International Tables for X-ray Crystallography*, 1968) reduced R to 0.048 and R_w to 0.065. A correction for secondary extinction was applied but

Table 1. Fractional coordinates and isotropic thermal parameters obtained in the final refinement of $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$

The coordinates for silver and iodine are multiplied by 10^5 , the others by 10^4 . Estimated standard deviations are given in parentheses.

	x	y	z	B (Å ²)		x	y	z	B (Å ²)
Ag	13351 (5)	4581 (6)	12536 (5)	[3.9]	C(12)	3268 (10)	3795 (11)	3930 (9)	6.2 (2)
I	10956 (4)	-9921 (6)	-9470 (4)	[3.9]	C(13)	1857 (7)	-838 (8)	3960 (7)	4.1 (1)
					C(14)	1565 (8)	390 (9)	4303 (7)	4.6 (2)
P(1)	2424 (2)	2713 (2)	1658 (2)	[3.6]	C(15)	1449 (9)	743 (11)	5400 (9)	6.0 (2)
P(2)	1921 (2)	-1238 (2)	2491 (1)	[3.7]	C(16)	1601 (10)	-209 (12)	6129 (10)	6.7 (2)
S	1250 (2)	4186 (3)	-1608 (2)	[4.2]	C(17)	1897 (10)	-1414 (12)	5829 (10)	6.8 (2)
C(1)	3987 (6)	2877 (8)	1697 (6)	3.7 (1)	C(18)	2040 (10)	-1806 (11)	4717 (9)	6.3 (2)
C(2)	4655 (8)	4130 (9)	1860 (7)	4.7 (2)	C(19)	3410 (7)	-1624 (8)	2526 (7)	4.1 (1)
C(3)	5842 (8)	4191 (9)	1845 (7)	4.8 (2)	C(20)	3669 (8)	-2134 (9)	1524 (7)	4.8 (2)
C(4)	6353 (8)	3059 (10)	1698 (8)	5.4 (2)	C(21)	4830 (9)	-2330 (11)	1505 (9)	6.0 (2)
C(5)	5711 (10)	1806 (11)	1554 (9)	6.2 (2)	C(22)	5703 (10)	-2020 (12)	2455 (10)	6.4 (2)
C(6)	4511 (8)	1724 (10)	1547 (8)	5.0 (2)	C(23)	5441 (12)	-1577 (14)	3455 (12)	8.1 (3)
C(7)	2313 (7)	3552 (8)	3018 (7)	4.1 (1)	C(24)	4302 (10)	-1286 (12)	3507 (10)	6.5 (2)
C(8)	1221 (8)	3761 (10)	3150 (8)	5.4 (2)	C(25)	1822 (7)	3875 (8)	665 (7)	4.1 (1)
C(9)	1068 (10)	4254 (12)	4224 (10)	6.8 (2)	C(26)	2124 (9)	3482 (11)	-439 (9)	6.0 (2)
C(10)	2036 (11)	4521 (12)	5119 (10)	7.0 (3)	C(27)	158 (9)	2776 (11)	-2297 (9)	6.0 (2)
C(11)	3105 (11)	4323 (12)	4990 (10)	7.1 (3)	C(28)	-1038 (7)	2893 (9)	-2029 (7)	4.4 (2)

did not improve the result. The quantity minimized was $\sum w_i(|F_o| - |F_c|)^2$, with $w_i^{-1} = \sigma^2(F_o) + a|F_o|^2 + b$. In the last cycle, with $a = 0.0014$ and $b = 1.0$, the average values of $w_i(|F_o| - |F_c|)^2$ were nearly constant in different $|F_o|$ and $\sin \theta$ intervals. A final difference map gave no peaks larger than $1 \text{ e } \text{Å}^{-3}$. No attempt to locate H atoms was made. The final positional and thermal parameters are given in Tables 1 and 2.* Selected interatomic distances and angles are presented in Table 3. All calculations were made on the UNIVAC 1108 computer in Lund.

Discussion. A stereo view of $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$ is given in Fig. 1. The angles in the distorted tetrahedra around Ag, P(1) and P(2) vary from 96.59 (3) to 119.87 (7), 103.2 (4) to 118.6 (3) and 103.2 (4) to 116.5 (3)°, respectively (Table 3). In the double halide bridge the

Ag–I–Ag angle of 83.41 (3)° may look small, but examples are known of bridges with M–X–M angles varying from 60 to 180° (Cotton & Wilkinson, 1972). For example, in $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$ (Stomberg, 1969), endless chains of AgI_4 tetrahedra sharing edges give double I bridges with Ag–I–Ag angles of 65.54 (5) and 81.31 (5)°. The small value of 65.54 (5)° is due to a Ni–I interaction, while the other unaffected I atom gives an Ag–I–Ag angle of 81.31° , in good agreement with the value 83.41 (3)° found in the present structure.

The major differences in distances and angles between the Cl and I compounds are illustrated in Fig. 2. In the Cl compound the two Ag atoms, together with the double bridging Cl atoms form a nearly square plane with Ag–Cl–Ag = 88.8 (1)° and Cl–Ag–Cl = 91.2 (1)°. In the I compound, the corresponding angles are Ag–I–Ag = 83.41 (3) and I–Ag–I = 96.59 (3)°. The Cl–Cl and I–I distances are 3.786 (8) and 4.323 (1) Å. The Ag–Ag distance is 3.708 (3) Å in the Cl and 3.852 (2) Å in the I compound. Thus the replacement of the Cl atoms by I in the double bridge causes not only a smaller Ag–X–Ag angle and a larger X–Ag–X angle, but also an elongation of the Ag–Ag distance

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30854 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Vibrational parameters for the silver, iodine, phosphorus and sulphur atoms of $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$*

The expression for the anisotropic thermal parameters is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. β_{ij} values of silver and iodine are multiplied by 10^5 , the others by 10^4 . Estimated standard deviations are given in parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1 (Å)	R_2 (Å)	R_3 (Å)
Ag	681 (5)	939 (14)	653 (4)	54 (4)	134 (3)	135 (4)	0.226	0.210	0.213
I	627 (4)	1438 (15)	569 (4)	290 (4)	168 (3)	161 (4)	0.279	0.184	0.206
P(1)	55 (1)	85 (2)	61 (1)	2 (1)	18 (1)	9 (1)	0.214	0.183	0.207
P(2)	54 (1)	91 (2)	61 (1)	7 (1)	10 (1)	17 (1)	0.223	0.189	0.201
S	81 (2)	138 (3)	86 (2)	–28 (2)	0 (1)	46 (2)	0.326	0.193	0.217

Table 3. *Selected interatomic distances (Å) and angles (°) in $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$*

Standard deviations are given in parentheses. For notation see Fig. 1.

Silver coordination		Phosphorus coordination				Sulphur coordination			
Ag–P(1)	2.461 (2)	P(1)–Ag	2.461 (2)	P(2)–Ag	2.461 (2)	S–C(26)	1.826 (11)	S–Ag	5.436 (3)
–P(2)	2.461 (2)	–C(1)	1.827 (8)	–C(13)	1.832 (8)	–C(27)	1.827 (11)		5.492 (3)
–I	2.879 (1)	–C(7)	1.830 (8)	–C(19)	1.823 (8)				
–I	2.911 (1)	–C(25)	1.859 (8)	–C(28)	1.853 (9)				

Carbon–carbon distances outside the phenyl rings

C(25)–C(26)	1.502 (13)	C(27)–C(28)	1.531 (13)
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Mean carbon–carbon distances of the phenyl rings

1.390 (5)	1.383 (6)	1.388 (6)	1.392 (6)
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Angles in the distorted tetrahedra around the silver and the phosphorus atoms

P(1)–Ag–P(2)	119.87 (7)	Ag–P(1)–C(7)	110.7 (3)	Ag–P(2)–C(13)	116.5 (3)
P(1)–Ag–I	103.32 (5)	Ag–P(1)–C(25)	113.8 (3)	Ag–P(2)–C(28)	113.9 (3)
P(1)–Ag–I	117.35 (5)	Ag–P(1)–C(1)	118.6 (3)	Ag–P(2)–C(19)	112.2 (3)
P(2)–Ag–I	102.49 (5)	C(1)–P(1)–C(25)	103.9 (4)	C(13)–P(2)–C(19)	105.8 (4)
P(2)–Ag–I	115.26 (5)	C(1)–P(1)–C(7)	105.2 (4)	C(13)–P(2)–C(28)	104.1 (4)
I–Ag–I	96.59 (3)	C(7)–P(1)–C(25)	103.2 (4)	C(28)–P(2)–C(19)	103.2 (4)

Angles between the methyl carbon atoms and the phosphorus or sulphur atom

P(1)–C(25)–C(26)	108.7 (6)	C(25)–C(26)–S	113.6 (7)	C(26)–S–C(27)	102.4 (5)
S–C(27)–C(28)	113.2 (7)	C(27)–C(28)–P(2)	107.7 (6)		

Angle in the bridge

Ag–I–Ag	83.41 (3)
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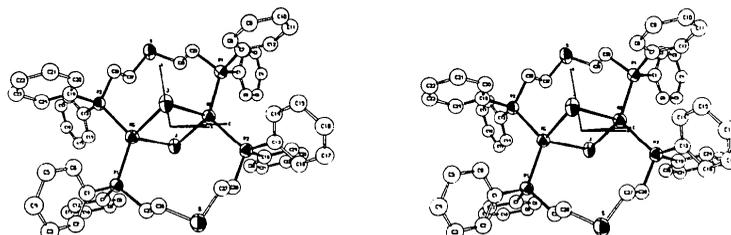


Fig. 1. A stereo view of the molecule $(\text{AgIP}_2\text{SC}_{28}\text{H}_{28})_2$. The hydrogen atoms are omitted.

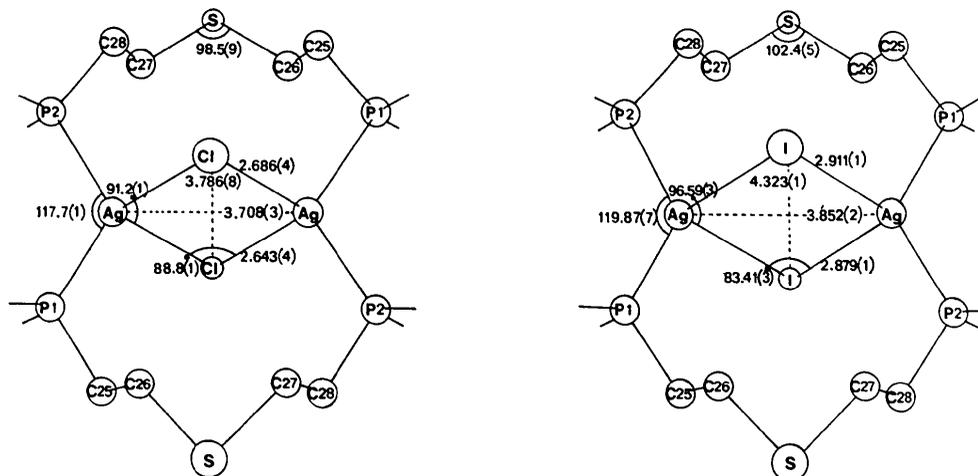


Fig. 2. Schematic drawings of $(\text{AgClIP}_2\text{SC}_{28}\text{H}_{28})_2$ and $(\text{AgIIP}_2\text{SC}_{28}\text{H}_{28})_2$. The phenyl groups and the methylene hydrogen atoms are omitted. Distances and angles which distinguish the two molecules from each other are denoted.

by 0.14 Å. This lengthening can be traced in other parts of the present molecule. The strain in the ligand is somewhat reduced at the S atom, as C(26)–S–C(27) (Fig. 2) increases from 98.5 (9) to 102.4 (5)°. This change makes C(26)–C(27) increase from 2.73 (3) Å in the Cl to 2.85 (2) Å in the I compound. The lengthening is not great enough, however, to compensate for the Ag–Ag elongation, and the P(1)–Ag–P(2) angle has thus increased from 117.7 (1) to 119.87 (7)°. The Ag–I distances of 2.911 (1) and 2.879 (1) Å agree well with the mean Ag–I distance of 2.87 Å given by Stomberg (1969). No further essential differences between the structures of the two compounds have been found.

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References

- AURIVILLIUS, K., CASSEL, A. & FÄLTH, L. (1974). *Chem. Script.* **5**, 9–12.
 COTTON, F. A. & WILKINSON, G. (1972). *Advanced Inorganic Chemistry*, 3rd ed., pp. 468–469. New York: John Wiley.
 DEGISCHER, G. (1968). Diss. 4163, E.T.H., Zürich, Switzerland.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., p. 214. Birmingham: Kynoch Press.
 STOMBERG, R. (1969). *Acta Chem. Scand.* **23**, 3498–3512.