

The Crystal Structure of $(\text{Pb}_{1-x}\text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$ ($x=0.88$)

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The crystal structure of $(\text{Pb}_{1-x}\text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$ ($x=0.88$) has been determined from three-dimensional intensity data. Four formula units of the compound are contained in the orthorhombic cell: $a=13.236$ (5), $b=23.630$ (16), $c=4.010$ (5) Å of the space group $Bbmm$. The structure was derived from Patterson, Fourier and difference syntheses, and was refined by a least-squares method. The final R for 725 independent reflexions is 7.4%. (Pb, Bi) and Bi have three nearest sulphur atoms and form trigonal pyramids. One of the two independent copper atoms is trigonally coordinated with three sulphur atoms. Two sulphur and two iodine atoms are arranged tetrahedrally around the second copper atom. The occupancy of this copper atom is 56%. The material has a layer structure, the layers being parallel to (010) and connected by weak Bi-I bonds.

Introduction

The compound $\text{PbBi}_2\text{Cu}_4\text{S}_5\text{I}_2$ has been synthesized by transport reactions. As only a few structures of bismuth sulphidides have been studied so far, the present investigation was undertaken to compare the coordination of iodine atoms around bismuth atoms in this material with iodine atoms in other bismuth sulphidides.

Experimental

The material was synthesized by chemical transport reaction from a mixture of appropriate proportion of PbS , Bi_2S_3 and Cu_2S . The mixed sulphides and 0.1 *N* HI solution were sealed in a silica glass tube and were kept at a temperature of 430°C with a gradient of about 15°C for 12 days. The crystals obtained were

needles of the length 0.1–0.7 mm, and of radius 0.005–0.05 mm.

Semi-quantitative electron microprobe analysis of the crystals revealed that the content of Pb, Bi and Cu varies for different crystals (Fig. 1) and that the chemical formula of these substances is expressed by $\text{Pb}_{1-x}\text{Bi}_{2+x}\text{Cu}_{4-x}\text{S}_5\text{I}_2$ ($0 \leq x \leq 1$).

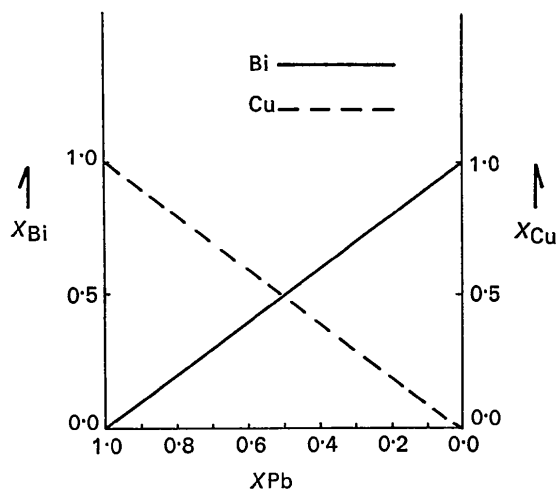


Fig. 1. Variations of the parameter x of Pb, Bi and Cu for different crystals.

Table 1. Crystal data

$(\text{Pb}_{1-x}\text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$
($x=0.88$: determined from the structure)
Orthorhombic, space group $Bbmm$
$a=13.236 \pm 0.005$, $b=23.630 \pm 0.016$, $c=4.010 \pm 0.005$ Å
($\lambda=1.5418$ Å)
$Z=4$
$D_{\text{calc}}=6.570$ g cm ⁻³
$\mu=1322$ cm ⁻¹ for Cu $K\alpha$ radiation

Table 2. Fractional coordinates, temperature factors in the expression $\exp[-(h^2\beta_{11}^2 + k^2\beta_{22}^2 + l^2\beta_{33}^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ and occupancies

Estimated standard deviations are in parentheses.

	Site	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	m
(Pb, Bi)	8(f)	0.1058 (2)	0.2407 (2)	$\frac{1}{2}$	0.00184 (9)	0.00105 (15)	0.0143 (9)	0.00002 (6)	0	0	$\frac{1}{2}$
Bi	8(f)	0.0546 (1)	0.0874 (1)	0	0.00324 (6)	0.00051 (2)	0.0169 (5)	0.00027 (3)	0	0	1
Cu(1)	8(f)	0.3671 (4)	0.1861 (2)	0	0.00336 (28)	0.00171 (11)	0.0167 (23)	0.00072 (15)	0	0	1
Cu(2)	8(f)	0.3159 (6)	0.1098 (4)	$\frac{1}{2}$	0.00189 (44)	0.00110 (16)	0.0685 (69)	0.00022 (22)	0	0	0.560 (13)
S(1)	4(c)	0.2393 (6)	$\frac{1}{2}$	0	0.00057 (40)	0.00170 (21)	0.0036 (39)	0	0	0	1
S(2)	8(f)	0.1593 (5)	0.1324 (3)	$\frac{1}{2}$	0.00216 (34)	0.00081 (11)	0.0126 (29)	0.00003 (16)	0	0	1
S(3)	8(f)	0.4487 (4)	0.1781 (3)	$\frac{1}{2}$	0.00134 (32)	0.00068 (11)	0.0148 (29)	0.00007 (15)	0	0	1
I	8(f)	0.3629 (1)	0.0406 (1)	0	0.00264 (11)	0.00073 (3)	0.0130 (9)	0.00010 (5)	0	0	1

The X-ray photographs of the crystals showed that the needles were always accompanied by small fragments of the same material, and that the *c* axis of the fragments was almost parallel to that of the hosts ($\approx 3^\circ$). The crystal used for the determination of the lattice parameters and the intensities was a needle 0.4 mm long and 0.012 mm diameter. Some extra reflexions from a fragment were observed in oscillation photographs ($\parallel c$) of this crystal. Since these reflexions were

very weak, their effect on the structure determination was not taken into account. The cell dimensions were measured on a single-crystal diffractometer. The observed diffraction symmetry, *mmmBb-*, permits *Bbmm* (No. 63), *Bbm2* (No. 40) and *Bb2,m* (No. 36) as possible space groups. The correct space group determined from the structure is *Bbmm*. The crystal data of the material are given in Table 1.

The intensities were measured from *hk0* to *hk4* on an automated Weissenberg diffractometer (STAD I-2 system from Stoe) using nickel-filtered copper radiation and were corrected for Lorentz and polarization effects. Absorption corrections for cylindrical shape were also applied. 74 of the 725 independent reflexions had $I < 2\sigma(I)$ and were designated unobservable reflexions.

Table 3. Observed and calculated structure factors

h	k	l	FO			FC			h	k	l	FO			FC			h	k	l	FO			FC			h	k	l	FO			FC		
			o	f	o	f	o	f				o	f	o	f	o	f				o	f	o	f	o	f				o	f	o	f	o	f
2	0	0	364	364	10	19	139	142	9	13	1	9	714	6	2	250	256	5	8	1	130	340	2	0	0	130	340	2	0	0					
4	0	0	620	636	12	19	276	284	18	13	1	227	221	6	2	291	289	5	8	1	260	79	4	0	0	260	79	4	0	0					
6	0	0	876	912	18	19	412	424	27	13	1	343	337	9	2	392	389	5	8	1	390	100	6	0	0	390	100	6	0	0					
8	0	0	1132	1184	24	19	548	568	36	13	1	451	445	12	2	500	497	5	8	1	490	130	8	0	0	490	130	8	0	0					
10	0	0	1388	1456	30	19	694	724	45	13	1	559	553	15	2	609	605	5	8	1	590	170	10	0	0	590	170	10	0	0					
12	0	0	1644	1728	36	19	840	880	54	13	1	667	661	18	2	718	713	5	8	1	690	210	12	0	0	690	210	12	0	0					
14	0	0	1900	1996	42	19	986	1036	63	13	1	775	769	21	2	827	821	5	8	1	790	250	14	0	0	790	250	14	0	0					
16	0	0	2156	2264	48	19	1132	1192	72	13	1	883	877	24	2	936	929	5	8	1	890	290	16	0	0	890	290	16	0	0					
18	0	0	2412	2532	54	19	1278	1348	81	13	1	991	985	27	2	1045	1037	5	8	1	990	330	18	0	0	990	330	18	0	0					
20	0	0	2668	2800	60	19	1424	1504	90	13	1	1100	1094	30	2	1154	1145	5	8	1	1090	370	20	0	0	1090	370	20	0	0					
22	0	0	2924	3068	66	19	1570	1660	99	13	1	1208	1202	33	2	1263	1253	5	8	1	1190	410	22	0	0	1190	410	22	0	0					
24	0	0	3180	3336	72	19	1716	1816	108	13	1	1316	1310	36	2	1378	1367	5	8	1	1290	450	24	0	0	1290	450	24	0	0					
26	0	0	3436	3604	78	19	1862	1972	117	13	1	1424	1418	39	2	1490	1479	5	8	1	1390	490	26	0	0	1390	490	26	0	0					
28	0	0	3692	3872	84	19	2008	2128	126	13	1	1532	1526	42	2	1606	1595	5	8	1	1490	530	28	0	0	1490	530	28	0	0					
30	0	0	3948	4140	90	19	2154	2284	135	13	1	1640	1634	45	2	1720	1709	5	8	1	1590	570	30	0	0	1590	570	30	0	0					
32	0	0	4204	4408	96	19	2300	2440	144	13	1	1748	1742	48	2	1846	1835	5	8	1	1690	610	32	0	0	1690	610	32	0	0					
34	0	0	4460	4676	102	19	2446	2596	153	13	1	1856	1850	51	2	1966	1955	5	8	1	1790	650	34	0	0	1790	650	34	0	0					
36	0	0	4716	4944	108	19	2592	2752	162	13	1	1964	1958	54	2	2076	2065	5	8	1	1890	690	36	0	0	1890	690	36	0	0					
38	0	0	4972	5212	114	19	2738	2908	171	13	1	2072	2066	57	2	2186	2175	5	8	1	1990	730	38	0	0	1990	730	38	0	0					
40	0	0	5228	5480	120	19	2884	3064	180	13	1	2180	2174	60	2	2296	2285	5	8	1	2090	770	40	0	0	2090	770	40	0	0					
42	0	0	5484	5748	126	19	3030	3220	189	13	1	2288	2282	63	2	2406	2395	5	8	1	2190	810	42	0	0	2190	810	42	0	0					
44	0	0	5740	6016	132	19	3176	3376	198	13	1	2396	2390	66	2	2516	2505	5	8	1	2290	850	44	0	0	2290	850	44	0	0					
46	0	0	6000	6280	138	19	3322	3532	207	13	1	2504	2498	69	2	2626	2615	5	8	1	2390	890	46	0	0	2390	890	46	0	0					
48	0	0	6260	6552	144	19	3468	3688	216	13	1	2612	2606	72	2	2736	2725	5	8	1	2490	930	48	0	0	2490	930	48	0	0					
50	0	0	6520	6816	150	19	3614	3836	225	13	1	2720	2714	75	2	2846	2835	5	8	1	2590	970	50	0	0	2590	970	50	0	0					
52	0	0	6780	7088	156	19	3760	3992	234	13	1	2828	2822	78	2	2956	2945	5	8	1	2690	1010	52	0	0	2690	1010	52	0	0					
54	0	0	7040	7360	162	19	3906	4156	243	13	1	2936	2930	81	2	3066	3055	5	8	1	2790	1050	54	0	0	2790	1050	54	0	0					
56	0	0	7300	7680	168	19	4052	4328	252	13	1	3044	3038	84	2	3176	3165	5	8	1	2890	1090	56	0	0	2890	1090	56	0	0					
58	0	0	7560	7960	174	19	4198	4500	261	13	1	3152	3146	87	2	3286	3275	5	8	1	2990	1130	58	0	0	2990	1130	58	0	0					
60	0	0	7820	8240	180	19	4344	4672	270	13	1	3260	3254	90	2	3396	3385	5	8	1	3090	1170	60	0	0	3090	1170	60	0	0					
62	0	0	8080	8512	186	19	4490	4844	279	13	1	3368	3362	93	2	3506	3495	5	8	1	3190	1210	62	0	0	3190	1210	62	0	0					
64	0	0	8340	8784	192	19	4636	5016	288	13	1	3476	3470	96	2	3616	3605	5	8	1	3290	1250	64	0	0	3290	1250	64	0	0					
66	0	0	8600	9080	198	19	4782	5188	297	13	1	3584	3578	99	2	3726	3715	5	8	1	3390	1290	66	0	0	3390	1290	66	0	0					
68	0	0	8860	9392	204	19	4928	5360	306	13	1	3692	3686	102	2	3836	3825	5	8	1	3490	1330	68	0	0	3490	1330	68	0	0					
70	0	0	9120	9616	210	19	5074	5532	315	13	1	3800	3794	105	2	3946	3935	5	8	1	3590	1370	70	0	0	3590	1370	70	0	0					
72	0	0	9380	9856	216	19	5220	5704	324	13	1	3908	3902	108	2	4056	4045	5	8	1	3690	1410	72	0	0	3690	1410	72	0	0					
74	0	0	9640	10104	222	19	5366	5876	333	13	1	4016	4010	111	2	4166	4155	5	8	1	3790	1450	74	0	0	3790	1450	74	0	0					
76	0	0	9900	10360	228	19	5512	6048	342	13	1	4124	4118	114	2	4276	4265	5	8	1	3890	1490	76	0	0	3890	1490	76	0	0					
78	0	0	10160	10624	234	19	5658	6220	351	13	1	4232	4226	117	2	4386	4375	5	8	1	3990	1530	78	0	0	3990	1530	78	0	0					
80	0	0	10420	10896	240	19	5804	6392	360	13	1	4340	4334	120	2	4496	4485	5	8	1	4090	1570	80	0	0	4090	1570	80	0	0					
82	0	0	10680	11176	246	19	5950	6564	369	13	1	4448	4442	123	2	4606	4595	5	8	1	4190	1610	82	0	0	4190	1610	82	0	0					
84	0	0	10940	11464	252	19	6096	6736	378	13	1	4556	4550	126	2	4716	4705	5	8	1	4290	1650	84	0	0	4290	1650	84	0	0					
86	0	0	11200	11752	258	19	6242	6908	387	13	1	4664	4658	129	2	4826	4815	5	8	1	4390	1690	86	0	0	4390	1690	86	0	0					
88	0	0	11460	12048	264	19	6388	7080	396	13	1	4772	4766	132	2	4936	4925	5	8	1	4490	1730	88	0	0	4490	1730	88	0	0					
90	0	0	11720	12344	270	19	6534	7252	405	13	1	4880	4874	135	2	5046	5035	5	8	1	4590	1770	90	0	0	4590	1770	90	0	0					
92	0	0	11980	12640	276	19	6680	7424	414	13	1	4988	4982	138	2	5156	5145	5	8	1	4690	1810	92	0	0	4690	1810	92	0	0					
94	0	0	12240	12936	282	19	6826	7596	423	13	1	5096	5090	141	2	5266	5255	5	8	1	4790	1850	94	0	0	4790	1850	94	0	0					
96	0	0	12500	13240	288	19	6972	7768	432	13	1	5204	5198	144	2	5376	5365	5	8	1	4890	1890	96	0	0	4890	1890	96	0	0					
98	0	0	12760	13544	294	19	7118	7940	441	13	1	5312																							

X-ray Crystallography (1968) were used. Corrections for anomalous dispersion were employed for all atoms using the values published by Cromer (1965). Individual weights, $1/\sigma^2(F_o)$, based on counting statistics were used during the course of the refinements. Five reflexions were excluded from the least-squares calculations because they seemed to be affected strongly by the parallel-grown crystal fragment.

The atomic positions, anisotropic temperature factors and the occupancies are listed in Table 2. The observed and the computed structure factors are presented in Table 3.

Discussion of the structure

The interatomic distances and angles computed by the program *ORFFE* (Busing, Martin & Levy, 1964) are given in Table 4. The structure is illustrated in Fig. 2.

The formula of this material is expressed as $(\text{Pb}_{1-x}, \text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$ and that of the crystal used for the structure determination corresponds to $x = 0.88$.

Since (Pb, Bi) is slightly shifted from a mirror plane, it is statistically distributed between two positions with a separation of 0.44 Å. Six sulphur atoms around (Pb, Bi) form a trigonal prism and two more bonds to sulphur atoms are arranged in the directions perpendic-

ular to the prism faces. This type of coordination is very common for lead atoms in many substances. However, the ratio of the occupancies, $m_{\text{Bi}}:m_{\text{Pb}}$, is 0.88:0.12 in the crystal studied and the space around (Pb, Bi) is probably too large for short Bi-S distances. This misfit of size should cause the statistical distribution of the (Pb, Bi). The distances between (Pb, Bi) and the three nearest sulphur atoms, being around 2.67 Å, coincide well with those values in Bi sulphosalts (Kupčik, 1972). The coordination of these three sulphur atoms to (Pb, Bi) is trigonal pyramidal.

Bi has three nearest S atoms at distances of 2.56 and 2.66 Å ($\times 2$), and forms with them a flat trigonal pyramid. One copper atom, Cu(2), and four iodine atoms also surround the bismuth atom at distances of 3.20, 3.42 ($\times 2$) and 3.79 Å ($\times 2$). An idealized drawing of the coordinations around Bi is illustrated in Fig. 3 together with those of bismuth atoms in $\text{Bi}(\text{Bi}_2\text{S}_3)_2\text{I}_3$ (Miehe & Kupčik, 1971) and BiSI (Haase-Wessel, 1973).

There are two independent copper atoms in the structure. Cu(1) is in nearly trigonal planar coordination with S and the mean Cu-S distance is 2.28 Å. This atom is not, however, on the triangle formed by the three sulphur atoms. The displacement of Cu(1) from the plane is about 0.4 Å and the sum of the three S-Cu-S angles is 350.7°. Cu(2) is in a tetrahedron, formed by two sulphur and two iodine atoms, with an occupancy 0.56. The mean Cu-S distance is 2.26 Å. The Cu-I distance, 2.66 Å, coincides with the published Cu-I distance of fourfold coordination (2.62 Å, *International Tables for X-ray Crystallography*, 1968) Table 5 lists some typical short Cu-Cu distances for comparison. The shortest distance between two copper atoms is 2.78 Å in this compound.

The structure of $(\text{Pb}_{1-x}, \text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$ consists of sheets parallel to (010). These layers are connected to each other by weak Bi-I bonds (3.79 Å).

Table 4. *Interatomic distances and angles*

Estimated standard deviations are in parentheses.

Superscript			
None			
i	$-\frac{1}{2} + x$	y	$\frac{1}{2} - z$
ii	$\frac{1}{2} - x$	$-y$	$\frac{1}{2} + z$
iii	x	y	$-z$
iv	$-\frac{1}{2} + x$	y	$-\frac{1}{2} - z$
v	x	$\frac{1}{2} - y$	z
vi	$-\frac{1}{2} + x$	$\frac{1}{2} - y$	$\frac{1}{2} - z$
vii	x	y	$1 + z$

Table 4 (cont.)

Distances (Å)		Angles (°)	
(Pb, Bi)-S(2)	2.655 (9)	S(2)-(Pb, Bi)-S(1)	84.5 (2)
(Pb, Bi)-S(1)	2.682 (6)	S(1)-(Pb, Bi)-S(1 ^{vi})	96.8 (3)
(Pb, Bi)-S(2 ^v)	3.083 (9)	S(2)-(Pb, Bi)-S(3 ⁱ)	74.5 (2)
(Pb, Bi)-S(3 ⁱ)	3.244 (6)	S(3 ⁱ)-(Pb, Bi) ⁱⁱⁱ -S(3 ^{iv})	76.4 (2)
(Pb, Bi)-Cu(1 ⁱ)	3.412 (6)	S(1)-(Pb, Bi)-S(3 ⁱ)	89.9 (2)
(Pb, Bi)-S(3 ^{vi})	3.468 (6)		
Bi-S(3 ⁱ)	2.563 (6)	S(3 ⁱ)-Bi-S(2)	87.1 (2)
Bi-S(2)	2.659 (5)	S(2)-Bi-S(2 ⁱⁱⁱ)	97.9 (2)
Bi-Cu(2 ⁱ)	3.204 (8)	S(3 ⁱ)-Bi-I ⁱ	82.2 (1)
Bi-I ⁱ	3.417 (3)	I ⁱ -Bi-I ^{iv}	71.9 (1)
Bi-I ⁱⁱ	3.789 (3)	S(2)-Bi-I ⁱ	94.2 (1)
Cu(1)-S(1)	2.267 (8)	S(1)-Cu(1)-S(3)	114.0 (2)
Cu(1)-S(3)	2.285 (4)	S(3)-Cu(1)-S(3 ⁱⁱⁱ)	122.7 (3)
Cu(1)-Cu(2)	2.781 (8)		
Cu(1)-Cu(1 ^v)	3.020 (11)	S(2)-Cu(2)-S(3)	123.0 (5)
		S(2)-Cu(2)-I	112.3 (3)
Cu(2)-S(2)	2.140 (11)	S(3)-Cu(2)-I	104.1 (2)
Cu(2)-S(3)	2.387 (11)	I-Cu(2)-I ⁱⁱ	97.8 (3)
Cu(2)-I	2.661 (7)		

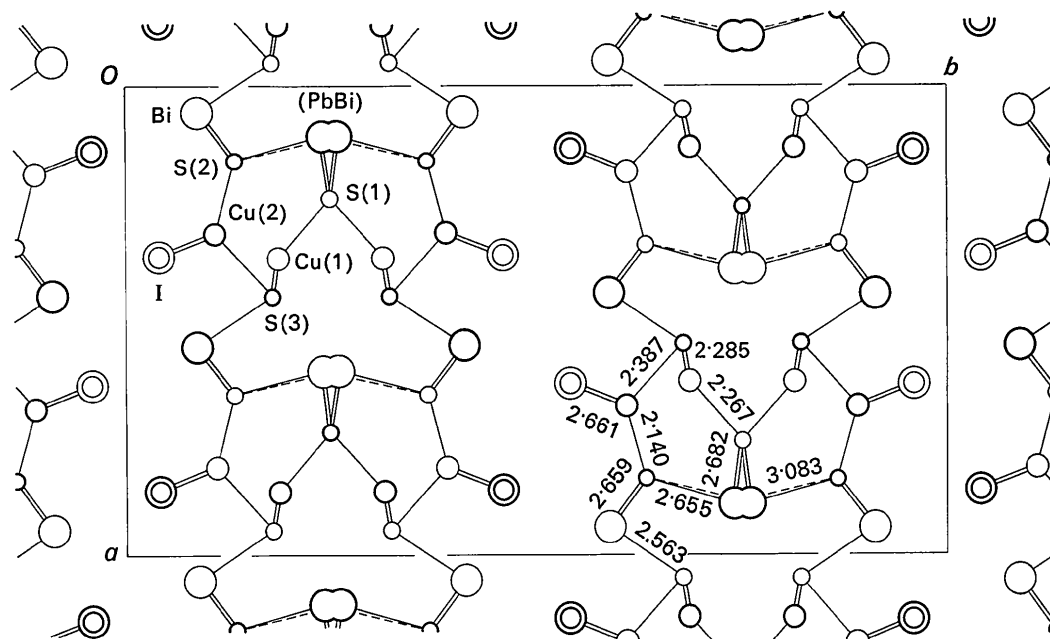


Fig. 2. Projection of the structure along the c axis. Thin circles indicate the atoms at $z=0$ and thick circles the atoms at $z=\frac{1}{2}$.

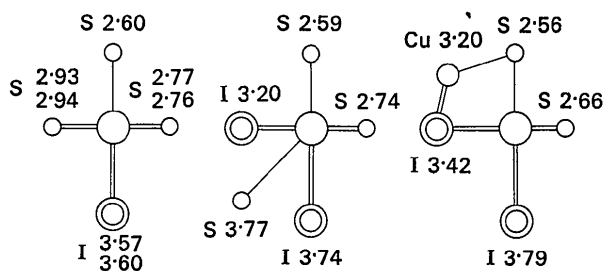


Fig. 3. Comparison of the coordinations around Bi in (a) $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{I}_3$, (b) BiSI and (c) $(\text{Pb}_{1-x}, \text{Bi}_x)\text{Bi}_2\text{Cu}_2\text{Cu}_{2-x}\text{S}_5\text{I}_2$. Distances from bismuth atoms to the corresponding atoms are indicated.

Table 5. Typical short Cu–Cu distances in some compounds

Cu (metal, at 20°C)	2.556 Å
$\text{C}_{12}\text{H}_{10}\text{N}_3\text{Cu}$ [diaminobenzene copper(I)] ^(a)	2.45
Cu_2S (chalcocite)	2.53*†
CuBi_5S_8 ^(b)	2.56
$\text{Bi}_2\text{Cu}_3\text{S}_4\text{Cl}_4$ ^(c)	2.79*
$\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ [dinuclear copper(II) acetate monohydrate] ^(d)	2.614

References: (a) Brown & Dunitz (1961). (b) Ohmasa & Nowacki (1973). (c) Lewis & Kupčik (1974). (d) Brown & Chidambaram (1973).

* The shortest distances are listed.

† This value was calculated from the data of Evans (1971).

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