

## Structure of Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Tetraiodogallate(III), (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>

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**Abstract.**  $2\text{C}_{10}\text{H}_8\text{S}_8^{1/2+}\cdot\text{GaI}_4^-$ ,  $M_r = 1346.6$ , triclinic,  $P\bar{1}$ ,  $a = 6.719$  (3),  $b = 14.950$  (7),  $c = 19.216$  (10) Å,  $\alpha = 81.27$  (4),  $\beta = 90.47$  (4),  $\gamma = 91.34$  (4)°,  $V = 1907$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.35$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70173$  Å,  $\mu = 4.79$  mm<sup>-1</sup>,  $F(000) = 1270$ ,  $T = 295$  K,  $R(F_o) = 0.048$  for 6694 observed reflections. The structure consists of layers of partially oxidized BEDT-TTF molecules within the  $ab$  plane, separated by isolated tetrahedral  $\text{GaI}_4^-$  anions along  $c$ . Short ( $< 3.60$  Å) S...S contacts connect the donor molecules in the  $a$  direction, resulting in one-dimensional chains within the donor layers. The  $\text{InI}_4^-$  salt is isostructural, with triclinic lattice parameters  $a = 6.715$  (1),  $b = 14.961$  (2),  $c = 19.440$  (3) Å,  $\alpha = 81.300$  (5),  $\beta = 90.356$  (5),  $\gamma = 91.117$  (4)°,  $V = 1930.2$  (5) Å<sup>3</sup>.  $(\text{BEDT-TTF})_2\text{GaI}_4$  is a semiconductor, with  $\sigma(300\text{ K}) \approx 10^{-5}$  ( $\Omega\text{ cm}$ )<sup>-1</sup>, and  $E_g \approx 0.07$  eV.

**Introduction.** Charge-transfer salts of BEDT-TTF with simple inorganic anions have been found with a wide variety of electrical conduction properties. Among them are superconductors, metals, semiconductors and insulators. For a recent review, see Williams *et al.* (1987). It has been suggested that large polarizable anions can facilitate the electron-phonon coupling necessary for superconductivity. Linear triatomic anions with I and Br atoms at the periphery, such as  $\text{I}_3^-$ ,  $\text{IBr}_2^-$  and  $\text{AuI}_2^-$ , indeed form superconducting salts with BEDT-TTF, with transition temperatures  $T_c$  of 1.5 K [at ambient pressure (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984); 8 K under applied pressure (Laukhin, Kostyuchenko, Sushko, Shchegolev & Yagubskii, 1985; Murata, Tokumoto, Anzai, Bando, Saito, Kajimura & Ishiguro, 1985)], 2.8 K [at ambient pressure (Williams *et al.*, 1984)], and

5 K [at ambient pressure (Wang *et al.*, 1985)], respectively. The use of tetrahedral iodo- and bromo-metallates as counter-ions with BEDT-TTF is still largely unexplored. Only  $(\text{BEDT-TTF})_2\text{InBr}_4$  (Beno, Cox, Williams & Kwak, 1984) and  $(\text{BEDT-TTF})_2(\text{I}_3)(\text{Tl}_4)$  (Beno *et al.*, 1987), both semiconductors, have been reported to date.

**Experimental.** Crystals of  $(\text{BEDT-TTF})_2\text{GaI}_4$  prepared by electrocrystallization (Pt electrodes,  $0.1\ \mu\text{A cm}^{-2}$ , 295 K) of 1.4 mM BEDT-TTF and 16.8 mM  $[\text{N}(n\text{-C}_4\text{H}_9)_4]\text{GaI}_4$  [precipitated from  $\text{N}(n\text{-C}_4\text{H}_9)_4\text{I}$  and  $\text{GaI}_3$  in absolute ethanol] in 1,1,2-trichloroethane. Black irregular plates  $0.36 \times 0.30 \times 0.14$  mm. Nicolet P3/F automated four-circle diffractometer. Unit-cell dimensions determined from a least-squares refinement of the setting angles of 25 reflections ( $24 < 2\theta < 29^\circ$ ). Intensity data collected using the  $\theta/2\theta$  scan technique ( $2.1\text{--}2.5^\circ$  width) with variable scan rates of 2 to  $12^\circ\text{ min}^{-1}$  to  $(\sin\theta)/\lambda = 0.650\ \text{\AA}^{-1}$  ( $2\theta < 55^\circ$ ;  $h = 0$  to 8,  $k = -19$  to 19,  $l = -24$  to 24). Three standard reflections, measured at interval of 96 reflections, small (3%) variations. Data corrected for Lorentz and polarization factors, and absorption effects using a Gaussian integration procedure;  $T_{\min} = 0.248$ ,  $T_{\max} = 0.520$ . 9888 reflections collected,  $(0kl)$  data and standards averaged to 8827 unique reflections,  $R_{\text{int}}(F_o) = 0.014$ ,  $R_{\text{int}}(wF_o) = 0.014$ , 6694 with  $I > 2\sigma(I)$  used for refinement. Centrosymmetric space group indicated by intensity statistics, confirmed by successful structure solution and refinement. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) which provided positions for the Ga and I atoms. Structure completed using Fourier methods. Atomic scattering factors including anomalous contributions from *International Tables for X-ray Crystallography* (1974). All computations carried out with a modified version of the *UCLA Crystallographic Package* (Strouse, 1978, 1986). Full-matrix least-squares refinement, all atoms with anisotropic thermal parameters. H atoms not located. One scale factor and isotropic secondary-extinction parameter (Larson, 1967) refined, total number of variables 371.

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters for (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ in units of } \text{\AA}^2.$$

	x	y	z	$U_{eq} (\text{\AA}^2 \times 10^4)$
Ga	0.46460 (10)	0.24307 (5)	0.00140 (3)	434 (2)
I1	0.68375 (8)	0.31364 (4)	-0.10042 (3)	754 (2)
I2	0.68173 (8)	0.17268 (4)	0.10291 (3)	698 (2)
I3	0.23876 (8)	0.12143 (4)	-0.03761 (3)	792 (2)
I4	0.25433 (8)	0.36463 (4)	0.04166 (3)	810 (2)
S1	0.1058 (2)	0.07249 (11)	0.64255 (7)	423 (5)
S2	-0.3156 (2)	0.07286 (12)	0.60170 (8)	490 (5)
S3	0.2316 (2)	0.13384 (12)	0.48151 (8)	459 (5)
S4	-0.1885 (2)	0.13070 (12)	0.43860 (8)	465 (5)
S5	0.0336 (2)	0.03336 (14)	0.79488 (8)	580 (6)
S6	-0.4661 (2)	0.02405 (14)	0.74636 (9)	587 (6)
S7	0.3870 (2)	0.20278 (14)	0.34177 (9)	602 (7)
S8	-0.1139 (2)	0.19650 (13)	0.28832 (8)	536 (6)
C1	-0.0704 (8)	0.0886 (4)	0.5752 (3)	365 (18)
C2	-0.0142 (8)	0.1139 (4)	0.5065 (3)	383 (19)
C3	-0.0679 (8)	0.0482 (4)	0.7101 (3)	349 (18)
C4	-0.2610 (8)	0.0469 (4)	0.6911 (3)	385 (19)
C5	0.1779 (8)	0.1705 (4)	0.3926 (3)	364 (18)
C6	-0.0132 (8)	0.1696 (4)	0.3729 (3)	371 (18)
C7	-0.3649 (13)	0.0560 (8)	0.8257 (5)	1061 (44)
C8	-0.1790 (12)	0.0233 (9)	0.8507 (4)	1200 (52)
C9	0.1044 (12)	0.2055 (8)	0.2368 (4)	1124 (48)
C10	0.2829 (11)	0.2314 (8)	0.2567 (4)	984 (42)
S11	0.1369 (2)	0.44399 (11)	0.35224 (8)	451 (5)
S12	-0.2809 (2)	0.40630 (12)	0.38939 (8)	513 (6)
S13	0.2643 (2)	0.38898 (12)	0.51472 (8)	497 (6)
S14	-0.1550 (2)	0.35304 (12)	0.55241 (8)	481 (5)
S15	0.0654 (3)	0.48839 (14)	0.19988 (9)	595 (6)
S16	-0.4328 (3)	0.4467 (2)	0.24441 (10)	902 (10)
S17	0.4207 (3)	0.3356 (2)	0.65721 (10)	821 (9)
S18	-0.0809 (2)	0.29198 (12)	0.70299 (8)	513 (6)
C11	-0.0351 (8)	0.4109 (4)	0.4178 (3)	384 (19)
C12	0.0195 (8)	0.3882 (4)	0.4872 (3)	393 (19)
C13	-0.0367 (8)	0.4571 (4)	0.2835 (3)	386 (19)
C14	-0.2270 (9)	0.4406 (4)	0.3006 (3)	448 (21)
C15	0.2110 (9)	0.3478 (4)	0.6030 (3)	460 (21)
C16	0.0211 (8)	0.3312 (4)	0.6201 (3)	397 (19)
C17	-0.329 (2)	0.4654 (10)	0.1618 (5)	1434 (64)
C18	-0.1403 (14)	0.4743 (10)	0.1430 (4)	1423 (62)
C19	0.3214 (11)	0.2652 (5)	0.7331 (4)	674 (28)
C20	0.1352 (11)	0.2977 (6)	0.7598 (4)	681 (29)

$\sum w(|F_o| - |F_c|)^2$  minimized, where  $w = 1/\sigma^2(F_o)$  and  $\sigma(F_o) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}/(2F_o)$ , with the value of  $\sigma(F_o^2)$  based on counting statistics.  $\Delta/\sigma \leq 0.07$  in final least-squares cycle which resulted in  $R(F_o) = 0.048$ ,  $wR(F_o) = 0.047$  and  $S = 2.27$ . Largest peaks ( $1.8 \text{ e } \text{\AA}^{-3}$ ) on difference Fourier synthesis near Ga and I atoms. Electrical conductivity measured using direct-current four-probe technique.

**Discussion.** Final positional parameters and equivalent isotropic thermal parameters are presented in Table 1.\* Bond lengths, angles and intermolecular distances less than the van der Waals radii sums (Bondi, 1964) are given in Table 2. The atomic numbering and molecular conformations of the two inequivalent BEDT-TTF entities are shown in Fig. 1. The unit cell (see Fig. 2) contains stacks of four donor radical cations (formal charge  $+1/2$  per molecule) per unit cell along the **b**

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51010 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) and bond angles (°) in (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>

Ga-I3	2.5372 (14)	C5-C6	1.336 (7)
Ga-I4	2.5420 (14)	S11-C11	1.725 (6)
S2-C1	1.729 (5)	S12-C14	1.744 (6)
S3-C5	1.751 (5)	S14-C12	1.738 (6)
S5-C3	1.745 (6)	S15-C18	1.784 (9)
S6-C7	1.790 (8)	S17-C15	1.743 (6)
S8-C6	1.748 (5)	S18-C20	1.817 (7)
C3-C4	1.345 (7)	C15-C16	1.329 (8)
C9-C10	1.323 (11)	Ga-I1	2.541 (2)
S12-C11	1.739 (6)	S1-C3	1.745 (5)
S13-C15	1.751 (6)	S3-C2	1.730 (6)
S15-C13	1.746 (6)	S4-C6	1.758 (5)
S16-C14	1.743 (6)	S6-C4	1.742 (5)
S18-C16	1.751 (6)	S7-C10	1.768 (8)
C13-C14	1.330 (8)	C1-C2	1.370 (7)
C19-C20	1.476 (10)	C7-C8	1.406 (12)
Ga-I2	2.538 (2)	S11-C13	1.746 (6)
S1-C1	1.740 (5)	S13-C12	1.724 (6)
S2-C4	1.741 (6)	S14-C16	1.750 (6)
S4-C2	1.740 (6)	S16-C17	1.722 (9)
S5-C8	1.783 (8)	S17-C19	1.789 (8)
S7-C5	1.734 (5)	C11-C12	1.373 (8)
S8-C9	1.768 (8)	C17-C18	1.317 (12)
I3-Ga-I2	109.25 (5)	S7-C5-S3	113.8 (3)
I2-Ga-I1	109.51 (5)	S8-C6-S4	114.5 (3)
C1-S1-C3	95.1 (3)	C10-C9-S8	125.8 (7)
C2-S4-C6	94.9 (3)	C11-S12-C14	95.2 (3)
I3-Ga-I1	109.78 (5)	C13-S15-C18	102.8 (4)
I2-Ga-I4	109.31 (5)	C16-S18-C20	101.4 (3)
C1-S2-C4	95.3 (3)	S11-C11-S12	115.1 (3)
C3-S5-C8	103.8 (3)	S13-C12-S14	115.8 (3)
C5-S7-C10	102.1 (3)	S15-C13-S11	114.7 (3)
C2-C1-S1	121.0 (4)	S16-C14-S12	114.9 (3)
C1-C2-S4	121.6 (4)	S17-C15-S13	113.8 (3)
C4-C3-S5	128.3 (4)	S14-C16-S18	114.3 (3)
C3-C4-S6	127.2 (4)	C20-C19-S17	114.4 (5)
C6-C5-S3	117.3 (4)	I3-Ga-I4	109.53 (5)
C5-C6-S4	116.9 (4)	I1-Ga-I4	109.46 (5)
C7-C8-S5	121.3 (7)	C2-S3-C5	95.2 (3)
C11-S11-C13	95.4 (3)	C4-S6-C7	100.1 (3)
C12-S14-C16	94.8 (3)	C2-C1-S2	123.6 (4)
C15-S17-C19	100.9 (3)	C1-C2-S3	122.8 (4)
C12-C11-S12	122.7 (4)	C4-C3-S1	116.9 (4)
C11-C12-S14	121.6 (4)	C3-C4-S2	117.2 (4)
C14-C13-S11	117.1 (4)	C6-C5-S7	129.0 (4)
C13-C14-S12	117.2 (5)	C5-C6-S8	128.4 (4)
C16-C15-S13	117.4 (5)	C8-C7-S6	119.6 (7)
C15-C16-S18	128.6 (5)	C9-C10-S7	125.5 (7)
C17-C18-S15	125.8 (7)	C12-S13-C15	94.9 (3)
C6-S8-C9	100.8 (3)	C17-S16-C14	103.5 (4)
S2-C1-S1	115.4 (3)	C12-C11-S11	122.2 (4)
S3-C2-S4	115.5 (3)	C11-C12-S13	122.6 (4)
S1-C3-S5	114.7 (3)	C14-C13-S15	128.2 (5)
S2-C4-S6	115.5 (3)	C13-C14-S16	127.9 (5)
		C16-C15-S17	128.7 (5)
		C15-C16-S14	117.1 (4)
		C18-C17-S16	130.0 (8)
		C19-C20-S18	115.1 (5)

Intermolecular I...S and S...S distances less than 3.9 and 3.6 Å, respectively

I1-S15 <sup>i</sup>	3.654 (3)	S11-S16 <sup>ii</sup>	3.567 (3)
S1-S6 <sup>ii</sup>	3.514 (3)	S17-S18 <sup>ii</sup>	3.506 (3)
S7-S8 <sup>ii</sup>	3.523 (3)	I3-S5 <sup>iii</sup>	3.889 (3)
S15-S16 <sup>ii</sup>	3.518 (3)	S5-S6 <sup>ii</sup>	3.508 (3)
I2-S8 <sup>ii</sup>	3.871 (3)	S14-S17 <sup>iv</sup>	3.486 (3)
S4-S7 <sup>iv</sup>	3.494 (3)		

Symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $1+x, y, z$ ; (iii)  $x, y, -1+z$ ; (iv)  $-1+x, y, z$ .

direction, with a stacking sequence  $(\dots A \dots A' \dots B \dots B' \dots)_n$ , where  $A$  and  $B$  denote the two inequivalent donor molecules, and primes indicate inversion-related units. The long axis of the molecules lies approximately along the **c** direction, but the small tilt of the long axis with respect to the **bc** plane has opposite signs for the two molecules  $A$  and  $B$ , respectively. Interdonor

contacts along the stacking direction are longer than the S...S van der Waals radii sum of 3.60 Å (Bondi, 1964): the distances between parallel planes through the center of the donor molecules are 3.60 Å (molecules *B* and *B'*; individual S...S distances are longer than 3.77 Å), 3.678 Å (molecules *A* and *A'*; shortest S...S distance 3.674 Å\*), and 3.746 Å (molecules *A* and *B*; no individual S...S distance shorter than 3.80 Å). Shorter interstack S...S contacts (of order 3.50 Å) occur between translationally equivalent donor molecules along the *a* direction (see Table 2). In contrast to the superconducting  $\beta$ -(BEDT-TTF)<sub>2</sub>X salts (X<sup>-</sup> = linear triatomic anion), the topology of short interstack interactions is strictly one-dimensional, without the honeycomb-like cross-linking which causes those compounds to become two-dimensional conductors.

\* Slight deviations from planarity make this distance shorter than the interplanar spacing.

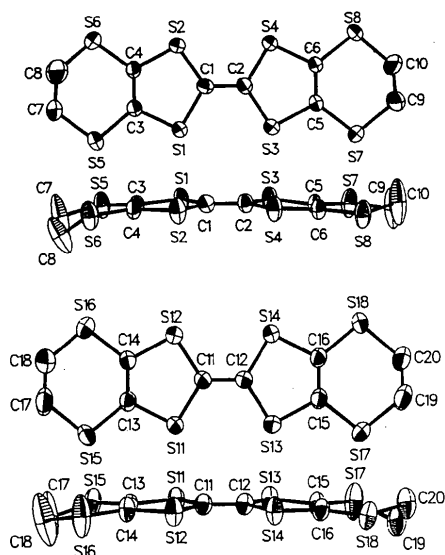


Fig. 1. Top and side views with atomic labeling of the crystallographically independent molecules *A* (top) and *B* (bottom) in (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>. Thermal ellipsoids are drawn at the 50% level.

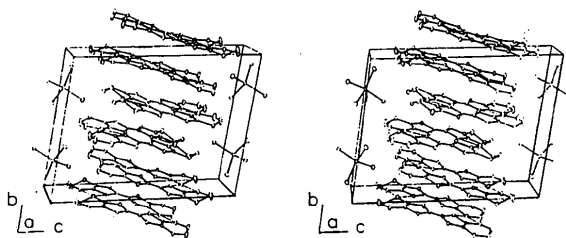


Fig. 2. Stereoview of the crystal packing in (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>. The donor molecule sequence from bottom to top is *A'*, *A*, *B*, *B'*, *A'*, *A*, where primes indicate molecules related to the corresponding reference molecule by inversion symmetry. S...S contacts less than 3.6 Å are drawn as thin lines.

After averaging chemically equivalent bond lengths and angles in the individual BEDT-TTF molecules, corresponding values in the two donors are equal within the accuracy of this structure determination. Furthermore, the distances within the tetrathiafulvalene portions are consistent with those found in BEDT-TTF molecules with formal charge +1/2 [see Table VII of Williams *et al.* (1987)]. It is therefore reasonable to assume that the total cationic charge of +1 per formula unit is divided approximately equally over the inequivalent donor molecules. The ethylene groups of both molecules exhibit considerable conformational disorder, as evidenced by the large anisotropic thermal parameters of the carbon atoms, the short C—C apparent bond lengths (average 1.40 Å between ellipsoid centers), and the large S—C—C angles (average 120.4°). Using Busing & Levy's (1964) procedure for averaging bond lengths over the thermal motion (assuming independently moving atoms), we find that the ethylene group C—C distances are 1.56 Å on the average, which is reasonable for a C—C single bond. Conformational disorder of this kind is frequently observed in BEDT-TTF salts and related compounds, and it is sometimes possible to resolve two conformations, or to freeze out one conformation upon cooling the crystals.

The GaI<sub>4</sub><sup>-</sup> anions separate the layers of stacks in the *c* direction. Anion-donor interactions therefore involve mainly the H atoms (not located in this structure determination) of the ethylene end groups. However, because of the slightly puckered donor stacking, one I atom (I1) approaches atom S15 within 3.65 Å, considerably less than the van der Waals radii S...I sum of 3.9 Å. The average Ga—I distance of 2.54 Å agrees very well with other structures containing the GaI<sub>4</sub><sup>-</sup> anion, e.g. Ga[GaI<sub>4</sub>], 2.56 (Gerlach, Höhle & Simon, 1982), and LiGaI<sub>4</sub>, 2.56 Å (Höhle, Hettich & Simon, 1987). The slight distortions from tetrahedral geometry are comparable to those found in the Li<sup>+</sup> and Ga<sup>+</sup> salts.

The structure of (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub> shares several features with that of the InBr<sub>4</sub><sup>-</sup> salt (Beno, Cox, Williams & Kwak, 1984). Common structural elements include the strictly side-by-side interdonor interactions, the stacking sequence (*A'*...*A*...*B*...*B'*...*A'*)<sub>n</sub>, and the overall arrangement of cations and anions in the unit cell. The major difference lies in the orientation of the normals to the BEDT-TTF molecular planes (essentially parallel to each other for the inequivalent donor cations in both structures) with respect to the stacking axis (*b* in the GaI<sub>4</sub><sup>-</sup>, *c* in the InBr<sub>4</sub><sup>-</sup> derivative). In the present structure the normals are essentially parallel to the stacking axis, whereas in the InBr<sub>4</sub><sup>-</sup> structure they form an angle of ca 30° with the *c* axis, leading to a markedly slipped stacking motif. Both salts are semiconductors with activation energies of the same order of magnitude [0.07 eV for (BEDT-TTF)<sub>2</sub>GaI<sub>4</sub>, 0.15 eV for (BEDT-TTF)<sub>2</sub>InBr<sub>4</sub>]. In light of the strictly transverse interdonor contacts and the

absence of a two-dimensional extended S...S network, it is no surprise that metallic conduction is not observed in these compounds.

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## Structure of Dibromo(1,10-phenanthroline)copper(II)

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**Abstract.**  $[\text{CuBr}_2(\text{C}_{12}\text{H}_8\text{N}_2)]_\infty$ ,  $M_r = 403.55$ , monoclinic,  $C_{21}$ ,  $a = 10.005$  (2),  $b = 6.526$  (2),  $c = 10.314$  (2) Å,  $\beta = 117.52$  (1)°,  $V = 597.3$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.243$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 8.963$  mm<sup>-1</sup>,  $F(000) = 386$ ,  $T = 291$  K,  $R = 0.057$  for 746 unique observed reflections. The Cu atom displays a tetragonally elongated (4 + 2) coordination. The four in-plane bonds are to the two N atoms of the 1,10-phenanthroline molecule and to the *cis* Br atoms. The out-of-plane bonds are to the Br atoms of the Cu centres above and below, which form the chain. The

complex is polymeric in the crystal  $[\text{Cu}-\text{N}(1) = 2.033$  (8),  $\text{Cu}-\text{N}(2) = 2.048$  (8),  $\text{Cu}-\text{Br}(1) = 2.386$  (2),  $\text{Cu}-\text{Br}(2) = 2.410$  (1),  $\text{Cu}-\text{Br}(2^{\text{ii}}) = \text{Cu}-\text{Br}(2^{\text{i}}) = 3.286$  (1) Å].

**Introduction.** Polymeric copper(II) compounds are known to have doubly bridged chains and singly bridged chains (Hatfield, 1985). However, polymeric structures in which one halide ligand is bound to three adjacent Cu atoms while the others are terminal are rare. This kind of bridging geometry is known for