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

References

BENO, M. A., COX, D. D., WILLIAMS, J. M. & KWAK, J. F. (1984). *Acta Cryst.* C**40**, 1334–1337.

BENO, M. A., GEISER, U., KOSTKA, K. L., WANG, H. H., WEBB, K. S., FIRESTONE, M. A., CARLSON, K. D., NUÑEZ, L., WHANGBO, M.-H. & WILLIAMS, J. M. (1987). *Inorg. Chem.* **26**, 1912–1920.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

GERLACH, G., HÖNLE, W. & SIMON, A. (1982). *Z. Anorg. Allg. Chem.* **486**, 7–21.

HÖNLE, W., HETTICH, B. & SIMON, A. (1987). *Z. Naturforsch. Teil B*, **42**, 248–250.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

LAUKHIN, V. N., KOSTYUCHENKO, E. E., SUSHKO, YU. V., SHCHEGOLEV, I. F. & YAGUBSKII, E. B. (1985). *JETP Lett.* (English transl.), **41**, 81–84.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MURATA, K., TOKUMOTO, M., ANZAI, H., BANDO, H., SAITO, G., KAJIMURA, K. & ISHIGURO, T. J. (1985). *J. Phys. Soc. Jpn*, **54**, 1236–1237.

STROUSE, C. (1978, 1986). *UCLA Crystallographic Package.* Univ. of California, Los Angeles, USA.

WANG, H. H., BENO, M. A., GEISER, U., FIRESTONE, M. A., WEBB, K. S., NUÑEZ, L., CRABTREE, G. W., CARLSON, K. D., WILLIAMS, J. M., AZEVEDO, L. J., KWAK, J. F. & SCHIRBER, J. E. (1985). *Inorg. Chem.* **24**, 2465–2466.

WILLIAMS, J. M., WANG, H. H., BENO, M. A., EMGE, T. J., SOWA, L. M., COPPS, P. T., BEHROOZI, F., HALL, L. N., CARLSON, K. D. & CRABTREE, G. W. (1984). *Inorg. Chem.* **23**, 3839–3841.

WILLIAMS, J. M., WANG, H. H., EMGE, T. J., GEISER, U., BENO, M. A., LEUNG, P. C. W., CARLSON, K. D., THORN, R. J., SCHULTZ, A. J. & WHANGBO, M.-H. (1987). *Prog. Inorg. Chem.* **35**, 51–218.

YAGUBSKII, E. B., SHCHEGOLEV, I. F., LAUKHIN, V. N., KONONOVICH, P. A., KARTSOVNIK, M. W., ZVARYKINA, A. V. & BURAVOV, L. I. (1984). *JETP Lett.* (English transl.), **39**, 12–15.

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

BY M. T. GARLAND AND D. GRANDJEAN

Université de Rennes I, Laboratoire de Cristallochimie, UA au CNRS n° 254, Campus de Beaulieu, F-35042 Rennes CEDEX, France

E. SPODINE AND A. M. ATRIA

Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile

AND J. MANZUR

Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

Abstract. $[CuBr_2(C_{12}H_8N_2)]_\alpha$, $M_r = 403.55$, monoclinic, $C2_1$, $a = 10.005$ (2), $b = 6.526$ (2), $c = 10.314$ (2) Å, $\beta = 117.52$ (1)°, $V = 597.3$ (4) Å^3, $Z = 2$, $D_x = 2.243$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 8.963$ mm^{-1}, $F(000) = 386$, $T = 291$ 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 [Cu—N(1) = 2.033 (8), Cu—N(2) = 2.048 (8), Cu—Br(1) = 2.386 (2), Cu—Br(2) = 2.410 (1), Cu—Br(2^{ii}) = Cu—Br(2^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

dibromo[2-(2-aminoethyl)pyridine]copper(II) and dibromo(2-methyl-1,2-diaminopropane)copper(II) (Helis, Goodman, Wilson, Morgan & Hodgson, 1977) and for hydrazinium trichlorocuprate(II) (Brown, Donner, Hall, Wilson, Wilson, Hodgson & Hatfield, 1979).

We here report the synthesis and structural determination of dibromo(1,10-phenanthroline)copper(II), $[Cu(phen)Br_2]_\infty$, which has a similar ladder-like bridging geometry.

Experimental. The complex was prepared by addition of 1 mmol of anhydrous $CuBr_2$ to a solution containing 1 mmol of 1,10-phenanthroline in freshly distilled ethanol. The reaction mixture was refluxed, and a microcrystalline solid formed when the solution was cooled. The solid was recrystallized from hot dimethylacetamide.

Crystal dimensions $0.10 \times 0.08 \times 0.08$ mm; Nonius CAD-4 four-circle diffractometer, cell dimensions from 2θ values of 25 reflections, $4.46 \le \theta \le 13.37°$, integrated reflections collected up to $(\sin\theta)/\lambda \le 0.595$ Å^{-1}, ω–2θ scan technique, scan width $(1.0 + 0.35\tan\theta)°$, $0 \le h \le 11, 0 \le k \le 6, -12 \le l \le 10$; variable scan rate with max. scan time 60 s per reflection; no significant decline in intensities of three standard reflections; decay 2.8% during 15 h of irradiation; no absorption correction and no time-decay corrections applied; 1079 unique reflections after averaging ($R_{int} = 0.22$), 746 reflections with $F^2 > 3\sigma(F^2)$; structure solution by $MULTAN80$ (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) refined by full-matrix least squares based on F_o, weights based on counting statistics: $1/w = \sigma^2(F) = \frac{1}{4}\{[\sigma^2(I) + (0.05I)^2]/I\}$ (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); H atoms placed at idealized positions with fixed isotropic thermal parameters and not refined (4.5 Å^2); anisotropic thermal parameters for all other atoms, refinement converged to $R = 0.057$ and $wR = 0.069$; goodness of fit $S = 1.576$ for 104 refined parameters; largest shift over e.s.d. in the last cycle $= 0.01$; largest residual peak in final Fourier map 0.88 e Å^{-3} except for four peaks of 1.87, 1.26, 1.25 and 1.18 e Å^{-3} in the neighbourhood of Br atoms. All computer programs from the Enraf–Nonius *SDP* package (Frenz, 1978).

Discussion. Table 1 lists the fractional atomic coordinates of non-H atoms, Table 2 the bond lengths and angles.*

Table 1. *Fractional atomic coordinates and equivalent isotropic B* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

	x	y	z	B_{eq}
Br(1)	0.0954 (1)	0.250	0.7823 (1)	5.53 (4)
Br(2)	−0.1475 (1)	0.250	0.9339 (1)	3.76 (3)
Cu	0.1219 (1)	0.250	1.0244 (1)	3.49 (4)
N(1)	0.3526 (9)	0.250	1.1220 (9)	2.6 (2)
N(2)	0.163 (1)	0.250	1.2369 (9)	3.4 (2)
C(1)	0.417 (1)	0.250	1.268 (1)	2.2 (2)
C(2)	0.571 (1)	0.250	1.359 (1)	3.3 (3)
C(3)	0.661 (1)	0.250	1.290 (1)	4.5 (4)
C(4)	0.600 (1)	0.250	1.142 (1)	5.2 (4)
C(5)	0.443 (1)	0.250	1.060 (1)	3.4 (3)
C(6)	0.070 (1)	0.250	1.292 (1)	5.1 (4)
C(7)	0.116 (1)	0.250	1.442 (1)	5.1 (4)
C(8)	0.262 (1)	0.250	1.537 (1)	3.6 (3)
C(9)	0.372 (1)	0.250	1.484 (1)	2.6 (3)
C(10)	0.311 (1)	0.250	1.330 (1)	2.4 (2)
C(11)	0.529 (1)	0.250	1.569 (1)	3.0 (3)
C(12)	0.622 (1)	0.250	1.514 (1)	3.9 (3)

Table 2. *Intramolecular bond lengths* (Å) *and bond angles* (°) *and selected intermolecular bond lengths* (Å) *with e.s.d.'s in parentheses*

Cu–Cu^i	3.964 (2)	C(1)–C(10)	1.464 (13)
Cu–Br(2^i)	3.286 (2)	C(2)–C(3)	1.38 (2)
Cu–Br(1)	2.386 (2)	C(2)–C(12)	1.43 (2)
Cu–Br (2)	2.410 (1)	C(3)–C(4)	1.36 (2)
Cu–N(1)	2.048 (8)	C(4)–C(5)	1.40 (2)
Cu–N(2)	2.033 (8)	C(6)–C(7)	1.39 (2)
N(1)–C(1)	1.338 (12)	C(7)–C(8)	1.34 (2)
N(1)–C(5)	1.324 (13)	C(8)–C(9)	1.426 (15)
N(2)–C(6)	1.304 (14)	C(9)–C(10)	1.417 (13)
N(2)–C(10)	1.341 (13)	C(9)–C(11)	1.400 (14)
C(1)–C(2)	1.388 (14)	C(11)–C(12)	1.30 (2)

Br(2^i)–Cu–Br(2)	93.23 (3)	C(3)–C(2)–C(12)	126· (1)
Cu^i–Cu–Cu^{ii}	110.81 (5)	C(2)–C(3)–C(4)	121· (1)
Br(1)–Cu–Br(2)	91.79 (6)	C(3)–C(4)–C(5)	118· (1)
Br(1)–Cu–N(1)	94.0 (2)	N(1)–C(5)–C(4)	122· (1)
Br(1)–Cu–N(2)	175.9 (3)	N(2)–C(6)–C(7)	123· (1)
Br(2)–Cu–N(1)	174.3 (2)	C(6)–C(7)–C(8)	120· (1)
Br(2)–Cu–N(2)	93.0 (2)	C(7)–C(8)–C(9)	119.7 (9)
N(1)–Cu–N(2)	81.2 (3)	C(8)–C(9)–C(10)	115.0 (9)
C(1)–N(1)–C(5)	117.8 (9)	C(8)–C(9)–C(11)	126.7 (9)
C(6)–N(2)–C(10)	117.6 (9)	C(10)–C(9)–C(11)	118· (1)
N(1)–C(1)–C(2)	125· (1)	N(2)–C(10)–C(1)	117.8 (8)
N(1)–C(1)–C(10)	115.2 (8)	N(2)–C(10)–C(9)	124.2 (9)
C(2)–C(1)–C(10)	120.3 (9)	C(1)–C(10)–C(9)	118.1 (9)
C(1)–C(2)–C(3)	116· (1)	C(9)–C(11)–C(12)	124· (1)
C(1)–C(2)–C(12)	118· (1)	C(2)–C(12)–C(11)	122· (1)

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

The crystal can be described as consisting of chains with ladder-like geometry along the y axis, in which the monomeric units are linked by Cu–Br bonds (Fig. 1). The monomeric molecule is planar and lies perpendicular to the b axis at $y = 0.25$ and $y = 0.75$. This unit is repeated along two polymeric chains related by two dimeric entities Cu_2Br_2 forming the ladder.

The dihedral angle between the two planar units Cu–Br(2)–Cu^i–Br(2^i) and Cu–Br(2)–Cu^{ii}–Br(2^{ii}) is 11.8°.

One bromo ligand is bound to three adjacent Cu atoms, while the other is terminal. The coordination around each Cu atom is a tetragonally elongated (4 + 2) octahedron. The coordination polyhedron is defined by two N atoms from the 1,10-phenanthroline molecule and by four Br atoms, two of which link the monomeric unit. The structure of the monomer is illustrated in Fig. 2, which also shows the atomic numbering scheme [Cu—N(1) = 2·033 (8), Cu—N (2) = 2·048 (8),   Cu—Br (1) = 2·386 (2),   Cu—Br (2) = 2·410 (1), Cu—Br (2^i) = Cu—Br (2^{ii}) = 3·286 (2) Å].

The C—N bonds are comparable, but somewhat shorter than those found for the mixed copper(II) complexes   (1,10-phenanthroline)(salicylaldehydato)-copper(II) nitrate (Solans, Ruiz-Ramirez, Gasque & Briansó, 1987) and (1,10-phenanthroline)(salicylaldehydato)copper(II) perchlorate (Garland, Grandjean & Spodine, 1987). The C—N bonds of the 1,10-phenanthroline molecule are C(1)—N(1) = 1·338 (12), C(5)—N(1) = 1·324 (13),   C(6)—N(2) = 1·304 (14), C(10)—N(2) = 1·341 (13) Å.

The same bonds in the mixed-copper complexes range from 1·312 (5) to 1·351 (5) Å for the nitrate and from 1·327 (4) to 1·357 (4) for the perchlorate complex. The same is observed for the C—C bonds.

The long axial distances are Cu—Br(2^i) = 3·286 (1) Å. These out-of-plane distances are longer than the values found for dibromo[2-(2-aminomethyl)-pyridine]copper(II)   [Cu—Br(2^i) = 3·260 (6) Å] and for dibromo(2-methyl-1,2-diaminopropane)copper(II), [Cu—Br(2^i) = 3·109 (2) Å] (Helis et al., 1977).

The Cu—Cu^i separation in the chain is 3·964 (1) Å. This Cu—Cu^i distance is also longer than the value found for dibromo[2-(2-aminomethyl)pyridine]-copper(II) [Cu—Cu^i = 3·737 (6) Å] and for the dibromo(2-methyl-1,2-diaminopropane)copper(II) complex [Cu—Cu^i = 3·866 (2) Å] (Helis et al., 1977). The 2-(2-aminomethyl)pyridine complex has a very acute Cu—Br—Cu^i angle of 80·77 (4)°, while the (2-methyl-1,2-diaminopropane)copper(II) complex has a Cu—Br—Cu^i angle of 87·56 (3)°. This last value is similar to the one found for the present 1,10-phenanthroline complex [Cu—Br—Cu^i angle: 86·77 (3)°]. These bridging angles are comparable with the reported values for other copper(II) dimers and polymers, which range from 85·7 to 100·4° (Hatfield, 1985).
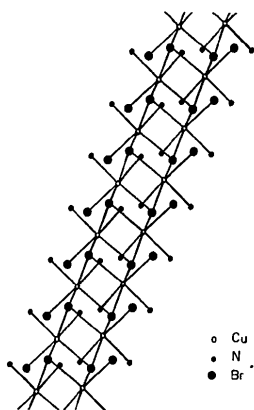
Fig. 1. A schematic view of the polymeric molecule.

Fig. 2. A perspective view of the monomeric molecule with H atoms excluded for clarity.

References

BROWN, D. B., DONNER, J. A., HALL, J. W., WILSON, S. R., WILSON, R. B., HODGSON, D. J. & HATFIELD, W. E. (1979). Inorg. Chem. 18, 2635–2641.

FRENZ, B. A. (1978). The Enraf–Nonius CAD-4 Structure Determination Package. A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. In Computing in Crystallography, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.

GARLAND, M. T., GRANDJEAN, D. & SPODINE, E. (1987). Acta Cryst. C43, 1910–1912.

HATFIELD, W. E. (1985). Magneto-Structural Correlations in Exchange Coupled Systems, edited by R. D. WILLETT et al., pp. 555–616. Dordrecht: Reidel.

HELIS, H. M., GOODMAN, W. H., WILSON, R. B., MORGAN, J. A. & HODGSON, D. J. (1977). Inorg. Chem. 16, 2412–2416.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

SOLANS, X., RUIZ-RAMIREZ, L., GASQUE, L. & BRIANSÓ, J. L. (1987). Acta Cryst. C43, 428–430.

STOUT, G. H. & JENSEN, L. H. (1968). X-ray Structure Determination. New York: Macmillan.