Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å^2)

H atoms were refined isotropically. For non-H atoms U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} matrix.

	x	y	z	U_{eq}
Ni	0	0	0	0.0403 (2)
S	0.3578 (1)	0	−0.6817 (2)	0.0579 (3)
C	0.2378 (2)	0	−0.4544 (5)	0.0379 (9)
N	0.1510 (2)	0	−0.3003 (5)	0.0529 (10)
N1	0.0835 (2)	0.1862 (3)	0.1599 (4)	0.0527 (8)
H1	0.123 (2)	0.256 (4)	0.054 (5)	0.10 (1)
H2	0.038 (2)	0.252 (4)	0.259 (5)	0.11 (1)
H3	0.128 (2)	0.152 (4)	0.238 (5)	0.10 (1)

Table 2. Interatomic distances (Å) and bond angles (°)

Ni—N	2.079 (3)	N—C	1.136 (3)
Ni—N1	2.103 (3)	C—S	1.615 (3)
N1—H1	0.86 (3)	N1—H3	0.80 (3)
N1—H2	0.85 (3)		
N—Ni—N1	88.7 (1)	Ni—N—C	175.8 (3)
N—C—S	177.6 (3)		

Fig. 1. Molecular structure with atom numbering.

kina, Dickareva & Jukhnov (1957), but refined structural data were necessary for a study of structure correlations (Jóna, Valach, Gažo, Fendrych & Šramko, 1983), for reactivity studies of solid nickel-(II) complexes (Jóna, Šramko & Gažo, 1975) and for comparison with related [Ni(NCS)$_2$L$_x$] complexes [L is an N-donor ligand such as ammonia, piperidine (pip) or pyridine (py)], e.g. [Ni(NCS)$_2$(pip)$_4$] (Koman, Handlovič, Ďurčanská & Gažo, 1983), [Ni(NCS)$_2$(py)$_4$] (Valach, Sivý & Koreň, 1984) and [Ni(NCS)$_2$(3-ethylpy)$_4$] (Ďurčanská, Jamnický, Koman, Wnęk & Głowiak, 1986), for $x = 4$.

References

Ďurčanská, E., Jamnický, M., Koman, M., Wnęk, I. & Głowiak, T. (1986). Acta Cryst. C42, 1157–1159.

Jóna, E., Šramko, T. & Gažo, J. (1975). J. Therm. Anal. 7, 551–560.

Jóna, E., Valach, F., Gažo, J., Fendrych, E. & Šramko, T. (1983). Koord. Khim. 9, 86–91.

Koman, M., Handlovič, M., Ďurčanská, E. & Gažo, J. (1983). Chem. Zvesti, 37, 741–749.

Nardelli, M. (1983). Comput. Chem. 7, 95–98.

Paraj-Kojic, M. A., Antzishkina, A. S., Dickareva, L. M. & Jukhnov, E. K. (1957). Acta Cryst. 10, 784–785.

Pavelčík, F. (1987). XP21. A computer program for Syntex P2$_1$ data reduction. J. A. Komenský Univ., Bratislava, Czechoslovakia.

Sheldrick, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

Valach, F., Sivý, P. & Koreň, B. (1984). Acta Cryst. C40, 957–959.

Structure of Bis(4-methylpyridine-N)copper(I) Bromide

By Marek J. Jedrzejas, Robert A. Martuch, Robert L. R. Towns,* Ronald J. Baker and Stan A. Duraj*

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

and Aloysius F. Hepp*

National Aeronautics and Space Administration, Lewis Research Center, Photovoltaic Branch, MS 302-1, Cleveland, OH 44135, USA

Abstract. Bromobis(4-methylpyridine)copper(I), [CuBr(C$_6$H$_7$N)$_2$], $M_r = 329.71$, triclinic, $P\bar{1}$, $a = 9.254$ (7), $b = 9.736$ (3), $c = 7.955$ (3) Å, $\alpha = 102.34$ (3), $\beta = 112.33$ (3), $\gamma = 95.09$ (4)°, $V = 636.2$ (6) Å^3, $Z = 2$, $D_m = 1.8$, $D_x = 1.721$ g cm^{-3}, λ(Mo $K\alpha$) = 0.710326 Å, $\mu = 50.84$ cm^{-1}, $F(000) =$

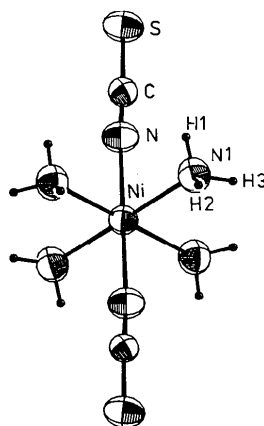* Authors to whom correspondence should be addressed.

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Br	0.2138 (1)	0.2461 (1)	0.2934 (2)	4.76 (3)
Cu	0.4557 (1)	0.3860 (1)	0.3107 (2)	4.49 (3)
N1B	0.4030 (8)	0.5347 (8)	0.179 (1)	3.7 (2)
N1A	0.6431 (8)	0.3045 (7)	0.4349 (9)	3.2 (2)
C2B	0.513 (1)	0.645 (1)	0.200 (1)	3.8 (2)
C2A	0.623 (1)	0.1745 (9)	0.466 (1)	3.7 (2)
C3A	0.753 (1)	0.1170 (9)	0.558 (1)	3.8 (2)
C3B	0.472 (1)	0.755 (1)	0.124 (1)	4.4 (3)
C4B	0.317 (1)	0.7624 (9)	0.024 (1)	3.5 (2)
C4AA	1.048 (1)	0.130 (1)	0.722 (1)	4.8 (3)
C4A	0.907 (1)	0.190 (1)	0.619 (1)	3.7 (2)
C4BB	0.272 (1)	0.890 (1)	−0.050 (1)	5.2 (3)
C5A	0.923 (1)	0.319 (1)	0.582 (1)	4.5 (3)
C5B	0.204 (1)	0.648 (1)	−0.002 (1)	3.7 (2)
C6A	0.790 (1)	0.373 (1)	0.488 (1)	4.3 (2)
C6B	0.251 (1)	0.541 (1)	0.078 (1)	4.4 (2)

Table 2. *Bond distances* (Å) *and angles* (°)

Br—Cu	2.455 (2)	C3A—C4A	1.387 (13)
Cu—N1B	1.956 (8)	C3B—C4B	1.367 (13)
Cu—N1A	1.973 (7)	C4B—C4BB	1.509 (15)
N1A—C2B	1.349 (12)	C4B—C5B	1.384 (13)
N1B—C6B	1.345 (12)	C4AA—C4A	1.493 (14)
N1A—C2A	1.353 (12)	C4AA—C5A	1.361 (15)
N1A—C6A	1.327 (12)	C5A—C6A	1.389 (14)
C2B—C3B	1.352 (15)	C5B—C6B	1.353 (15)
C2A—C3A	1.388 (13)		

Br—Cu—N1B	110.6 (2)	C2A—C3A—C4A	121.4 (9)
Br—Cu—N1A	110.4 (2)	C2B—C3—CB4	122.2 (9)
N1B—Cu—N1A	138.7 (3)	C3B—C4B—C4BB	121.8 (9)
Cu—N1B—C2B	122.8 (6)	C3B—C4B—C5B	116.2 (9)
Cu—N1B—C6B	120.9 (7)	C4BB—C4B—C5B	122.0 (8)
C2B—N1B—C6B	115.9 (8)	C3A—C4A—C5A	116.3 (8)
Cu—N1A—C2A	119.7 (6)	C4AA—C4A—C5A	122.3 (9)
Cu—N1A—C6A	121.8 (6)	C4A—C5A—C6A	121.0 (9)
C2A—N1A—C6A	118.5 (8)	C4B—C5B—C6B	119.4 (8)
N1B—C2B—C3B	121.9 (8)	N1A—C6A—C5A	122.2 (9)
N1A—C2A—C3A	120.5 (8)	N1B—C6B—C5B	124.3 (9)

328, $T = 293$ K, $R = 0.057$, $wR = 0.088$, for 1517 independent observed $[I > 3\sigma(I)]$ reflections. An interesting structural feature of this compound is a distance between Cu atoms of 3.101 (2) Å within the same unit cell compared to a distance of 6.124 (2) Å between Cu atoms of different unit cells.

Experimental. All reactions were performed in a dry box or on a vacuum line under inert atmosphere using standard Schlenk techniques. The title compound was prepared by the reaction of copper(I) bromide–dimethyl sulfide complex with 4-methylpyridine. A solution of copper(I) bromide–dimethyl sulfide [CuBr·S(CH$_3$)$_2$, 0.62 g, 3 mmol] in 25 ml of 4-methylpyridine was stirred for 3 d at 293 K under argon. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexanes produced colorless crystals of the title compound. Density was measured by flotation in dichloromethane and tetrabromoethane.

A single crystal of dimensions 0.37 × 0.31 × 0.23 mm was sealed inside a glass capillary. The determination of the unit cell was accomplished by collecting 25 reflections having $11.62 < \theta < 22.78°$, using an Enraf–Nonius CAD-4 automated diffrac-

tometer (Mo $K\alpha$ radiation and graphite monochromator). Intensity data were collected with ω–2θ scans at room temperature in the range $4 < 2\theta < 50°$. The scan rate varied from 2 to $10° \, \text{min}^{-1}$ with ω-scan width $(1.00 + 0.350\tan\theta)°$. Intensities were corrected for Lorentz–polarization effects and for absorption (North, Phillips & Mathews, 1968), the latter ranging from 0.795 to 1.000; a secondary-extinction correction of the form $F_c = F_c/(1 + gI_c)$ was also applied, with $g = 1.459 \times 10^{-6}$. Three standard reflections, monitored every 60 min, showed 2.6% variation in intensity; decay correction applied. A total of 2381 independent reflections were measured $(0 \le h \le 11, \ -11 \le k \le 11, \ -9 \le l \le 9)$, of which 1517 had $I > 3\sigma(I)$ and were used to solve the structure. Positions of Br and Cu atoms were determined by solving a Patterson map. All remaining non-H atoms and most of the H atoms were found by analysis of difference electron density maps and least-squares refinements (on F). The few remaining H atoms were calculated assuming reasonable bond distances and angles. All non-H atoms were refined anisotropically. H atoms had fixed positional and displacement parameters throughout the refinements. The entire structure was refined to convergence to give reliability factors $R = 0.057$, $wR =$
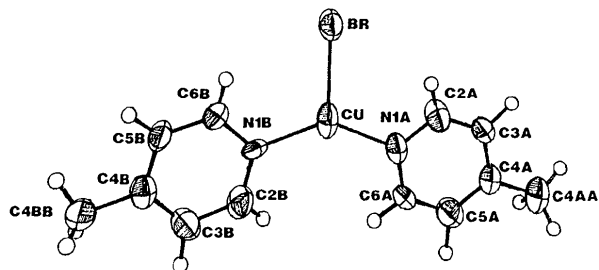

Fig. 1. *ORTEP*II (Johnson, 1976) drawing depicting the stereochemistry of the [CuBr(C$_6$H$_7$N)$_2$] complex and the atomic labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitrary size.
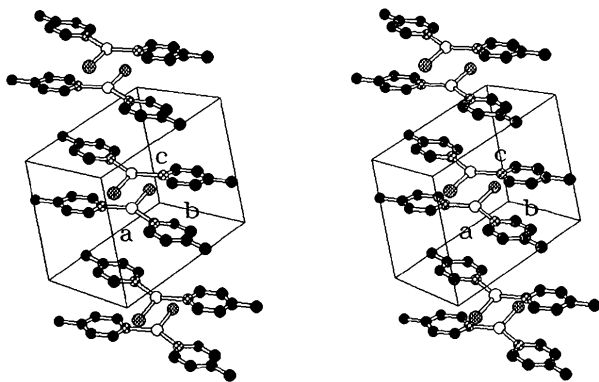

Fig. 2. Stereoview of the packing diagram of the [CuBr(C$_6$H$_7$N)$_2$] complex.

0.088 $\{w = 4(F_o)^2/[\sigma(F_o)^2]^2\}$ and quality of fit indicator $S = 2.967$. All shifts of 146 refined parameters were found to be smaller than 0.001σ. The highest peaks remaining on the resulting electron density map, measuring from 0.825 to 0.500 e Å^{-3}, were in the immediate vicinity of the Cu and Br atoms. Atomic scattering factors were taken from Cromer & Waber (1974). All calculations were performed utilizing a PDP-11/60 minicomputer and Enraf–Nonius (1983) *SDP-Plus* software.

Final positional parameters and equivalent isotropic displacement parameters are listed in Table 1. Bond distances and angles between atoms are listed in Table 2.* An *ORTEP*II (Johnson, 1976) drawing and the atomic labeling scheme are shown in Fig. 1. A packing diagram is presented in Fig. 2.

---

* Lists of structure factors, complete bond distances and angles, anisotropic displacement parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55497 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1000]

Related literature. X-ray structures of the following two adducts were recently determined: copper(I) bromide with 2-bromopyridine and copper(I) chloride with 2-benzylpyridine (Healy, Kildea, Skelton, Waters & White, 1991).

References

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Enraf–Nonius (1983). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
Healy, P. C., Kildea, J. D., Skelton, B. W., Waters, A. F. & White, A. H. (1991). *Acta Cryst.* C47, 1721–1723.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Structure of Bis(benzenesulfonato-O)tetrakis(pyridine-N)copper(II)

By Marek J. Jedrzejas, Robert L. R. Towns,* Ronald J. Baker and Stan A. Duraj*

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

and Aloysius F. Hepp*

National Aeronautics and Space Administration, Lewis Research Center, Photovoltaic Branch, MS 302-1, Cleveland, OH 44135, USA

Abstract. [Cu(C$_6$H$_5$O$_3$S)$_2$(C$_5$H$_5$N)$_4$], $M_r = 694.29$, monoclinic, $C2/c$, $a = 15.180$ (6), $b = 14.431$ (5), $c = 15.269$ (6) Å, $\beta = 96.38$ (4)°, $V = 3324$ (2) Å^3, $Z = 4$, $D_x = 1.388$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 8.54$ cm^{-1}, $F(000) = 1436$, $T = 295$ K, $R = 0.067$, $wR = 0.087$ for 1141 independent reflections with $I \geq 3\sigma(I)$ and 207 variables. The [Cu(O$_3$SC$_6$H$_5$)$_2$(C$_5$H$_5$N)$_4$] complex has a distorted *trans* octahedral stereochemistry. The bond angles about the Cu atom are consistent with this structure type. The important bond distances and angles are: Cu—O1 2.471 (8), S—C1 1.785 (10) Å, Cu—O1—S 154.1 (6), O1—S—O2 112.3 (5), O1—S—O3 111.5 (5)°.

---

* Authors to whom correspondence should be addressed.

Experimental. The title compound was prepared by reaction of metallic copper powder with diphenyl disulfide in pyridine solution. Slow diffusion of hexanes into the reaction solution afforded regular prismatic blue crystals at room temperature. A suitable single crystal for X-ray crystallography (0.26 × 0.34 × 0.31 mm) was mounted inside a glass capillary using fast drying epoxy glue. The unit-cell parameters were determined from 25 reflections with $12.78 < \theta < 24.16°$. A total number of 2919 unique reflections with $2 < \theta < 25°$ ($0 \leq h \leq 19$, $0 \leq k \leq 19$, $-19 \leq l \leq 19$) were collected (ω–2θ scans) using an Enraf–Nonius X-ray automated diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Three standard reflections, monitored every 60 min, showed 3.3% variation in intensity; decay correction