*Acta Cryst.* (1996). C**52**, 635–637

# Bromo(*N*,*N*-dibutyl-*N*′-phenylthiourea-*S*)bis(triphenylphosphine-*P*)copper(I), [Cu(PPh$_3$)$_2$(dbptH)Br]

Ramsharan Singh† and Sheo Kant Dikshit

*Department of Chemistry, Indian Institute of Technology – Kanpur, Kanpur (UP) 208 016, India*

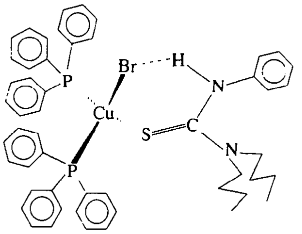
(*Received 17 January 1995; accepted 16 May 1995*)

## Abstract

The coordination around the Cu-metal centre in the title compound, [CuBr(C$_{15}$H$_{24}$N$_2$S)(C$_{18}$H$_{15}$P)$_2$], is distorted tetrahedral with bond lengths Cu—S 2.367 (1), Cu—Br 2.469 (1), Cu—P(1) 2.279 (2) and Cu—P(2) 2.284 (2) Å, and bond angles S—Cu—Br 111.86 (5), S—Cu—P(1) 111.28 (6), S—Cu—P(2) 98.01 (6), Br—Cu—P(1) 103.08 (5), Br—Cu—P(2) 108.60 (5) and P(1)—Cu—P(2) 124.11 (6)°. The H atom of the NH group is intramolecularly hydrogen bonded to the Br atom, with an NH···Br distance of 2.411 Å.

## Comment

Copper complexes of sulfur-donor ligands have attracted considerable attention mainly because of their relevance to biological systems (Karlin & Zubieta, 1983; Patch, Choi, Chapman, Bau, McKee & Reed, 1990) and their stereochemistry. Since the prediction of a structure for the title compound, (*A*), was by no means straightforward, it was deemed worthwhile to carry out the X-ray crystal structure determination.



(*A*)

An *ORTEP* diagram (Johnson, 1965) of the title molecule with the atom labelling is shown in Fig. 1 and a two-dimensional packing diagram viewed down the *c* axis is shown in Fig. 2. The Cu atom is surrounded, in the form of a distorted tetrahedron, by the two P atoms of the phosphine ligands, one Br atom and one S atom. This is a consequence of the approximately equal steric factors acting on the Cu coordination sphere.

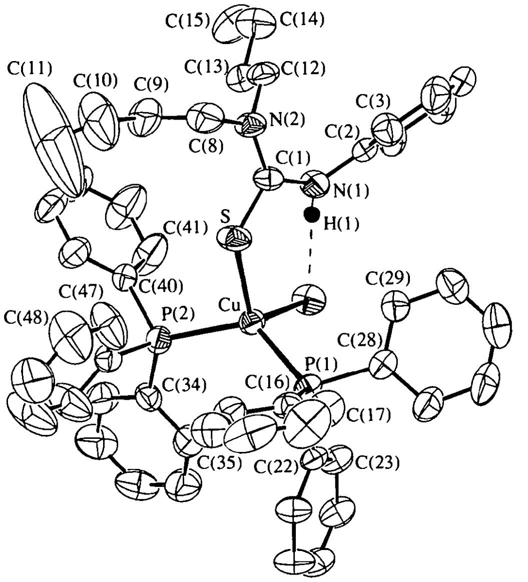


Fig. 1. An *ORTEP* (Johnson, 1965) diagram of [Cu(PPh$_3$)$_2$(dbptH)Br] (*A*) showing 50% probability ellipsoids and the atom-numbering scheme. H atoms are omitted for clarity except for H(1). The hydrogen bond is shown by a dashed line.

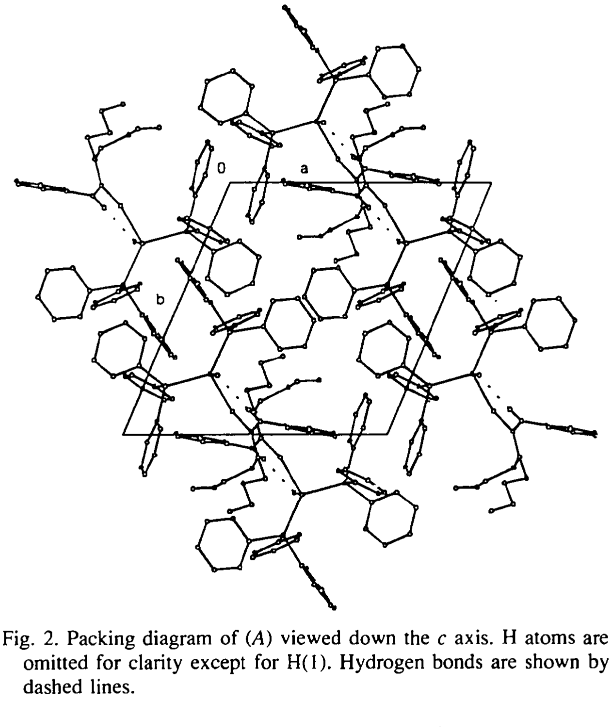


Fig. 2. Packing diagram of (*A*) viewed down the *c* axis. H atoms are omitted for clarity except for H(1). Hydrogen bonds are shown by dashed lines.

The Cu—S bond length of 2.367 (1) Å, the Cu—P(1) and Cu—P(2) distances of 2.279 (2) and 2.284 (2) Å, respectively, and the Cu—Br distance of 2.469 (1) Å, are in good agreement with the distances found in [Cu(PPh$_3$)$_2$(meimtH)Br] (where meimtH is 1-methyl-1,3-imidazoline-2-thione) (Karagiannidis, Aslanidis, Papastefanou, Mentzafos, Hountas & Terzis, 1990) and in [Cu(PPh$_3$)$_2$(py2SH)Br] (where py2SH is pyridine-2-

---

† Present address: Institute of Chemistry, Academica Einica, Taipei, Taiwan.

thione) (Karagiannidis, Aslanidis, Kessissoglou, Krebs & Dartmann, 1989) for tetrahedrally coordinated copper(I) with similar donor ligands. For comparison purposes, selected interatomic distances and angles of the three related complexes $[Cu(PPh_3)_2(dbptH)Br]$, (*A*), $[Cu(PPh_3)_2(meimtH)Br]$, (*B*), and $[Cu(PPh_3)_2(py2SH)Br]$, (*C*), are included in Table 3. Three of the angles around the Cu atom in the two related complexes, as well as in the present complex, approach those of a regular tetrahedron. The P(1)—Cu—P(2) angle deviates considerably from the tetrahedral value of 109.47°. A possible explanation for the large value is the steric interaction between the $PPh_3$ group and the CuSBr entity, but as the angle has been opened up considerably, these steric interactions are not likely to be the sole cause of the distortion. In comparison with complexes (*B*) and (*C*), it is seen that the Cu—S distance in (*A*) is between the values for (*B*) and (*C*), which suggests that the $\pi$ character in this bond is quite comparable.

Geometries of the triphenylphosphine and thione ligands are standard. The average P—C (1.826 Å) and S—C (1.691 Å) bond lengths are close to those found in similar complexes. It appears that the exchange of the cyclic thione ligand for an acyclic thione ligand produces no significant change in the $CuP_2SBr$ core. The H atom of the NH group is intramolecularly hydrogen bonded to the Br atom. The NH···Br distance is 2.411 Å. The intramolecular NH···Br hydrogen bond is also important with respect to the orientation of the dbptH ligand (Fig. 1).

## Experimental

The title compound was available from earlier studies (Singh & Dikshit, 1992). Synthesis of the title compound was carried out by reaction of $[Cu(PPh_3)_3Br]$ and dbptH (molar ratio 1:1) in benzene solution for 2 h at refluxing temperature in a round-bottomed flask. The resulting solution was filtered and the volume of the reaction mixture reduced under vacuum. Excess petroleum ether (333–353 K) was added to induce crystallization. The colourless crystals thus obtained were suitable for X-ray structure investigation. The density $D_m$ was measured by flotation in $CCl_4$/petroleum ether solution.

*Crystal data*

$[CuBr(C_{15}H_{24}N_2S)(C_{18}H_{15}P)_2]$
$M_r = 932.46$
Triclinic
$P\overline{1}$
$a = 13.226\,(2)$ Å
$b = 13.230\,(2)$ Å
$c = 14.908\,(3)$ Å
$\alpha = 87.63\,(1)^\circ$
$\beta = 78.64\,(2)^\circ$
$\gamma = 66.76\,(1)^\circ$
$V = 2348.1\,(7)$ Å$^3$
$Z = 2$
$D_x = 1.319$ Mg m$^{-3}$
$D_m = 1.321$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$25^\circ$
$\mu = 1.46$ mm$^{-1}$
$T = 293$ K
Cubic
0.6 × 0.3 × 0.2 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
6438 measured reflections
6117 independent reflections
3973 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.013$
$\theta_{max} = 22.48^\circ$
$h = 0 \rightarrow 14$
$k = -12 \rightarrow 14$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: <1%

*Refinement*

Refinement on $F$
$R = 0.037$
$wR = 0.032$
$S = 2.225$
3973 reflections
523 parameters
H atoms refined isotropically
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.27 \times 10^{-3}$
$\Delta\rho_{max} = 0.671$ e Å$^{-3}$
$\Delta\rho_{min} = -0.555$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cu | 0.23099 (5) | 0.24074 (5) | 0.25189 (4) | 0.0390 (7) |
| Br | 0.26009 (5) | 0.23488 (5) | 0.41091 (4) | 0.0508 (6) |
| S | 0.3728 (1) | 0.0917 (1) | 0.1592 (1) | 0.055 (2) |
| P(1) | 0.2374 (1) | 0.4046 (1) | 0.2048 (1) | 0.038 (1) |
| P(2) | 0.0834 (1) | 0.1928 (1) | 0.2495 (1) | 0.040 (2) |
| N(1) | 0.4937 (4) | 0.0534 (3) | 0.2878 (3) | 0.046 (5) |
| N(2) | 0.5439 (4) | −0.0924 (3) | 0.1835 (3) | 0.047 (5) |
| C(1) | 0.4771 (4) | 0.0121 (4) | 0.2126 (4) | 0.041 (6) |
| C(2) | 0.5978 (5) | 0.0348 (4) | 0.3111 (4) | 0.040 (6) |
| C(3) | 0.6892 (6) | 0.0260 (5) | 0.2440 (4) | 0.058 (7) |
| C(4) | 0.7905 (6) | 0.0050 (5) | 0.2691 (5) | 0.072 (8) |
| C(5) | 0.8009 (6) | −0.0058 (5) | 0.3585 (6) | 0.074 (9) |
| C(6) | 0.7072 (7) | 0.0079 (6) | 0.4254 (5) | 0.074 (9) |
| C(7) | 0.6060 (5) | 0.0284 (5) | 0.4009 (4) | 0.057 (7) |
| C(8) | 0.5381 (5) | −0.1344 (5) | 0.0954 (4) | 0.065 (7) |
| C(9) | 0.4530 (6) | −0.1876 (5) | 0.1072 (5) | 0.088 (9) |
| C(10) | 0.4299 (8) | −0.2113 (9) | 0.0185 (7) | 0.15 (2) |
| C(11) | 0.350 (1) | −0.216 (2) | 0.0053 (9) | 0.41 (4) |
| C(12) | 0.6048 (4) | −0.1766 (4) | 0.2435 (4) | 0.049 (6) |
| C(13) | 0.5292 (5) | −0.1957 (4) | 0.3273 (4) | 0.055 (7) |
| C(14) | 0.5956 (5) | −0.2828 (5) | 0.3845 (4) | 0.071 (7) |
| C(15) | 0.5244 (6) | −0.3095 (5) | 0.4675 (4) | 0.084 (9) |
| C(16) | 0.2452 (5) | 0.4310 (4) | 0.0826 (4) | 0.045 (6) |
| C(17) | 0.3149 (6) | 0.4756 (5) | 0.0312 (4) | 0.068 (8) |
| C(18) | 0.3152 (8) | 0.4931 (7) | −0.0596 (5) | 0.10 (1) |
| C(19) | 0.2472 (9) | 0.4662 (6) | −0.1024 (5) | 0.10 (1) |
| C(20) | 0.1771 (7) | 0.4223 (6) | −0.0544 (5) | 0.084 (9) |
| C(21) | 0.1765 (5) | 0.4019 (5) | 0.0394 (4) | 0.063 (7) |
| C(22) | 0.1173 (4) | 0.5252 (4) | 0.2605 (4) | 0.038 (6) |
| C(23) | 0.0981 (5) | 0.5362 (4) | 0.3555 (4) | 0.052 (6) |
| C(24) | 0.0025 (5) | 0.6216 (5) | 0.4015 (4) | 0.057 (7) |
| C(25) | −0.0723 (5) | 0.6934 (5) | 0.3548 (4) | 0.058 (7) |
| C(26) | −0.0544 (5) | 0.6831 (5) | 0.2613 (5) | 0.067 (7) |
| C(27) | 0.0415 (5) | 0.5996 (5) | 0.2131 (4) | 0.054 (6) |
| C(28) | 0.3558 (5) | 0.4272 (5) | 0.2320 (3) | 0.041 (6) |
| C(29) | 0.4532 (5) | 0.3375 (5) | 0.2355 (4) | 0.051 (7) |
| C(30) | 0.5441 (5) | 0.3485 (6) | 0.2609 (4) | 0.067 (8) |
| C(31) | 0.5370 (6) | 0.4514 (7) | 0.2824 (4) | 0.074 (9) |
| C(32) | 0.4407 (7) | 0.5412 (6) | 0.2780 (5) | 0.079 (9) |
| C(33) | 0.3490 (5) | 0.5311 (5) | 0.2524 (4) | 0.063 (7) |
| C(34) | −0.0486 (4) | 0.2734 (5) | 0.3246 (4) | 0.043 (6) |
| C(35) | −0.0693 (5) | 0.3797 (5) | 0.3511 (4) | 0.059 (7) |
| C(36) | −0.1681 (6) | 0.4438 (5) | 0.4097 (5) | 0.075 (8) |

| | | | | |
|---|---|---|---|---|
| C(37) | −0.2456 (6) | 0.4002 (6) | 0.4430 (5) | 0.077 (8) |
| C(38) | −0.2271 (5) | 0.2952 (6) | 0.4178 (5) | 0.084 (9) |
| C(39) | −0.1290 (5) | 0.2324 (5) | 0.3589 (5) | 0.071 (8) |
| C(40) | 0.1089 (4) | 0.0525 (4) | 0.2858 (4) | 0.043 (6) |
| C(41) | 0.1327 (7) | 0.0255 (5) | 0.3710 (5) | 0.09 (1) |
| C(42) | 0.1532 (7) | −0.0796 (6) | 0.4028 (5) | 0.11 (1) |
| C(43) | 0.1460 (6) | −0.1574 (5) | 0.3525 (5) | 0.075 (9) |
| C(44) | 0.1223 (6) | −0.1322 (5) | 0.2682 (5) | 0.077 (9) |
| C(45) | 0.1030 (5) | −0.0278 (5) | 0.2347 (4) | 0.062 (7) |
| C(46) | 0.0450 (5) | 0.1920 (4) | 0.1390 (4) | 0.047 (7) |
| C(47) | 0.1292 (6) | 0.1448 (6) | 0.0636 (5) | 0.09 (1) |
| C(48) | 0.1044 (8) | 0.1407 (7) | −0.0214 (5) | 0.11 (1) |
| C(49) | 0.0002 (9) | 0.1837 (7) | −0.0351 (5) | 0.10 (1) |
| C(50) | −0.0832 (7) | 0.2327 (8) | 0.0364 (7) | 0.13 (1) |
| C(51) | −0.0612 (6) | 0.2370 (6) | 0.1239 (5) | 0.095 (9) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu—S | 2.367 (1) | P(1)—C(16) | 1.831 (6) |
| Cu—Br | 2.469 (1) | P(1)—C(22) | 1.831 (4) |
| Cu—P(1) | 2.279 (2) | P(1)—C(28) | 1.827 (7) |
| Cu—P(2) | 2.284 (2) | C(1)—N(1) | 1.359 (8) |
| S—C(1) | 1.691 (5) | C(1)—N(2) | 1.347 (6) |
| N(1)—C(2) | 1.411 (8) | P(2)—C(34) | 1.816 (5) |
| N(2)—C(8) | 1.474 (8) | P(2)—C(40) | 1.830 (6) |
| N(2)—C(12) | 1.477 (7) | P(2)—C(46) | 1.819 (7) |
| | | | |
| S—Cu—Br | 111.86 (5) | Br—Cu—P(2) | 108.60 (5) |
| S—Cu—P(1) | 111.28 (6) | N(1)—C(2)—C(3) | 120.5 (6) |
| S—Cu—P(2) | 98.01 (6) | C(1)—N(1)—C(2) | 126.8 (4) |
| S—C(1)—N(1) | 119.6 (3) | C(1)—N(2)—C(8) | 119.6 (4) |
| S—C(1)—N(2) | 121.9 (5) | C(1)—N(2)—C(12) | 123.3 (4) |
| Cu—S—C(1) | 114.0 (2) | P(1)—Cu—P(2) | 124.11 (6) |
| Cu—P(1)—C(16) | 117.5 (2) | P(1)—C(16)—C(17) | 124.9 (6) |
| Cu—P(1)—C(22) | 114.0 (2) | P(1)—C(22)—C(23) | 117.5 (4) |
| Cu—P(1)—C(28) | 113.5 (2) | P(1)—C(28)—C(29) | 118.6 (5) |
| Cu—P(2)—C(34) | 116.6 (2) | P(2)—C(34)—C(35) | 119.2 (5) |
| Cu—P(2)—C(40) | 112.9 (2) | P(2)—C(40)—C(41) | 118.4 (5) |
| Cu—P(2)—C(46) | 116.8 (2) | P(2)—C(46)—C(47) | 118.7 (5) |
| Br—Cu—P(1) | 103.08 (5) | | |

Table 3. *Interatomic distances (Å) and angles (°) in [Cu(PPh$_3$)$_2$(dbptH)Br], (A), [Cu(PPh$_3$)$_2$(meimtH)Br], (B), and [Cu(PPh$_3$)$_2$(py2SH)Br], (C)*

| | *(A)** | *(B)*† | *(C)*‡ |
|---|---|---|---|
| Cu—S | 2.367 (1) | 2.375 (1) | 2.302 (4) |
| Cu—Br | 2.469 (1) | 2.509 | 2.462 (2) |
| Cu—P | 2.279 (2) | 2.281 (1) | 2.263 (4) |
| | 2.284 (2) | 2.268 (1) | 2.267 (4) |
| | | | |
| P—Cu—P | 124.11 (6) | 130.9 | 125.0 (2) |
| P—Cu—Br | 103.08 (5) | 106.7 | 104.4 (1) |
| | 108.60 (5) | 98.3 | 105.9 (1) |
| S—Cu—Br | 111.86 (5) | 112.6 | 114.9 (1) |
| S—Cu—P | 111.28 (6) | 102.9 | 104.5 (2) |
| | 98.01 (6) | 105.3 | 102.8 (2) |

* Present work. † Karagiannidis *et al.* (1990). ‡ Karagiannidis *et al.* (1989).

All H atoms were calculated as riding on their C atoms at a distance of 0.95 Å, except for the amine H atom, which was calculated as riding on the N atom at a distance of 0.87 Å. Refined parameters were calculated by using anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for all H atoms.

Data collection: *CAD*-4 *MACH-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *MACH-PC Software*. Data reduction: *Xtal*3.2 *DIFDAT SORTRF ADDREF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*3.2 *SIMPEL*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *CIFIO*.

The data for the X-ray crystal structure analysis were collected at the DST-funded National Facility on Single Crystal X-ray Diffraction, Department of Chemistry, Indian Institute of Technology, Kanpur, India. The authors are thankful to Dr P. K. Bharadwaj for his help in the solution and refinement of the X-ray data. One of the authors (RS) wishes to acknowledge the Indian Institute of Technology, Kanpur, India, for providing financial support in the form of a Research Associateship.

---

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

## References

Enraf–Nonius (1993). *CAD*-4 *MACH-PC Software*. Version 4.0. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Karagiannidis, P., Aslanidis, P., Kessissoglou, D. P., Krebs, B. & Dartmann, M. (1989). *Inorg. Chim. Acta*, **156**, 47–56.

Karagiannidis, P., Aslanidis, P., Papastefanou, S., Mentzafos, D., Hountas, A. & Terzis, A. (1990). *Polyhedron*, **9**, 981–986.

Karlin, K. D. & Zubieta, J. (1983). In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*. New York: Adenine.

Patch, M. G., Choi, H., Chapman, D. R., Bau, R., McKee, V. & Reed, C. A. (1990). *Inorg. Chem.* **29**, 110–119.

Singh, R. & Dikshit, S. K. (1992). *Polyhedron*, **11**, 2099–2107.

---

*Acta Cryst.* (1996). **C52**, 637–640

# Lithium Tetraphenylborate.2thf.2H$_2$O

Holger Schödel, Thorsten Vaupel and Hans Bock*

*Institut für Anorganische Chemie der Universität Frankfurt,*
*Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany.*
*E-mail: schoedel@bock.anorg.chemie.uni-frankfurt.de*

(*Received 23 May 1995; accepted 6 September 1995*)

## Abstract

The structure of diaquabis(tetrahydrofuran)lithium tetraphenylborate, [Li(C$_4$H$_8$O)$_2$(H$_2$O)$_2$](C$_{24}$H$_{20}$B), has been determined at 200 K. The Li$^+$ cation is coordinated by two water and two tetrahydrofuran molecules, whereas the tetraphenylborate anion does not show any contact. A crystallographic mirror plane bisects the lithium complex and the tetraphenylborate anion.

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1996