

[(OW2)] and intramolecularly with an oxalate oxygen [O(4)]. This latter oxygen is an acceptor for three additional hydrogen bonds, while O(2) accepts three hydrogen bonds from water [O(W1)] and amine hydrogens and O(3) accepts one from water [O(W2)]. The protonated oxalate oxygen [O(1)] does not accept any hydrogen bonds. The intramolecular hydrogen bond O(1) to O(4) is of moderate strength [O...O = 2.681 (3) Å]. In compound (1) the hydrogen bonding involves all amine H atoms with the nitrate oxygen atoms as primary acceptors and apparent weak intramolecular interactions with the coordinated chloro ligands.

Despite these rather large differences in crystalline environments for the rhodium complexes in the two salts there is little difference in molecular structure (Fig.

1, Table 3), suggesting that this structure may be very similar to that in solution.

Financial support by DOE Grant No. FG02-86ER60400 is gratefully acknowledged.

References

- BAIDINA, I. A., POBEREZSKAYA, N. V., BELYAEV, A. V. & BAKAKIN, V. V. (1979). *Zh. Strukt. Khim.* **20**, 1096–1102 (Engl. transl. pp. 934–938).
 Enraf–Nonius (1984). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, S. A. & BASOLO, F. (1962). *Inorg. Chem.* **1**, 925–932.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1988). **C44**, 34–38

Structures of *N*-Benzylpiperazinium Tetrabromocuprate(II) Hydrate and Bis[methyl(2-phenylethyl)ammonium] Tetrabromocuprate(II)

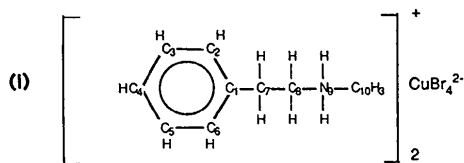
BY HELEN PLACE AND ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, WA 99164-4630, USA

(Received 17 July 1986; accepted 10 August 1987)

Abstract. [C₁₁H₁₈N₂][CuBr₄].H₂O, *M_r* = 579.5, monoclinic, *P*₂₁/*c*, *a* = 7.413 (2), *b* = 16.459 (10), *c* = 14.961 (8) Å, β = 104.78 (4)°, *V* = 1765 Å³, *Z* = 4, *D_x* = 2.18 g cm⁻³, *F*(000) = 1108, μ = 102.1 cm⁻¹, Mo *K*α radiation (λ = 0.71069 Å), *T* = 293 K. 2720 unique reflections of which 1863 had *F* ≥ 3σ(*F*) were refined to a final *R* = 0.0588 for the 3σ data set (*wR* = 0.0511). The structure consists of discrete CuBr₄²⁻ anions, *N*-benzylpiperazinium cations and water molecules, held together in the lattice with hydrogen bonding. The CuBr₄²⁻ ion has nearly tetrahedral geometry and is therefore different from other CuCl₄²⁻ and CuBr₄²⁻ ions seen in similar compounds. [NH₂(CH₃)(C₈H₉)₂][CuBr₄], *M_r* = 655.6, monoclinic, *C*2/*c*, *a* = 25.98 (2), *b* = 9.045 (5), *c* = 10.986 (5) Å, β = 111.08 (4)°, *V* = 2408.6 Å³, *Z* = 4, *D_x* = 1.81 g cm⁻³, *F*(000) = 1276, μ = 74.9 cm⁻¹, Mo *K*α radiation (λ = 0.71069 Å), *T* = 293 K. 1130 unique reflections, 748 reflections with *F* > 3σ(*F*) were refined to a final *R* = 0.0618 for the 3σ set (*wR* = 0.0595). The structure consists of discrete CuBr₄²⁻ anions and methyl(2-phenylethyl)ammonium cations. The CuBr₄²⁻ anion has geometry intermediate between square planar and tetrahedral. The crystal packing shows distinct layers of anions and cations, held together in the lattice with hydrogen bonding.

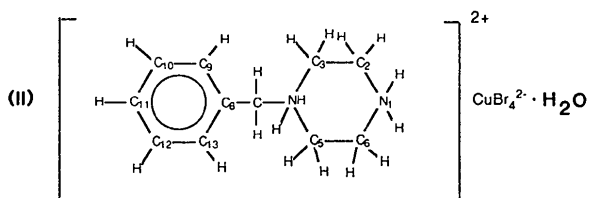
Introduction. A series of copper chloride and copper bromide salts containing quasi-planar Cu_{*n*}X_{2*n*+2}⁻ ions has been sought in order to study their magnetic and structural correlations (Geiser, Willett, Lindbeck & Emerson, 1986). The structure of methyl(2-phenylethyl)ammonium heptachloromonoethanolatetetracuprate(II) has been studied (Grigereit, 1986; Grigereit, Ramakrishna, Place, Willett, Pellacani, Manfredini, Menabue, Bonamartini-Corradi & Battaglia, 1987) and shown to contain the unusual Cu₃Cl₇(EtOH)⁻ anion. In an attempt to make the analogous bromide salt, the crystalline product turned out to be bis[methyl(2-phenylethyl)ammonium] tetrabromocuprate(II), hereafter (NMPH)₂CuBr₄ (I).



Tetrabromocuprate and tetrachlorocuprate anions such as this have routinely shown up in this laboratory in the attempted preparation of such oligomeric species, resulting in a separate study of the varying geometries

of these anions. One emphasis of this study is the change in structure resulting from replacing the chloride ion with the larger bromide ion.

In this respect, the structures of both the low- and the high-temperature phases of bis[methyl(2-phenylethyl)ammonium] tetrachlorocuprate(II) have been reported (Harlow, Wells, Watt & Simonsen, 1974). This study compares the tetrabromocuprate salt with the low-temperature phase of the tetrachlorocuprate salt. Similarly, the *N*-benzylpiperazinium (NBPZ) tetrachlorocuprate(II) salts (hemihydrate and anhydrous) contain CuCl_4^{2-} ions with different geometries (Antolini, Pellacani, Sandrolini, Marcotrigiano & Porzio, 1981). An attempt to prepare the corresponding bromide salts resulted in the formation of a monohydrate salt (II). The structure of the latter is reported and compared with the chloride salts.



Experimental. (NBPZ) $\text{CuBr}_4 \cdot \text{H}_2\text{O}$ was prepared from a 2:1 mixture of copper(II) bromide and *N*-benzylpiperazine in methanol to which enough hydrobromic acid was added to neutralize the amine. The black plate-like crystals separated upon controlled evaporation of the solvent. A thin crystal, approximately $0.56 \times 0.50 \times 0.08$ mm, was selected for data collection. Data were collected with an ω scan on a Nicolet R3m/E diffractometer system with $\text{MoK}\alpha$ radiation, and a graphite monochromator (Campana, Shepherd & Litchman, 1981). Agreement between equivalent reflections (Ok): $R = 0.0323$. The monoclinic unit cell and orientation matrix were defined by a least-squares refinement of 25 centered reflections in the $24\text{--}26^\circ 2\theta$ range. Data were collected for $h \geq 0$, $k \geq 0$ and all l . (The maximum values of h , k and l were 8, 18 and 32, respectively.) The faces of the crystal were indexed and absorption corrections were calculated from these faces and the size of the crystal (minimum transmission = 0.031, maximum transmission = 0.413). Three standards were monitored every 100 reflections, with variations within counting statistics. Scan speeds ranged from 4.00 to $29.30^\circ \text{min}^{-1}$. 3434 total reflections with $2\theta \leq 47^\circ$, 2720 unique reflections with 1863 having $F \geq 3\sigma(F)$. The structure was solved *via* direct methods, yielding the Cu and Br positions. The *N*-benzylpiperazinium rings were found on subsequent difference maps. Final refinement on F for all observed reflections with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0588$ and $wR = 0.0511$ with an average $|\Delta/\sigma| = 0.015$ (SHELXTL;

Sheldrick, 1984), where $w = [\sigma^2(F_o) + g|F_o|^2]$, $g = 0.0005$, number of least-squares parameters refined = 172. The goodness of fit was 1.270. H atoms were fixed at calculated positions ($r_{\text{C-H}} = r_{\text{N-H}} = 0.96 \text{ \AA}$) with isotropic thermal parameters approximately 20% larger than the corresponding heavy atom. The largest residual on the final difference map was 0.9 e \AA^{-3} near one of the Br atoms, the largest negative residual being -0.8 e \AA^{-3} . Scattering factors, corrected for dispersion effects, were taken from *International Tables for X-ray Crystallography* (1974). Final positional parameters are listed in Table 1, with selected bond distances and angles reported in Table 2.*

(NMPH) $_2\text{CuBr}_4$ formed dark brown-red crystals which separated out of a saturated solution of the complex. The complex was prepared by mixing together approximately stoichiometric amounts of *N*-methyl-2-phenylethylamine and copper bromide in aqueous solution with sufficient HBr to neutralize the amine. The product was recrystallized from water. A thin platelike crystal measuring $0.22 \times 0.14 \times 0.02$ mm was selected for data collection. Data were collected with an ω scan on a Nicolet R3m/E diffractometer system with $\text{MoK}\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1981). Agreement between equivalent reflections (Ok): $R = 0.0206$. The monoclinic unit cell and the orientation matrix were defined by least-squares refinement of 25 centered reflections with $18 < 2\theta < 20^\circ$. Empirical absorption corrections were applied assuming an ellipsoidally shaped crystal (minimum transmission 0.088, maximum transmission 0.131). Data were collected for $h \geq 0$, $k \geq 0$ and all l . (The maximum values of h , k and l were 24, 8 and 10, respectively.) Three standards were monitored every 100 reflections, variation was within counting statistics. 1262 total reflections with $2\theta \leq 40^\circ$, 1130 unique reflections, 748 with $F > 3\sigma(F)$. Direct methods yielded the Cu and Br positions. Subsequent difference maps yielded all other non-hydrogen-atom positions. Final refinement on F for all observed reflections, with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the H atoms, gave a final value of $R = 0.0618$ and $wR = 0.0597$ with an average $|\Delta/\sigma| = 0.052$ (Sheldrick, 1984) where w is as above; number of least-squares parameters refined = 115. The goodness of fit was 1.241. H atoms were fixed at calculated positions ($r_{\text{C-H}} = r_{\text{N-H}} = 0.96 \text{ \AA}$) with isotropic thermal parameters approximately 20% larger than the corresponding heavy atom. The largest residual on the final difference map was 0.61 e \AA^{-3} near Br(2), the largest negative

* Lists of anisotropic thermal parameters, H-atom positions and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44311 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for (NBPZ)CuBr₄.H₂O

The equivalent isotropic U values are defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	615 (2)	8735 (1)	1662 (1)	44 (1)
Cu	3899 (2)	8726 (1)	2139 (1)	37 (1)
Br(2)	4599 (2)	80 (1)	2650 (1)	48 (1)
Br(3)	4690 (2)	3499 (1)	4146 (1)	51 (1)
Br(4)	4533 (2)	7555 (1)	3077 (1)	49 (1)
O	2325 (11)	488 (5)	478 (6)	46 (3)
N(1)	1115 (15)	6083 (5)	4347 (7)	42 (4)
C(2)	542 (19)	6930 (7)	4122 (9)	51 (6)
C(3)	-753 (17)	6970 (6)	3138 (8)	38 (5)
N(4)	175 (12)	6632 (5)	2438 (6)	28 (3)
C(5)	742 (16)	5761 (6)	2704 (8)	35 (4)
C(6)	2008 (15)	5713 (6)	3663 (8)	32 (4)
C(7)	-1093 (16)	6683 (7)	1485 (7)	36 (4)
C(8)	-211 (18)	6423 (6)	723 (8)	39 (5)
C(9)	-1383 (18)	6126 (7)	-87 (8)	45 (5)
C(10)	-709 (24)	5915 (7)	-804 (9)	61 (6)
C(11)	1175 (25)	5959 (7)	-728 (10)	60 (7)
C(12)	2358 (22)	6236 (7)	80 (8)	53 (6)
C(13)	1678 (17)	6461 (6)	776 (8)	42 (5)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) for (NBPZ)CuBr₄.H₂O

Br(1)—Cu	2.356 (2)	Cu—Br(4)	2.359 (2)
Cu—Br(2a)	2.369 (2)	Cu—Br(3a)	2.442 (2)
N(1)—C(2)	1.470 (14)	N(1)—C(6)	1.483 (16)
C(2)—C(3)	1.540 (16)	C(3)—N(4)	1.499 (16)
N(4)—C(5)	1.518 (12)	N(4)—C(7)	1.497 (12)
C(5)—C(6)	1.504 (14)	C(7)—C(8)	1.515 (18)
C(8)—C(9)	1.387 (15)	C(8)—C(13)	1.384 (18)
C(9)—C(10)	1.339 (21)	C(10)—C(11)	1.375 (26)
C(11)—C(12)	1.378 (18)	C(12)—C(13)	1.320 (20)
Br(1)—Cu—Br(4)	102.7 (1)	Br(2)—Cu—Br(3)	107.2 (1)
Br(4)—Cu—Br(2a)	125.6 (1)	Br(1)—Cu—Br(2a)	102.5 (1)
Br(4)—Cu—Br(3a)	106.4 (1)	Br(1)—Cu—Br(3a)	112.3 (1)
N(1)—C(2)—C(3)	109.5 (9)	C(2)—N(1)—C(6)	112.7 (10)
C(3)—N(4)—C(5)	108.3 (9)	C(2)—C(3)—N(4)	111.5 (10)
C(5)—N(4)—C(7)	111.6 (8)	C(3)—N(4)—C(7)	110.8 (8)
N(1)—C(6)—C(5)	110.9 (9)	N(4)—C(5)—C(6)	111.3 (8)
C(7)—C(8)—C(9)	117.6 (11)	N(4)—C(7)—C(8)	114.5 (9)
C(9)—C(8)—C(13)	117.8 (12)	C(7)—C(8)—C(13)	124.6 (10)
C(9)—C(10)—C(11)	119.9 (12)	C(8)—C(9)—C(10)	120.8 (13)
C(11)—C(12)—C(13)	120.0 (15)	C(10)—C(11)—C(12)	119.7 (15)
		C(8)—C(13)—C(12)	121.7 (11)

residual being -0.5 e \AA^{-3} . Final positional parameters are given in Table 3 with selected bond distances and angles reported in Table 4.*

Discussion. (NBPZ)CuBr₄.H₂O contains discrete *N*-benzylpiperazinium cations, CuBr₄²⁻ anions and water molecules (Fig. 1). Distances and angles within the cation are normal. The CuBr₄²⁻ anion is unusual in that it has a very small distortion from tetrahedral. The extent of this distortion can be seen from the largest *trans* Br—Cu—Br angle which is only 125.6°. However, the average *trans* Br—Cu—Br angle is only 119°. This is a much smaller value for the *trans* angle than is

seen in the CuBr₄²⁻ anions in the *N*-benzylpiperazinium tetrachlorocuprate(II) salts (Antolini *et al.*, 1981). In the hemihydrate salt the *trans* Cl—Cu—Cl angle is 133° and in the anhydrous salt it is 144° (average). This angle is also smaller than that seen in several other tetrabromocuprates with substituted aminopyridine cations (Place & Willett, 1987b). Bond angles and distances are given in Table 2.

Table 3. Positional ($\times 10^4$) and equivalent isotropic thermal ($\text{\AA}^2 \times 10^3$) parameters for (NMPH)₂CuBr₄

The equivalent isotropic U values are defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	5000	9057 (4)	2500	72 (1)
Br(1)	4496 (1)	10850 (2)	915 (2)	84 (1)
Br(2)	5732 (1)	7340 (3)	2966 (2)	109 (1)
C(1)	2779 (9)	846 (29)	1895 (23)	98 (12)
C(2)	2374 (14)	1668 (30)	2059 (30)	131 (17)
C(3)	1844 (12)	1560 (32)	1135 (34)	120 (16)
C(4)	1738 (15)	580 (41)	215 (31)	128 (18)
C(5)	2142 (19)	-219 (37)	-10 (29)	145 (21)
C(6)	2651 (11)	-61 (31)	894 (30)	111 (14)
C(7)	3385 (9)	836 (22)	2893 (22)	112 (13)
C(8)	2640 (9)	2245 (22)	2945 (20)	101 (11)
N(9)	4224 (7)	2265 (19)	3851 (17)	90 (9)
C(10)	4485 (9)	3679 (24)	3900 (24)	115 (14)

Table 4. Bond lengths (\AA) and bond angles ($^\circ$) for (NMPH)₂CuBr₄

Cu(1)—Br(1)	2.395 (3)	Cu(1)—Br(2)	2.364 (3)
Cu(1)—Br(1a)	2.395 (3)	Cu(1)—Br(2a)	2.364 (3)
C(1)—C(2)	1.353 (45)	C(1)—C(6)	1.315 (39)
C(1)—C(7)	1.560 (28)	C(2)—C(3)	1.389 (39)
C(3)—C(4)	1.297 (48)	C(4)—C(5)	1.368 (62)
C(5)—C(6)	1.347 (45)	C(7)—C(8)	1.428 (30)
C(8)—N(9)	1.485 (24)	N(9)—C(10)	1.439 (28)
Br(1)—Cu(1)—Br(2)	142.1 (1)	Br(1)—Cu(1)—Br(1a)	94.8 (1)
Br(2)—Cu(1)—Br(1a)	95.8 (1)	Br(1)—Cu(1)—Br(2a)	95.8 (1)
Br(2)—Cu(1)—Br(2a)	97.9 (2)	C(2)—C(1)—C(6)	118.7 (22)
C(2)—C(1)—C(7)	123.1 (23)	C(6)—C(1)—C(7)	118.1 (23)
C(1)—C(2)—C(3)	118.5 (28)	C(2)—C(3)—C(4)	119.7 (32)
C(3)—C(4)—C(5)	122.7 (31)	C(4)—C(5)—C(6)	115.1 (30)
C(1)—C(6)—C(5)	124.7 (31)	C(1)—C(7)—C(8)	111.0 (17)
C(7)—C(8)—N(9)	112.7 (16)	C(8)—N(9)—C(10)	112.9 (15)

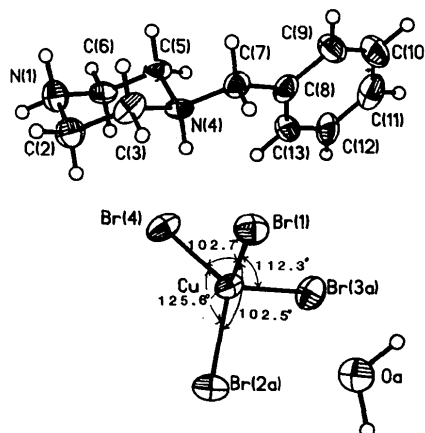


Fig. 1. Illustration of the asymmetric unit for (NBPZ)CuBr₄.H₂O.

* See deposition footnote.

The lattice is held together with hydrogen bonds between the N—H groups in the ring and the water molecules, between the N—H groups and the bromine, and between the water molecules and the bromide ions. These hydrogen-bonding distances are given in Table 5. The hydrogen-bonding distances between the N from the cation and the Br on the anion are longer than in the other CuBr_4^{2-} anions reported by this laboratory (Place & Willett, 1987a). This evidence for weaker hydrogen bonding would account for the nearly tetrahedral geometry of this ion. It has been argued (Geiser & Willett, 1984) that strong hydrogen bonding stabilizes a square-planar configuration for CuCl_4^{2-} anions through charge removal from the chloride ions, allowing crystal-field stabilization effects to become dominant. With weak hydrogen bonding, electrostatic forces would dominate and a geometry close to tetrahedral would result. Also, it is expected that the replacement of chloride ions by the larger bromide ions would further compress the coordination sphere towards tetrahedral geometry.

The structure of $(\text{NMPH})_2\text{CuBr}_4$ consists of discrete methyl(2-phenylethyl)ammonium cations and tetrabromocuprate(II) anions (Fig. 2). The Cu has a geometry intermediate between tetrahedral and square planar, and occupies a special position on a twofold axis. The *trans* Br(1)—Cu—Br(2) angle is 142.1° (109° would be tetrahedral, 180° square planar). The Cu—Br

distance (average) is 2.379 \AA . The dihedral angle is 51.6° . The dihedral angle is a measure of the amount of distortion from square planar (0° would be square planar, 90° would be tetrahedral). These angles and distances are compared with those reported in other CuCl_4^{2-} and CuBr_4^{2-} ions (Table 6).

In the room-temperature phase of the tetrachlorocuprate(II) salt of this same cation, the CuCl_4^{2-} anion is square planar (Harlow *et al.*, 1974). This changes to a geometry intermediate between square planar and tetrahedral in the high-temperature phase, where the dihedral angle is 66.4° . The geometry of this ion can again be correlated with the extent of hydrogen bonding. In the low-temperature form the N—Cl distances average 3.310 \AA and the H—Cl distance averages 2.60 \AA . N—Cl (average) for the high-temperature form is 3.45 \AA . In the tetrabromocuprate(II) salt

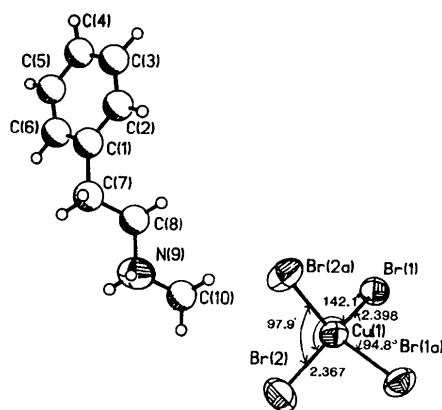


Fig. 2. Illustration of the cation and anion in $(\text{NMPH})_2\text{CuBr}_4$.

Table 5. H-bond lengths (\AA) for $(\text{NBPZ})\text{CuBr}_4 \cdot \text{H}_2\text{O}$

O—Br(1)	3.62 (1)	N(1)—Br(1)	3.59 (1)
H(O2)—Br(1)	3.20	H(1A)—Br(1)	3.01
O—N(1)	2.81 (1)	O—Br(3)	3.41 (1)
O—H(1B)	1.88	H(O1)—Br(3)	2.51

Table 6. Average bond distances and angles and dihedral angles in some $A_2\text{CuX}_4$ salts

Cation Anion	Cu—Cl distance (\AA)	Cl—Cu—Cl angle ($^\circ$) (ave.)	Cu—Br distance (\AA)	Br—Cu—Br angle ($^\circ$) (ave.)	Dihedral angle ($^\circ$)	Reference
Methyl(2-phenylethyl)ammonium CuCl_4 (low-temperature phase)	2.262	180			0	Harlow <i>et al.</i> (1974)
CuCl_4 (high-temperature phase)	2.223	130.5			66.4	Harlow <i>et al.</i> (1974)
CuBr_4			2.383	142.1	51.6	This work
5-Methyl-2-aminopyridinium CuCl_4	2.240	140			54.5	Place & Willett (1987a)
CuBr_4			2.376	137	57.9	Place & Willett (1987a)
<i>N</i> -Benzylpiperazinium $\text{CuCl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	2.250	133.0			~ 63	Antolini <i>et al.</i> (1981)
CuCl_4	2.240	144.0			~ 49	Antolini <i>et al.</i> (1981)
$\text{CuBr}_4 \cdot \text{H}_2\text{O}$			2.382	118.8	80.4	This work
5-Bromo-3-methyl-2-aminopyridinium, 3-Methyl-2-aminopyridinium CuBr_4			2.376	131.3	65.4	Place & Willett (1987b)
Caesium CuCl_4	2.20	124			73.8	Helmholz & Kruh (1952)
CuBr_4			2.374	128.4	68.7	Morosin & Lingafelter (1961) Morosin & Lingafelter (1960)

reported in this paper, the dihedral angle is 51.6° and the geometry of the CuBr₄²⁻ ion, although intermediate between square planar and tetrahedral, is nearer to square planar than the high-temperature form of the CuCl₄²⁻ salt. The N—Br distance is 3.480 Å (ave.) and the H—Br distance is 2.66 Å (ave.). In other compounds studied in this laboratory, where both the CuCl₄²⁻ salt and the CuBr₄²⁻ salt of the same cation have been prepared, the tetrabromocuprate(II) ion has usually shown a larger dihedral angle than the tetrachlorocuprate(II) ion (Table 6). This is as expected for the larger Br atom since distortion towards a tetrahedral geometry will lessen ligand–ligand repulsions. This argument would hold for the bis(NMPH) salts if the tetrabromocuprate(II) is compared directly with the low-temperature form of the tetrachlorocuprate(II). The high-temperature form contains disordered organic cations which exhibit decreased hydrogen bonding; it is therefore able to adopt a more tetrahedral configuration. The role of hydrogen bonding in CuCl₄²⁻ ions has been discussed previously (Geiser & Willett, 1984), and in CuBr₄²⁻ versus CuCl₄²⁻ ions (Place & Willett, 1987a).

In the NMPH salt, the distances and angles within the cations are normal. The lattice is held together with hydrogen bonding between the ammonium nitrogen N(9) and the Br ions. The N(9)—Br(1) distance is 3.485, H(9A)—Br(1) is 2.726 Å. N(9)—Br(2) is 3.476, H(9B)—Br(2) is 2.593 Å. The packing shows distinct layers of anions and cations. The 2-phenylethyl groups form a contiguous layer with the charged methyl-ammonium group alternating either side of, and protruding from, this layer.

The authors acknowledge the support of NSF grants DMR-8219430 and INT-8219425. In addition, the X-ray diffraction facility was established through funds supplied by NSF grant CHE-8408407 and by The Boeing Company.

References

- ANTOLINI, L. M., PELLACANI, G. C., SANDROLINI, M., MARCOTRIGIANO, G. & PORZIO, W. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1753–1759.
- CAMPANA, C. F., SHEPHERD, D. F. & LITCHMAN, W. N. (1981). *Inorg. Chem.* **20**, 4039–4044.
- GEISER, U. & WILLETT, R. D. (1984). *Chem. Croat. Acta*, **57**, 737–747.
- GEISER, U., WILLETT, R. D., LINDBECK, M. & EMERSON, K. (1986). *J. Am. Chem. Soc.* **108**, 1173–1179.
- GRIGEREIT, T. E. (1986). MS Thesis, Washington State Univ.
- GRIGEREIT, T. E., RAMAKRISHNA, B. L., PLACE, H., WILLETT, R. D., PELLACANI, G. C., MANFREDINI, T., MENABUE, L. B., BONAMARTINI-CORRADI, A. & BATTAGLIA, L. P. (1987). *Inorg. Chem.* **26**, 2235–2243.
- HARLOW, R. L., WELLS, W. J. III, WATT, G. W. & SIMONSEN, S. J. (1974). *Inorg. Chem.* **13**, 2106–2111.
- HELMHOLZ, L. & KRUEH, R. F. (1952). *J. Am. Chem. Soc.* **74**, 1176–1181.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MOROSIN, B. & LINGAFELTER, E. C. (1960). *Acta Cryst.* **13**, 807–809.
- MOROSIN, B. & LINGAFELTER, E. C. (1961). *J. Phys. Chem.* **65**, 50–51.
- PLACE, H. & WILLETT, R. D. (1987a). *Acta Cryst.* **C43**, 1050–1053.
- PLACE, H. & WILLETT, R. D. (1987b). *Acta Cryst.* **C43**, 1497–1500.
- SHELDRIK, G. (1984). *SHELXTL* Version 4.1, Nicolet Analytical Instrument Corporation, Madison, WI, USA.

Acta Cryst. (1988). **C44**, 38–41

Three Forms of (Triphenylarsine)diiodine: Two Polymorphs of C₁₈H₁₅AsI₂ and a 1:3/2 Toluene Solvate C₁₈H₁₅AsI₂.3/2C₇H₈

BY B. BEAGLEY, C. B. COLBURN,* O. EL-SAYRAFI, G. A. GOTT, D. G. KELLY, A. G. MACKIE, C. A. MCAULIFFE, P. P. MACRORY AND R. G. PRITCHARD

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(Received 26 May 1987; accepted 9 September 1987)

Abstract. (I): C₁₈H₁₅AsI₂, $M_r = 560.05$, orthorhombic, $P2_12_12_1$, $a = 10.990$ (4), $b = 12.056$ (4), $c = 13.963$ (3) Å, $V = 1850.0$ Å³, $Z = 4$, $F(000) = 1048$, $D_x = 2.01$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 5.04$ mm⁻¹, $T = 293$ K, $R = 0.037$ for

2880 reflexions with $F > 3\sigma(F)$. (II): C₁₈H₁₅AsI₂, $M_r = 560.05$, monoclinic, $P2_1/c$, $a = 9.228$ (3), $b = 10.079$ (2), $c = 20.348$ (3) Å, $\beta = 93.78$ (2)°, $V = 1888.4$ Å³, $Z = 4$, $F(000) = 1048$, $D_x = 1.97$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 4.94$ mm⁻¹, $T = 293$ K, $R = 0.059$ for 1585 reflexions with $F > 3\sigma(F)$. (III): C₁₈H₁₅AsI₂.1.5C₇H₈, $M_r = 698.16$, rhombohedral indexed on hexagonal axes, $R\bar{3}c$, a

* Permanent address: Department of Chemistry, Auburn University, Auburn, AL 36849, USA.