

$M-N(\text{oxime})$  angle decreases in the order  $[\{\text{Cu}(\text{EnAO-H})\}_2](\text{ClO}_4)_2 > [\text{Cu}(\text{PnAO-H})](\text{ReO}_4) > [\text{Cu}(6,6\text{-Me}_2\text{-PnAO-H})(\text{H}_2\text{O})](\text{ClO}_4) > [\text{Cu}(\text{BnAOH})(\text{H}_2\text{O})](\text{ClO}_4)$  and  $[\{\text{Cu}(\text{BnAO-H})\}_2](\text{ClO}_4)_2$ . This is related to two factors: (1) the size of the central chelate ring and (2) the number of the C-methyl groups of the central chelate ring. Generally, the  $N(\text{amine})-M-N(\text{amine})$  angle increases and the average  $N(\text{amine})-M-N(\text{oxime})$  angle decreases as the size of the central chelate ring increases and as the number of the C-methyl groups of the central ring increases. The average  $M-N(\text{amine})$  bond distance is slightly longer than the average  $M-N(\text{oxime})$  bond distance. It is significant to note that the  $M-N(\text{amine})$  bond distances of these complexes are shorter than those of the analogous copper(II) complexes of tetraamines (Fawcett, Rudich, Toby, Lalancette, Potenza & Schuger, 1980). The  $O\cdots O$  distance increases in the order:  $[\text{Cu}(\text{BnAO-H})(\text{H}_2\text{O})](\text{ClO}_4) < [\text{Cu}(\text{PnAO-H})](\text{ReO}_4) < [\text{Cu}(6,6\text{-Me}_2\text{-PnAO-H})(\text{H}_2\text{O})](\text{ClO}_4) < [\{\text{Cu}(\text{BnAO-H})\}_2](\text{ClO}_4)_2 < [\{\text{Cu}(\text{EnAO-H})\}_2](\text{ClO}_4)_2$ . As pointed out by Pal *et al.* (1986) there are two factors which tend to elongate the  $O\cdots O$  separation: (1) the constraint caused by the diaminedioxime ligand in the complex and (2) dimerization through a hydrogen-bonded oxime oxygen of copper(II). The constraint due to the C-methyl groups in  $[\text{Cu}(6,6\text{-Me}_2\text{-PnAO-H})(\text{H}_2\text{O})](\text{ClO}_4)$  contributes to the elongation of the  $O\cdots O$  distance; therefore, the  $O\cdots O$  distance in  $[\text{Cu}(6,6\text{-Me}_2\text{-PnAO-H})(\text{H}_2\text{O})](\text{ClO}_4)$  is larger than that in  $[\text{Cu}(\text{PnAO-H})](\text{ReO}_4)$ . Among

these complexes the constraint imposed by the ethylene bridge in  $\text{EnAO-H}$  is the largest (Pal *et al.*, 1986); consequently, the  $O\cdots O$  distance in  $[\{\text{Cu}(\text{EnAO-H})\}_2](\text{ClO}_4)_2$  is larger than that in any other complex.

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## Structure of $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$ at 293 K

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**Abstract.** Tetramethylphosphonium tetrabromocuprate(II),  $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$ ,  $M_r = 565.08$ , monoclinic,  $P2_1/b11$ ,  $a = 9.493$  (2),  $b = 31.673$  (1),  $c = 13.046$  (1) Å,  $\alpha = 90.17$  (2)°,  $V = 3922.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.909$  (3),  $D_x = 1.911$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 9.874$  mm<sup>-1</sup>,  $F(000) = 2168$ ,  $T = 293$  K,  $R = 0.064$  for 2368 unique observed reflections. Differential scanning calorimetry showed two phase transitions at 193 and 404 K, respectively. The space group, *Pm* $\bar{c}$ *n*, and the cell parameters of the

high-temperature phase have also been determined by X-ray precession photographs. The monoclinic structure can be described as a commensurate distortion (with wave vector  $\mathbf{q} = 1/2 \mathbf{b}_0^*$ ) of the orthorhombic phase.

**Introduction.** Compounds belonging to the  $A_2BX_4$  family have been exhaustively studied in the last few years. The main reason is the rich variety of commensurate and incommensurate (IC) phases pre-

sented by these materials. The majority of members of this family are known to have a common orthorhombic high-temperature phase with space group *Pmcn*. Among them, those compounds with the tetramethylammonium (TMA) group as monovalent cation constitute an important subfamily for which a common pressure-temperature phase diagram has been proposed (Axe, Iizumi & Shirane, 1986). Nevertheless, and apparently as a general rule, compounds in which the central atom of the anion is Cu present special features and cannot be put in such a phase diagram. As an additional difficulty,  $\text{CuX}_4$  tetrahedra show a strong Jahn-Teller distortion (Clay, Murray-Rust & Murray-Rust, 1975; Trouelan, Lefebvre & Derollez, 1984; Hasebe, Mashiyama & Tanisaki, 1985; Madariaga, Zúñiga, Paciorek & Bocanegra, 1990) which probably contributes to their unusual phase-transition scheme.

In contrast to what happens in the chloride compounds, there is no evidence of IC phases in the  $(\text{TMA})_2\text{ZnBr}_4$ ,  $(\text{TMA})_2\text{CoBr}_4$  or  $(\text{TMA})_2\text{MnBr}_4$  compounds, although an IC structure appears in the isomorphous  $(\text{TMA})_2\text{CuBr}_4$ . However, a new feature arises in this material: the modulation wave vector direction in its IC phase ( $\mathbf{b}^*$ ) is perpendicular to the common direction ( $\mathbf{c}^*$ ) shown by the other incommensurate TMA compounds.

It has been argued, given the characteristic behaviour of bromide compounds as well as the experimental results for deuterated derivatives, that the anion and cation sizes play an important role in the stability range of the phases of these materials. In this way, the study of analogous compounds containing different cations could represent an important advance in the systematization of the phase behaviour exhibited by these materials.

Up to now only four derivatives have been investigated:  $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$  (Pressprich, Bond, Willet & White, 1989),  $[\text{As}(\text{CH}_3)_4]_2\text{CoCl}_4$ ,  $[\text{As}(\text{CH}_3)_4]_2\text{ZnCl}_4$  (Zúñiga *et al.*, 1990) and the present compound  $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$ .

From a structural point of view  $[\text{As}(\text{CH}_3)_4]_2\text{CoCl}_4$  constitutes a surprising material since it exhibits tetragonal symmetry above and below all the detected phase-transition temperatures.

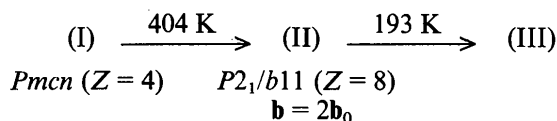
Starting from its high-temperature phase,  $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$  shows an initial sequence of phase transitions [*Pmcn*-IC-*P12<sub>1</sub>/c1* ( $\mathbf{q} = \frac{1}{3}\mathbf{c}^*$ )], very similar to the corresponding one in  $(\text{TMA})_2\text{CuCl}_4$  but significantly shifted to higher temperatures.

As will be shown, the phase transition scheme in the  $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$  compound is simpler than those observed in  $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$  and  $(\text{TMA})_2\text{CuBr}_4$ , and apparently does not contain any IC phase. However, its room-temperature structure, presented here, can be related (in spite of the symmetry differences) to the IC and lock-in phases (Madariaga, Zúñiga,

Paciorek & Bocanegra, 1990) which are present in  $(\text{TMA})_2\text{CuBr}_4$ .

**Experimental.** Dark violet crystals were kindly supplied by M. R. Pressprich from Washington State University. Differential scanning calorimetry measurements were obtained on a Perkin-Elmer DSC7 using a scan rate of  $5 \text{ K min}^{-1}$ . Only two clear anomalies were observed relating the three phases, labelled, as the temperature decreases, (I), (II) and (III), respectively.

The space groups of phases (I) (at 433 K) and (II) (at 293 K) were determined from the systematic absences detected in precession photographs. Phase (I) was found to be orthorhombic with space group *Pmcn*, assuming the existence of a symmetry centre. For this phase, lattice constants are  $a_0 = 9.56$ ,  $b_0 = 16.07$  and  $c_0 = 13.29 \text{ \AA}$  and  $Z = 4$ . At room temperature, the presence of strong superstructure reflections indicated a duplication of the lattice along  $\mathbf{b}_0$ . Therefore, the phase sequence can be schematized as follows:



Intensity data collection at 293 K was made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation on which a prismatic crystal ( $0.26 \times 0.36 \times 0.4 \text{ mm}$ ) was mounted.  $D_m$  by flotation. Unit-cell parameters were refined using a set of 25 reflections ( $5.9 < \theta < 15.4^\circ$ ). Intensity data were collected by the  $\omega$ - $2\theta$  scan technique, up to  $\sin\theta/\lambda = 0.7 \text{ \AA}^{-1}$ . Range of *hkl*:  $0 < h < 9$ ,  $0 < k < 38$ ,  $-15 < l < 15$ . Three check reflections were measured every 2 h without significant variation. Absorption correction was carried out by Gaussian integration ( $\text{Abs}_{\text{max/min}} = 7.67\text{--}20.91$ ). A total of 15114 reflections collected, 6147 unique reflections ( $R_{\text{int}} = 0.054/0.057$  with and without absorption correction, respectively) of which 2368, with the criterion  $I > 3\sigma(I)$ , were labelled observed. Lorentz and polarization corrections were applied. Cu and Cl atoms were located by direct methods. The rest of the atoms were found by successive difference Fourier syntheses.

Refinements based on  $|F|$ , in full-matrix mode. Final agreement factors were  $R = 0.064$ ,  $wR = 0.08$  with  $w = 1/\sigma^2(F)$ ;  $S = 1.74$ ,  $(\Delta/\sigma)_{\text{max}} = 0.51$ . Scattering factors for neutral atoms from Cromer & Mann (1968) and anomalous-dispersion correction for Cu and Br atoms, from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 55, 99, 149). No attempt was made to locate the H atoms. A final difference synthesis showed peaks of  $1.3 \text{ e \AA}^{-3}$ .

Table 1. Positional and equivalent isotropic atomic displacement parameters of  $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$  with *e.s.d.*'s in parentheses
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{Å}^2)$
Cu(1)	0.2156 (2)	0.19563 (5)	0.2208 (1)	0.0678 (6)
Br(11)	0.1883 (2)	0.17909 (5)	0.0439 (1)	0.0834 (6)
Br(12)	0.0247 (2)	0.15616 (5)	0.2856 (1)	0.1059 (7)
Br(13)	0.1816 (2)	0.25960 (5)	0.3168 (1)	0.1036 (7)
Br(14)	0.4620 (2)	0.18917 (8)	0.2336 (1)	0.146 (1)
Cu(2)	0.7702 (2)	0.44474 (5)	0.2753 (1)	0.0732 (6)
Br(21)	0.9808 (2)	0.40782 (5)	0.2369 (1)	0.1053 (7)
Br(22)	0.7469 (2)	0.42763 (5)	0.4510 (1)	0.1131 (8)
Br(23)	0.8179 (2)	0.51016 (5)	0.1916 (1)	0.1147 (8)
Br(24)	0.5316 (2)	0.43648 (9)	0.2310 (2)	0.168 (1)
P(1)	0.2442 (4)	0.2096 (1)	0.6162 (2)	0.062 (1)
C(11)	0.259 (2)	0.2653 (4)	0.601 (1)	0.091 (6)
C(12)	0.378 (2)	0.1860 (4)	0.537 (1)	0.093 (6)
C(13)	0.273 (2)	0.1966 (5)	0.747 (1)	0.124 (8)
C(14)	0.075 (2)	0.1919 (5)	0.574 (1)	0.109 (7)
P(2)	0.2432 (4)	0.3264 (1)	0.0178 (3)	0.066 (1)
C(21)	0.069 (1)	0.3132 (5)	0.058 (1)	0.093 (6)
C(22)	0.360 (2)	0.3337 (6)	0.1287 (9)	0.124 (8)
C(23)	0.306 (2)	0.2865 (4)	-0.064 (1)	0.098 (7)
C(24)	0.232 (2)	0.3760 (4)	-0.054 (2)	0.137 (9)
P(3)	0.2476 (4)	0.0425 (1)	0.1201 (3)	0.069 (1)
C(31)	0.379 (2)	0.0727 (4)	0.054 (1)	0.106 (7)
C(32)	0.075 (2)	0.0563 (4)	0.076 (1)	0.111 (7)
C(33)	0.268 (2)	0.0518 (6)	0.259 (1)	0.130 (9)
C(34)	0.278 (2)	-0.0133 (4)	0.099 (1)	0.097 (7)
P(4)	0.2457 (4)	0.4237 (1)	0.5193 (3)	0.080 (2)
C(41)	0.403 (2)	0.4427 (5)	0.584 (1)	0.116 (7)
C(42)	0.282 (2)	0.3800 (5)	0.435 (3)	0.119 (8)
C(43)	0.165 (4)	0.4629 (6)	0.452 (3)	0.25 (2)
C(44)	0.126 (3)	0.4023 (9)	0.618 (2)	0.24 (2)

These high values of  $\Delta\rho$  will be discussed below. Computer programs: *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), *MULTAN84* (Main, Germain & Woolfon, 1984) and *SCHAKAL88* (Keller, 1989).

**Discussion.** Final positional coordinates and equivalent atomic displacement parameters are given in Table 1.\* The most relevant interatomic distances and bond angles are listed in Table 2.

The structure, excluding H atoms, consists of  $\text{CuBr}_4$  and  $\text{PC}_4$  tetrahedra occupying general positions close to the  $\sigma_x$  mirror plane present in the high-temperature phase. Their small displacements from this plane are indeed responsible for the symmetry breaking and cause the appearance of a two-fold commensurate superstructure along the *b* axis. A projection of the structure parallel to the [001] direction can be seen in Fig. 1. The stacking of the tetrahedra along the *b* axis is shown in Fig. 2.

The  $\text{CuBr}_4$  groups adopt a flattened shape characteristic of the Jahn–Teller distortion, which also appears in the isomorphous  $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$  (Clay, Murray-Rust & Murray-Rust, 1975) and  $[\text{N}$

Table 2. Interatomic distances (Å) and bond angles (°) of  $[\text{P}(\text{CH}_3)_4]_2\text{CuBr}_4$  with *e.s.d.*'s in parentheses

Distances corrected for libration are included in square brackets.

Atom 1	Central Atom	Atom 2	Interatomic distance	Bond Angle
	Cu(1)	Br(11)	2.379 (2)	[2.393]
		Br(12)	2.360 (2)	[2.394]
		Br(13)	2.401 (2)	[2.423]
		Br(14)	2.354 (3)	[2.388]
Br(11)	Cu(1)	Br(12)		98.53 (8)
Br(11)		Br(13)		132.41 (8)
Br(12)		Br(13)		99.03 (8)
Br(11)		Br(14)		99.09 (8)
Br(12)		Br(14)		133.7 (1)
Br(13)		Br(14)		99.80 (9)
	Cu(2)	Br(21)	2.369 (3)	[2.404]
		Br(22)	2.367 (2)	[2.392]
		Br(23)	2.388 (2)	[2.415]
		Br(24)	2.351 (3)	[2.393]
Br(21)	Cu(2)	Br(22)		99.74 (7)
Br(21)		Br(23)		99.89 (7)
Br(22)		Br(23)		131.43 (8)
Br(21)		Br(24)		134.9 (1)
Br(22)		Br(24)		97.0 (1)
Br(23)		Br(24)		99.5 (1)
	P(1)	C(11)	1.78 (1)	[1.818]
		C(12)	1.80 (1)	[1.835]
		C(13)	1.77 (2)	[1.815]
		C(14)	1.78 (2)	[1.826]
C(11)	P(1)	C(12)		106.7 (7)
C(11)		C(13)		109.2 (7)
C(12)		C(13)		110.2 (8)
C(11)		C(14)		110.1 (7)
C(12)		C(14)		109.0 (7)
C(13)		C(14)		111.2 (8)
	P(2)	C(21)	1.78 (1)	[1.806]
		C(22)	1.83 (1)	[1.874]
		C(23)	1.75 (1)	[1.803]
		C(24)	1.83 (2)	[1.880]
C(21)	P(2)	C(22)		110.7 (7)
C(21)		C(23)		108.8 (7)
C(22)		C(23)		111.4 (8)
C(21)		C(24)		107.3 (8)
C(22)		C(24)		109.3 (9)
C(23)		C(24)		108.9 (8)
	P(3)	C(31)	1.80 (2)	[1.845]
		C(32)	1.79 (2)	[1.825]
		C(33)	1.85 (2)	[1.900]
		C(34)	1.80 (1)	[1.840]
C(31)	P(3)	C(32)		110.6 (7)
C(31)		C(33)		108.3 (8)
C(32)		C(33)		111.9 (8)
C(31)		C(34)		109.6 (7)
C(32)		C(34)		109.6 (7)
C(33)		C(34)		106.5 (8)
	P(4)	C(41)	1.81 (2)	[1.879]
		C(42)	1.80 (2)	[1.868]
		C(43)	1.70 (3)	[1.810]
		C(44)	1.84 (3)	[1.948]
C(41)	P(4)	C(42)		112.3 (8)
C(41)		C(43)		111.5 (1)
C(42)		C(43)		109.0 (1)
C(41)		C(44)		107.8 (1)
C(42)		C(44)		105.1 (1)
C(43)		C(44)		110.7 (1)

$(\text{CH}_3)_4]_2\text{CuBr}_4$  (Trouelan, Lefebvre & Derollez, 1984; Hasebe, Mashiyama & Tanisaki, 1985; Madariaga, Zúñiga, Paciorek & Bocanegra, 1990) compounds. Cu(1)—Br distances (see Table 2) range from 2.354 to 2.401 Å with a mean value of 2.377 Å. Distances involving Cu(2) and Br atoms show a similar dispersion with minimum and maximum values of 2.351 and 2.388 Å, respectively, around their mean value, 2.369 Å. The distortion of both  $\text{CuBr}_4$  groups with respect to the ideal tetrahedral configuration can be deduced from the values of the Br—Cu—Br bond angles presented in Table 2. Each  $\text{PC}_4$  tetrahedron

\* Lists of structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53182 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shows a more homogeneous distribution of bond angles [all C—P—C bond angles can be covered by the interval (105.2, 111.9°)], indicating a geometrical distortion smaller than that of the inorganic groups. The mean length of the P—C bond is 1.798 Å.

The anisotropic atomic displacement parameters of Br and C atoms show very large values. This is usual in other  $A_2BX_4$  compounds with organic cations. Hence, a librational thermal motion analysis based on the atomic temperature tensors was performed. Results indicate that the thermal motion of the tetrahedra can be well described by the T and L tensors (Schomaker & Trueblood, 1968) whereas the S tensor is, in all cases, almost negligible. In general the translational and librational displacements seem to be isotropic and anisotropic, respectively, although no clear conclusions (about the most important libration axis, for example) can be extracted from this. Residual deformations obtained from the agreement between the observed and calculated anisotropic atomic displacement parameters are significantly higher for  $PC_4$  groups.

When the bond lengths are corrected for thermal motion the mean values of Cu—Br and P—C are 2.400 and 1.848 Å, respectively.

As mentioned in *Experimental*, the final difference synthesis showed peaks with significant values. The

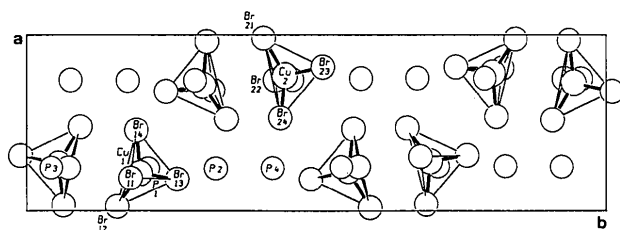


Fig. 1. Projection of the structure onto the  $ab$  plane. C atoms have been omitted for clarity.

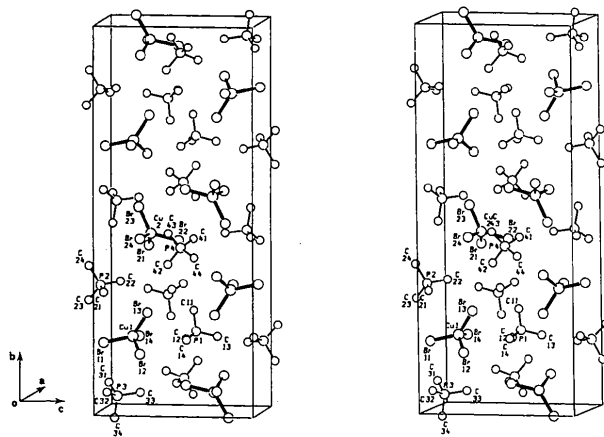


Fig. 2. Stereoscopic view of the unit cell at 293 K. The frame indicates the orientation of the cell axes.

most important appear to be in the Br—Cu—Br planes and very close to Cu atoms. This fact has already been observed in the isomorphous  $[N(CH_3)_4]_2CuBr_4$  (Trovellan, Lefebvre & Derollez, 1984) and could be another indication of the above cited Jahn–Teller distortion.

Phase (II) of  $[P(CH_3)_4]_2CuBr_4$  can be considered as a displacive commensurate modulation of the orthorhombic high-temperature structure, with wave vector  $q = 1/2 b_0^*$  [ $b_0^*$  being the reciprocal axis of the phase (I) structure]. Recently the structure of the IC phase of the TMA derivative has been solved (Madariaga, Zúñiga, Paciorek & Bocanegra, 1990). From the amplitudes and phases of the incommensurate modulation, both the lock-in phase of  $[N(CH_3)_4]_2CuBr_4$  and the present structure were extrapolated. This important result shows that the distortion in both compounds is formally identical and the difference in the space groups of the mentioned commensurate phases is only due to a different value in the global phase of the modulation. Moreover, the difference in the cation size seems to be irrelevant in the structural distortion, affecting only the stability range of the phases shown by these materials.

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