$$[Co(C_4H_{13}N_3)(C_6H_{17}N_3)]^{3+}.S_2O_6^{2-}.ClO_4^-.H_2O$$

Also, the conformational geometry observed in the solid-state structure of each of the three isomers is either that with the calculated minimum energy or a conformation of energy close to the minimum. Table 2 gives a comparison of the solid-state structure with that calculated by the energy-minimization method for the same conformer of the *s-fac* isomer. The molecular-mechanics model represents an isolated complex molecule, so that some discrepancies can be expected because of the influence of packing and hydrogen bonding on the solid-state structure. However, good general agreement is observed, and in particular the above-mentioned distortions are well reproduced in the theoretical model.

In D_2O solution, the ^{13}C NMR spectrum indicates that the complex cation has effective mirror symmetry (point group C_s) due to conformational averaging (Searle & Hambley, 1982b).

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Studies on Tetramethylammonium Tetrabromometallates. I. Structures of Tetramethylammonium Tetrabromocuprate(II), [N(CH₃)₄]₂[CuBr₄], and —zincate(II), [N(CH₃)₄]₂[ZnBr₄], at Room Temperature

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Abstract. Cu isomorph: $M_r = 531\cdot1$, orthorhombic, *Pnma*, $a = 12\cdot600$ (4), $b = 9\cdot326$ (2), $c = 15\cdot825$ (6) Å, $V = 1860$ (2) Å^3, $Z = 4$, $D_m = 1\cdot92$ (1), $D_x = 1\cdot898$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0\cdot7107$ Å, $\mu = 103$ cm^{-1}, $F(000) = 1020$, $T = 293$ (2) K, final $R = 0\cdot060$ for 585 observed reflections. Zn isomorph: $M_r = 533\cdot0$, orthorhombic, *Pnma*, $a = 12\cdot681$ (4), $b = 9\cdot239$ (3), $c = 16\cdot025$ (6) Å, $V = 1877$ (2) Å^3, $Z = 4$, $D_m = 1\cdot91$ (1), $D_x = 1\cdot887$ g cm^{-3}, $\mu = 104$ cm^{-1}, $F(000) = 1024$, final $R = 0\cdot059$ for 898 observed reflections. The ZnBr₄ tetrahedron is slightly distorted as explained by the crystal-field effect; Br—Cu—Br angles of the CuBr₄ tetrahedron range from 102·0 to 126·6° due to a Jahn–Teller distortion. The mean bond length is 2·426 Å for Cu—Br and 2·447 Å for Zn—Br. The N(CH₃)₄ groups are affected by large oscillations.

Introduction. Recently, physical properties of tetramethylammonium tetrahalogenometallate crystals $\{[N(CH_3)_4]_2[MX_4]$, with $M = $ Zn, Co, Ni, Fe, Cu, Hg and $X = $ Cl, Br, I$\}$ have been intensively studied because of the existence of successive phase transitions. Some of these compounds show a modulated phase: [N(CH₃)₄]₂[ZnCl₄], [N(CH₃)₄]₂[CoCl₄] (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978), [N(CH₃)₄]₂[CuBr₄] (Gesi, 1982). These compounds are known to have an orthorhombic high-temperature phase with space group *Pnma*. But an important difference occurs between the members of this series for the modulated phase: for tetramethylammonium tetrachlorozincate and -cobaltate, the modulation direction is along **a*** and for tetramethylammonium tetrabromocuprate, it is along **c***.

In this paper, the structures of $[N(CH_3)_4]_2[CuBr_4]$ and $[N(CH_3)_4]_2[ZnBr_4]$ (hereafter named TMAT BrCu and TMAT BrZn respectively) are reported at room temperature in the high-temperature phase. The former undergoes a commensurate–incommensurate phase transition at 272 K, while the latter has a commensurate–commensurate phase transition at 286 K (Gesi, 1982). The aim of this study is to show structural differences allowing us to explain the existence of a modulated phase for the Cu compound in comparison with the Zn one. This paper forms part of a more complete study of the structures of tetramethylammonium tetrabromomometallates in their different phases.

Experimental. TMAT BrCu and TMAT BrZn prepared from a mixture of tetramethylammonium bromide and copper or zinc bromide respectively in water; single crystals obtained by cooling these mixtures. Crystal sizes: $0.20 \times 0.20 \times 0.15$ and $0.25 \times 0.20 \times 0.15$ mm for Cu and Zn compounds respectively. D_m determined pycnometrically. Diffraction intensity measurements at room temperature collected using a Philips PW 1100 automatic diffractometer with monochromated Mo $K\alpha$ radiation. 25 reflections used for measuring lattice parameters. θ–2θ technique up to $\theta = 26°$ ($\sin \theta/\lambda = 0.62$ Å^{-1}), scan width $1.2°$, scan speed $0.016°$ s^{-1}. Background counted for half total scan on each side of $K\alpha$ position. Three standard reflections monitored every hour ($1\bar{2}3$, 020 and 111 for Cu compound, 022, $0\bar{2}2$ and 104 for Zn derivative), no significant change in intensities observed. For TMAT BrCu, 2468 reflections measured corresponding to 585 non-equivalent reflections with $I > 3\sigma(I)$ in range $0 \le h \le 15$; $0 \le k \le 12$; $0 \le l \le 19$. For TMAT BrZn, 2173 reflections measured with 898 non-equivalent reflections in same conditions. Data corrected for Lorentz and polarization effects. Calculated absorption coefficients are 103 cm^{-1} for TMAT BrCu and 104 cm^{-1} for TMAT BrZn. Because of the complicated shape of the TMAT BrZn single crystal, it was difficult to correct for absorption effects. Furthermore, systematic measurements of four equivalent reflections showed a maximum discrepancy of 3% in intensity. For TMAT BrCu, absorption corrections have been computed by *ABSORB* (Templeton & Templeton, 1973).

Some discrepancies are noted between values of the parameters obtained by Gesi (1982) and our determinations, particularly for the Cu compound. Systematic absences of $hk0$ reflections for $h = 2n+1$ and $0kl$ for $k+l = 2n+1$ confirm $Pn2_1a$ and $Pnma$ as possible space groups for the two compounds. The positions of the heavy atoms of chlorine isomorphs have been taken as starting parameters for the least-squares procedure (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967; Clay, Murray-Rust & Murray-Rust, 1975). Refinements with isotropic tem-

perature factors gave an R of 0.194 for TMAT BrCu and 0.186 for TMAT BrZn in the centrosymmetric $Pnma$ space group. N and C atoms were located by subsequent series of Fourier syntheses and least-squares refinement. Refinement of positional and isotropic thermal parameters for all atoms reduced R to 0.176 and 0.172 for Cu and Zn compounds respectively. Finally, introduction of anisotropic thermal parameters for all atoms reduced R to 0.060 for TMAT BrCu and 0.059 for TMAT BrZn ($wR = 0.063$ for both compounds, unit weights). Shifts in atomic parameters at final cycle < 0.2 σ. Six reflections for Cu compound and seven for Zn compound with a low-angle reflection and a high intensity were removed, because of the possibility of extinction effects.

Attempts were made with the non-centrosymmetric space group $Pn2_1a$. From the final values found with the $Pnma$ space group, refinements have been performed with the $Pn2_1a$ space group. Despite the higher number of parameters the R factors for the two structures are approximately the same as for the $Pnma$ space group. In addition, most of the anisotropic thermal parameters increase abnormally. For these reasons, it seems that the centrosymmetric $Pnma$ space group agrees with the description of the structure of TMAT BrCu and TMAT BrZn compounds.

Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion effects for heavy atoms taken into account (Cromer & Liberman, 1970). A final difference synthesis showed peaks of 0.92 e Å^{-3} for TMAT BrCu and 0.75 e Å^{-3} for TMAT BrZn. The high value of the Fourier difference peak for TMAT BrCu will be discussed below. Because of the high thermal vibrations of the C atoms of the methylammonium ions, no H atom could be located. Calculations carried out with *SHELX*76 (Sheldrick, 1976).

Discussion. The final atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.* An *ORTEP*II (Johnson, 1976) drawing of the structure of TMAT BrCu is shown in Fig. 1.

The $Pnma$ space group requires the $[MBr_4]^{2-}$ and the two independent $[N(CH_3)_4]^+$ tetrahedra to lie on the mirror plane parallel to (010) at $y = \frac{1}{4}$.

The most exceptional feature exhibited by the structures is the unusually large values of the thermal parameters. This fact has been observed in many isomorphous compounds: $[N(CH_3)_4]_2[MCl_4]$ with M = Co, Ni, Zn (Wiesner et al., 1967), M = Cu (Clay et al., 1975). In the present case where Cl atoms have

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* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39005 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

been replaced by heavier Br atoms, the mean r.m.s. displacement for these atoms is of the order of 0·35 Å. For the C atoms of the $[N(CH_3)_4]^+$ ions, this value increases to ~ 0·5 Å with very large anisotropic values for the thermal parameters.

A rigid-body analysis (Schomaker & Trueblood, 1968) has been made using U_{ij} values calculated by *SHELX*76 and the results are given in Table 3 for heavy tetrahedra. In both cases, the translational tensor **T** is almost isotropic: only the T_{11} value for TMAT BrZn is a little lower than T_{22} and T_{33}. The librational tensor **L** exhibits a large anisotropy: L_{11} is about two times higher than L_{22} and L_{33} for the two compounds. For the $[N(CH_3)_4]^+$ ions, the thermal parameters are very large for the C atoms. These results suggest either rotational thermal vibrations for these ions or a rotational disorder.

When the bond lengths are corrected for thermal motion, the mean values for Cu−Br and Zn−Br become 2·426 and 2·447 Å respectively. The $[MBr_4]^{2-}$ tetrahedra appear to be distorted in the form of flattened tetrahedra. For TMAT BrZn, the tetrahedron angles range from 108·6 to 112·2°. This small distortion can be attributed to the simple crystal-field effect. For TMAT BrCu, angles of the $[CuBr_4]^{2-}$ tetrahedron range from 102·0 to 126·6° and in this case, it is a Jahn–Teller distortion. This is a well-known effect in tetrahedra with Cu as the central atom: for example, there is a similar distortion in $[N(CH_3)_4]_2[CuCl_4]$ (Clay *et al.*, 1975) where angles of the $[CuCl_4]^{2-}$ tetrahedron range from 100·8 to 132·1°. In our case, with the values for Cu−Br bond lengths and Br−Cu−Br angles mentioned above, the calculated Br−Br contact lengths appear to be of the order of 3·78 Å for smaller values of the Br−Cu−Br angle and 4·30 Å for the larger values. It should be noted that the smaller Br−Br lengths correspond to just twice the van der Waals radii (1·89 Å; Scott & Sheraga, 1965). As mentioned above, the final difference synthesis
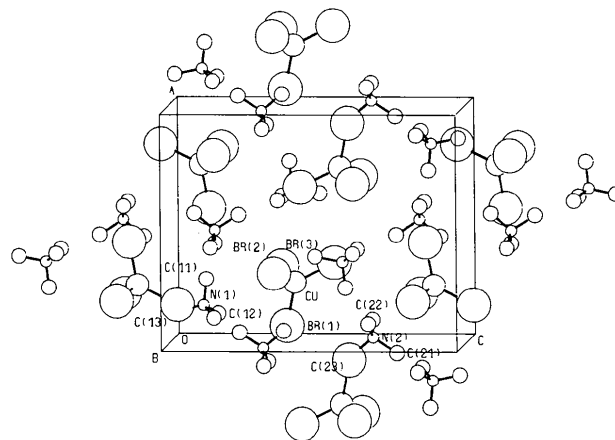

Fig. 1. *ORTEP*II drawing of the unit-cell contents of TMAT BrCu.

showed peaks with significant values. The two highest peaks, corresponding to 0·92 and 0·59 e Å⁻³, are located in the Br(2)−Cu−Br′(2) plane. In the same manner the deepest hole of −0·52 e Å⁻³ is in the Br(1)−Cu−Br(3) plane. It can be suggested that these peaks and this hole are due to the electronic-shell distortion generally known as the Jahn–Teller effect.

For $[N(CH_3)_4]^+$ tetrahedra, C−N−C angles range from 104 to 115° with an error bar of 3° for the two compounds. It is difficult to determine if there is a distortion of the tetrahedra. The C−N bond lengths range from 1·38 to 1·51 Å when thermal vibrations are not taken into account and from 1·62 to 1·77 Å when corrections are applied. The uncorrected mean values for the C−N bond (1·45 Å for TMAT BrCu and 1·44 Å for TMAT BrZn) are comparable with the mean values found in isomorphs (see, for instance, Kamenar & Nagl, 1976). The corrected values of C−N bond lengths seem to be too high. In $[N(CH_3)_4]_2[CdI_4]$, the corrected mean value is 1·53 Å (Kallel, Bats & Daoud, 1981).

Table 1. *Positional parameters and equivalent Debye–Waller factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} trace \, \mathbf{U}.$$

	TMAT BrCu				TMAT BrZn			
	x	y	z	U_{eq}	x	y	z	U_{eq}
M^*	0·2377 (3)	$\frac{1}{4}$	0·4072 (2)	72 (2)	0·2491 (2)	$\frac{1}{4}$	0·4081 (1)	56 (1)
Br(1)	0·0532 (3)	$\frac{1}{4}$	0·3804 (3)	124 (4)	0·0605 (2)	$\frac{1}{4}$	0·4034 (2)	95 (2)
Br(2)	0·2903 (2)	0·0272 (3)	0·3503 (2)	146 (3)	0·3128 (2)	0·0375 (2)	0·3384 (1)	114 (2)
Br(3)	0·3208 (3)	$\frac{1}{4}$	0·5413 (2)	135 (4)	0·3148 (3)	$\frac{1}{4}$	0·5479 (2)	120 (3)
N(1)	0·139 (2)	$\frac{1}{4}$	0·099 (2)	102 (21)	0·152 (1)	$\frac{1}{4}$	0·098 (1)	78 (12)
N(2)	0·003 (2)	$\frac{1}{4}$	0·670 (2)	84 (18)	−0·017 (1)	$\frac{1}{4}$	0·671 (1)	67 (11)
C(11)	0·250 (3)	$\frac{1}{4}$	0·108 (4)	229 (53)	0·261 (2)	$\frac{1}{4}$	0·099 (3)	240 (39)
C(12)	0·094 (3)	0·124 (3)	0·141 (3)	232 (38)	0·112 (3)	0·124 (4)	0·145 (2)	279 (38)
C(13)	0·115 (4)	$\frac{1}{4}$	0·007 (3)	229 (53)	0·104 (3)	$\frac{1}{4}$	0·016 (2)	266 (38)
C(21)	−0·062 (4)	$\frac{1}{4}$	0·750 (3)	183 (40)	−0·058 (3)	$\frac{1}{4}$	0·757 (2)	153 (28)
C(22)	0·069 (3)	0·127 (3)	0·662 (2)	228 (35)	0·046 (3)	0·127 (3)	0·657 (2)	243 (29)
C(23)	−0·069 (4)	$\frac{1}{4}$	0·601 (3)	243 (55)	−0·097 (3)	$\frac{1}{4}$	0·607 (2)	223 (39)

* Either Cu or Zn.

Table 2. *Molecular geometry*

	TMAT BrCu		TMAT BrZn	
	Uncorrected	Corrected	Uncorrected	Corrected
(a) Bond lengths (Å)				
M–Br(1)	2·364 (5)	2·426	2·393 (3)	2·445
M–Br(2)	2·360 (3)	2·423	2·398 (2)	2·452
M–Br(3)	2·366 (5)	2·430	2·390 (3)	2·443
N(1)–C(11)	1·42 (4)	1·62	1·38 (3)	1·66
N(1)–C(12)	1·46 (3)	1·68	1·48 (3)	1·77
N(1)–C(13)	1·49 (4)	1·71	1·46 (3)	1·75
N(2)–C(21)	1·51 (4)	1·74	1·47 (3)	1·73
N(2)–C(22)	1·42 (3)	1·63	1·41 (2)	1·65
N(2)–C(23)	1·42 (5)	1·64	1·44 (3)	1·69
Br(1)–Br(2)	3·670 (4)	3·768	3·896 (3)	3·981
Br(1)–Br(3)	4·226 (5)	4·338	3·969 (5)	4·057
Br(2)–Br(3)	3·689 (4)	3·787	3·889 (3)	3·974
Br(2)–Br'(2)	4·155 (4)	4·267	3·926 (3)	4·013
(b) Angles (°)				
Br(1)–M–Br(2)	102·0 (1)		108·8 (1)	
Br(1)–M–Br(3)	126·6 (2)		112·2 (1)	
Br(2)–M–Br(3)	102·6 (1)		108·6 (1)	
Br(2)–M–Br'(2)	123·4 (2)		109·9 (1)	
C(11)–N(1)–C(12)	109 (2)		110 (2)	
C(11)–N(1)–C(13)	107 (4)		115 (3)	
C(12)–N(1)–C(13)	112 (2)		109 (2)	
C(12)–N(1)–C'(12)	107 (4)		104 (4)	
C(21)–N(2)–C(22)	113 (2)		110 (2)	
C(21)–N(2)–C(23)	107 (3)		114 (3)	
C(22)–N(2)–C(23)	107 (3)		107 (2)	
C(22)–N(2)–C'(22)	108 (3)		108 (3)	

The primed atoms correspond to the atom obtained from the original atom by the symmetry plane at $y = \frac{1}{4}$.

This study is part of a more general study of tetramethylammonium tetrabromometallate compounds. In particular, a study at low temperature is planned in the near future.

Table 3. *Rigid-body vibration parameters for the heavy tetrahedra*

	[CuBr₄]²⁻			[ZnBr₄]²⁻		
T(Å² × 10⁴)	653 (34)	0	48 (45)	474 (10)	0	12 (14)
		765 (37)	0		636 (12)	0
			768 (44)			537 (12)
L(rad² × 10⁴)	272 (10)	0	64 (18)	215 (3)	0	−8 (7)
		114 (18)	0		88 (5)	0
			150 (11)			136 (5)
S(Å rad × 10⁴)	0	−45 (19)	0	0	−16 (6)	0
	28 (18)	0	7 (15)	29 (6)	0	5 (5)
	0	−44 (16)	0	0	29 (5)	0
R.m.s. ($U^o − U^c$) (Å² × 10⁴)	55			17		
E.s.d. U^o_{ij} (Å² × 10⁴)	57			17		

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Structure of Disodium Uridine Diphosphoglucose Dihydrate, C₁₅H₂₂N₂O₁₇P₂²⁻.2Na⁺.2H₂O, and Refinement of Dipotassium Glucose 1-Phosphate Dihydrate, C₆H₁₁O₉P²⁻.2K⁺.2H₂O (Monoclinic Form)

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Abstract. C₁₅H₂₂N₂O₁₇P₂²⁻.2Na⁺.2H₂O: $M_r = 646·3$, monoclinic, $P2_1$, $a = 8·950$ (2), $b = 18·724$ (4), $c = 7·289$ (2) Å, $\beta = 101·98$ (2)°, $V = 1194·9$ (4) Å³, $Z = 2$, $D_x = 1·796$, $D_m = 1·80$ Mg m⁻³, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 0·329 mm⁻¹, $F(000) = 668$, $T = 293$ K, $R = 0·049$ for 5895 observed reflections. C₆H₁₁O₉P²⁻.2K⁺.2H₂O: $M_r = 372·3$, $P2_1$, $a = 10·458$ (3), $b = 9·027$ (1), $c = 7·532$ (2) Å, $\beta =$