

## The Crystal Structure of Bis(3,4,5-trimethoxyphenethylammonium) Tetrachlorocuprate(II) Monohydrate, a Complex Salt of Mescaline

BY H. J. BUSER AND GEORGE W. WATT

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

(Received 8 December 1977; accepted 7 September 1978)

### Abstract

The title compound,  $[\text{NH}_3(\text{C}_{11}\text{H}_{15}\text{O}_3)]_2[\text{CuCl}_4] \cdot \text{H}_2\text{O}$ ,  $\text{C}_{22}\text{H}_{36}\text{Cl}_4\text{CuN}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , forms triclinic crystals, space group  $P\bar{1}$ ,  $Z = 2$ ,  $M_r = 647.92$ , with  $a = 8.698$  (1),  $b = 23.145$  (3),  $c = 7.427$  (1) Å,  $\alpha = 93.99$  (1),  $\beta = 99.22$ ,  $\gamma = 99.20$  (1)°,  $V = 1449.9$  Å<sup>3</sup> at 238 K, and  $a = 8.732$  (2),  $b = 23.184$  (5),  $c = 7.467$  (1) Å,  $\alpha = 93.99$  (1),  $\beta = 99.19$  (1),  $\gamma = 99.09$  (1)°,  $V = 1466.6$  Å<sup>3</sup>,  $d_x = 1.460$ ,  $d_m = 1.467$  Mg m<sup>-3</sup> at 297 K. Of the 6662 independent intensities, measured on an automated four-circle diffractometer (Syntex P2<sub>1</sub>) at 238 K, 5153 were used for the anisotropic full-matrix least-squares refinement to a conventional  $R$  of 0.037 and a weighted  $R$  of 0.043. The structure consists of separated  $\text{CuCl}_4^{2-}$  ions which are two-dimensionally linked by a network of hydrogen bonds involving the  $\text{NH}_3^+$  groups and the water molecules. The  $\text{CuCl}_4^{2-}$  ion has nearly  $D_{2d}$  symmetry with two large Cl–Cu–Cl angles in the ‘flattened tetrahedron’ of 130.2 and 132.8°. The hydrophobic part of the two independent mescaline molecules fills the space between the layers containing the polar portions of the structure. Both mescaline molecules have a similar conformation with maximally spaced methoxy groups and an  $\text{NH}_3^+$  group approaching the benzene ring. The conformation is equivalent to that of mescaline hydrobromide, but different from that of the hydrochloride.

### Introduction

In the course of investigations of first row transition-metal complexes of hallucinogenic drugs, it was found that mescaline hydrochloride forms well-defined complex salts with the general formula  $(\text{mescH})_2\text{MCl}_4 \cdot n\text{H}_2\text{O}$  where mescH represents the protonated 3,4,5-trimethoxyphenethylamine (mescaline) molecule. In the case of the Cu compounds several products with marked differences in color and physical properties were obtained; the details will be published elsewhere. The monohydrate obtained at 298 K was found to undergo a slow, reversible color change from orange to green at *ca* 278 K, similar to the thermochromism

reported for a few other anhydrous tetrachlorocuprates (Wang & Drickamer, 1973; Harlow, Wells, Watt & Simonsen, 1974; Willett, Haugen, Lebsack & Morrey, 1974). In these examples from the literature a change of the coordination of the Cu from distorted tetrahedral to square planar is considered responsible for the color change. Many other cases of varying coordination geometry are known for Cu<sup>II</sup> compounds, a characteristic that has been termed the plasticity of the coordination sphere of Cu<sup>II</sup> (Gažo *et al.*, 1976). The shape of the Cu ligand sphere in the solid state is largely determined by the nature of the ligands and their interactions, such as hydrogen bonds. In the present study the structure of the orange room-temperature modification of  $(\text{mescH})_2\text{CuCl}_4 \cdot \text{H}_2\text{O}$  is described. This structure determination was primarily aimed at investigating the Cu coordination and its relation to the presence of the protonated mescaline molecule, and at comparing the room-temperature modification with the structure of the green low-temperature modification of  $(\text{mescH})_2\text{CuCl}_4 \cdot \text{H}_2\text{O}$  which remains to be determined.

### Experimental

Orange crystals of  $(\text{mescH})_2\text{CuCl}_4 \cdot \text{H}_2\text{O}$  were grown by evaporation of an aqueous solution of stoichiometric amounts of  $(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}$  (mescaline hydrochloride) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at 298 K; a complete characterization of this compound will be published elsewhere. Weissenberg photographs showed the pinacoidal crystals to be triclinic and identified the best developed faces as {010}. The crystal selected for the lattice parameter and intensity measurements had dimensions of 0.29 × 0.24 × 0.44 mm perpendicular to (100), (010), (001), respectively. It showed a uniform extinction under the polarizing microscope and was mounted with the  $c$  axis approximately parallel to the diffractometer  $\phi$  axis.

34 high-angle reflections ( $81 < 2\theta < 115^\circ$ ) were centered at 297 K on a Ge XRD-5 three-circle diffractometer with Cu  $K\alpha_1$  radiation,  $\lambda = 1.54050$  Å, and 60 reflections ( $24 < 2\theta < 26^\circ$ ) were automatically centered at 238 K on a Syntex P2<sub>1</sub> four-circle

diffractometer with Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å. The lattice parameters (*cf. Abstract*) were calculated by least-squares refinement from the measured  $2\theta$  values. The density was measured at 297 K by flotation in a mixture of chloroform and 1-bromo-2-methylpropane.

The intensity data were collected on a computer-controlled Syntex P2<sub>1</sub> diffractometer supplemented with a low-temperature attachment. Throughout the measurements the crystal was kept at 238 K with a stream of nitrogen in order to reduce thermal motion. Using the  $\omega$  scan technique, the reflections were measured in a range of  $\pm 0.5$  about the calculated center with Mo K $\alpha$  radiation, monochromatized with a graphite crystal. The scan rate varied from 2 to 5° min<sup>-1</sup>, depending on the intensity. A coincidence correction was applied to the data based on the dead time of the detector circuit. By inspecting a 19-step profile of all reflections it was ascertained that the crystal orientation and the scan width were adequate. Background measurements were taken on both sides of each reflection at 1° from the calculated center for half the scan time each; 6662 independent reflections were measured with  $2\theta$  ranging from 4 to 55°, not including the four standard reflections recorded after every 96 ordinary reflections. The net intensities  $I$  were calculated for a scan rate of 1° min<sup>-1</sup>; their estimated standard deviations  $\sigma(I)$  were derived from counting statistics.

By comparing selected intensities with room-temperature Weissenberg photographs it was verified that no phase change had occurred in the crystal after the instantaneous cooling to 238 K. The transition to the green modification seems to be immeasurably slow at this low temperature; even under favorable conditions, around 273 K, the phase change took several days. A slight trend of the standard reflections towards higher intensity in the course of the measurement, probably of instrumental origin, was compensated with a quadratic function of the exposure time. The correction factors applied to the measured intensities were between 1.000 and 0.984. Based on the shape of the crystal and a calculated  $\mu$  of 1.192 mm<sup>-1</sup>, the intensities were also corrected for absorption, with transmission coefficients ranging from 0.727 to 0.773. Before the intensities were converted to structure amplitudes, the Lorentz and polarization factors were applied to the data.

### Solution and refinement of the structure

The structure was solved by the heavy-atom method. The positions of the Cu and Cl atoms in relation to the assumed center of inversion were found from a Patterson synthesis. A subsequent Fourier map showed all but six of the non-hydrogen atoms, the rest of which were found on a difference density map. The param-

eter refinement was carried out with the full-matrix least-squares program *NUCLS*, a modification by J. A. Ibers of the program *ORFLS* by Busing, Martin & Levy (1962). Scattering factors for the non-hydrogen atoms and anomalous-dispersion coefficients for Cu and Cl from *International Tables for X-ray Crystallography* (1974) were used. For the hydrogen atoms the scattering factors were taken from Stewart, Davidson & Simpson (1965):  $\sum w(F_o - F_c)^2$  was minimized with weights  $w = \sigma^{-2}(F_o)$ . Only the 5153 reflections for which  $I > 3\sigma(I)$  were included in the refinement. The discrepancy indices  $R = \sum |F_o - F_c| / \sum F_o$

Table 1. *Final positional parameters of the non-hydrogen atoms with estimated standard deviations in parentheses*

Cu and Cl positional parameters are multiplied by 10<sup>5</sup>, the others by 10<sup>4</sup>.

	x	y	z
Anion			
Cu	19822 (4)	25555 (1)	-914 (4)
Cl(1)	25795 (10)	20750 (3)	23662 (9)
Cl(2)	2381 (11)	30576 (4)	8305 (16)
Cl(3)	45083 (9)	28679 (3)	-4752 (11)
Cl(4)	9314 (14)	22542 (4)	-29957 (12)
Cation (1)			
O(1)	896 (2)	249 (1)	-1595 (2)
O(2)	2236 (2)	-713 (1)	-2033 (2)
O(3)	5173 (2)	-632 (1)	-2680 (2)
N(1)	6132 (3)	1755 (1)	1046 (3)
C(1)	4840 (3)	936 (1)	-2310 (3)
C(2)	3295 (3)	890 (1)	-2015 (3)
C(3)	2409 (3)	339 (1)	-1921 (3)
C(4)	3069 (3)	-164 (1)	-2170 (3)
C(5)	4621 (3)	-113 (1)	-2466 (3)
C(6)	5510 (3)	438 (1)	-2527 (3)
C(7)	5803 (3)	1541 (1)	-2344 (4)
C(8)	6943 (3)	1756 (1)	-576 (4)
C(9)	243 (3)	757 (1)	-1149 (4)
C(10)	1072 (4)	-941 (1)	-3619 (5)
C(11)	6758 (3)	-594 (1)	-3038 (4)
Cation (2)			
O(21)	8201 (2)	4823 (1)	1631 (2)
O(22)	7366 (2)	5751 (1)	3411 (2)
O(23)	6574 (2)	5683 (1)	6707 (2)
N(21)	3913 (3)	3230 (1)	5203 (3)
C(21)	7009 (3)	4145 (1)	5640 (3)
C(22)	7537 (3)	4197 (1)	3984 (3)
C(23)	7710 (3)	4735 (1)	3258 (3)
C(24)	7343 (3)	5224 (1)	4188 (3)
C(25)	6867 (3)	5175 (1)	5876 (3)
C(26)	6693 (3)	4634 (1)	6601 (3)
C(27)	6781 (3)	3548 (1)	6359 (4)
C(28)	5530 (3)	3099 (1)	5134 (4)
C(29)	8884 (4)	4361 (1)	855 (4)
C(30)	8918 (4)	6080 (1)	3500 (5)
C(31)	6325 (4)	5677 (1)	8570 (4)
Water			
O(41)	8337 (3)	2478 (1)	3694 (3)

$|F_c|/|\sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$  were used as criteria for the quality of the model.

After two cycles of isotropic and one cycle of anisotropic refinement ( $R = 0.065$ ,  $R_w = 0.088$ ) a difference density map revealed the positions of all H atoms. The positional and individual isotropic thermal parameters of all H atoms were refined during one least-squares cycle, giving  $R = 0.051$  and  $R_w = 0.060$ . The low value of the discrepancy indices and the satisfactory geometry of all portions of the structure at this stage were considered sufficient proof that the space group is indeed  $P1$ . In subsequent least-squares cycles all positional parameters were refined alternately with all

Table 2. Final positional and thermal parameters of the hydrogen atoms with estimated standard deviations in parentheses

All parameters are multiplied by  $10^3$ ;  $U$  is the mean-square amplitude of vibration in  $\text{\AA}^2$ .

	$x$	$y$	$z$	$U$
Cation (1)				
H(1)	284 (3)	123 (1)	-193 (3)	29 (7)
H(2)	650 (3)	49 (1)	-268 (3)	29 (7)
H(3)	642 (3)	154 (1)	-334 (3)	31 (7)
H(4)	512 (3)	179 (1)	-260 (4)	37 (7)
H(5)	777 (3)	151 (1)	-34 (4)	42 (8)
H(6)	749 (3)	217 (1)	-61 (4)	51 (8)
H(7)	684 (5)	196 (2)	228 (5)	88 (12)
H(8)	540 (4)	194 (1)	88 (4)	55 (10)
H(9)	575 (4)	139 (1)	126 (4)	54 (9)
H(10)	4 (3)	96 (1)	-217 (4)	45 (8)
H(11)	-75 (4)	62 (1)	-86 (4)	51 (9)
H(12)	92 (3)	99 (1)	-18 (4)	46 (8)
H(13)	50 (4)	-132 (1)	-331 (4)	64 (10)
H(14)	157 (4)	-105 (2)	-474 (5)	81 (12)
H(15)	32 (4)	-70 (2)	-389 (5)	69 (11)
H(16)	750 (4)	-39 (1)	-196 (4)	53 (9)
H(17)	684 (3)	103 (1)	-328 (4)	47 (8)
H(18)	692 (3)	-42 (1)	-414 (4)	39 (7)
Cation (2)				
H(21)	779 (3)	386 (1)	342 (4)	40 (8)
H(22)	634 (3)	459 (1)	770 (3)	27 (6)
H(23)	774 (3)	340 (1)	649 (4)	39 (8)
H(24)	647 (3)	360 (1)	763 (4)	46 (8)
H(25)	565 (3)	309 (1)	382 (4)	36 (7)
H(26)	556 (3)	274 (1)	551 (3)	28 (7)
H(27)	379 (3)	358 (1)	480 (4)	51 (9)
H(28)	377 (4)	322 (1)	633 (5)	66 (10)
H(29)	325 (4)	297 (2)	436 (5)	60 (10)
H(30)	976 (4)	429 (1)	172 (4)	53 (9)
H(31)	918 (3)	447 (1)	-23 (4)	36 (7)
H(32)	792 (4)	395 (1)	48 (4)	65 (10)
H(33)	960 (3)	584 (1)	313 (4)	43 (8)
H(34)	925 (4)	621 (1)	462 (5)	62 (10)
H(35)	870 (4)	639 (1)	268 (5)	64 (10)
H(36)	624 (3)	607 (1)	899 (4)	41 (8)
H(37)	545 (4)	541 (1)	865 (4)	46 (8)
H(38)	726 (4)	557 (1)	934 (4)	49 (8)
Water				
H(41)	878 (4)	241 (1)	459 (5)	52 (10)
H(42)	908 (6)	262 (2)	308 (7)	120 (17)

thermal parameters, until the shift to e.s.d. ratio for most parameters was below 0.1. An extinction correction was not included in the final cycles because it did not improve the agreement factors noticeably in earlier cycles.

The final discrepancy indices were  $R = 0.037$  and  $R_w = 0.043$  with the 5153 reflections used for the refinement,  $R = 0.052$  and  $R_w = 0.045$  if all 6662 reflections were included. The largest shift to e.s.d. ratio in the two last cycles was 0.39 for a H parameter and 0.21 for a nonhydrogen parameter. The largest positive peak,  $0.65 \text{ e \AA}^{-3}$ , and the largest negative peak,  $-0.56 \text{ e \AA}^{-3}$ , in a difference density map with the final parameters, are close to Cl(4). A few smaller peaks are located in the vicinity of the Cu and Cl atoms. A list of the final positional and hydrogen thermal parameters is found in the Tables 1 and 2.\*

## Discussion

### General description

The  $(\text{mescH})_2\text{CuCl}_4 \cdot \text{H}_2\text{O}$  complex contains isolated  $\text{CuCl}_4^{2-}$  anions with a minimum Cu-Cu distance equal to the length of the  $c$  axis,  $7.43 \text{ \AA}$ . As in most other known structures with  $\text{CuCl}_4^{2-}$  anions, the coordination polyhedron around the Cu is approximately a flattened tetrahedron with only a slight deviation from  $D_{2d}$  symmetry (Harlow, Wells, Watt & Simonsen, 1974, and literature cited therein; Larsen *et al.*, 1975; Harlow & Simonsen, 1976). The  $\text{CuCl}_4^{2-}$  ions are linked into chains extending along the  $c$  axis by hydrogen bonds to the water molecules and the amino groups of the mescaline (2) molecules. The chains are connected in a plane parallel to the  $a$  and  $c$  axes by hydrogen bonds

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33944 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

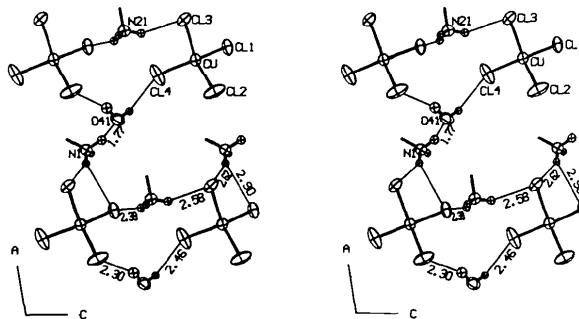


Fig. 1. Stereoscopic view of the hydrogen-bonding network with 50% probability ellipsoids for non-hydrogen atoms and 10% probability spheres for hydrogen atoms.

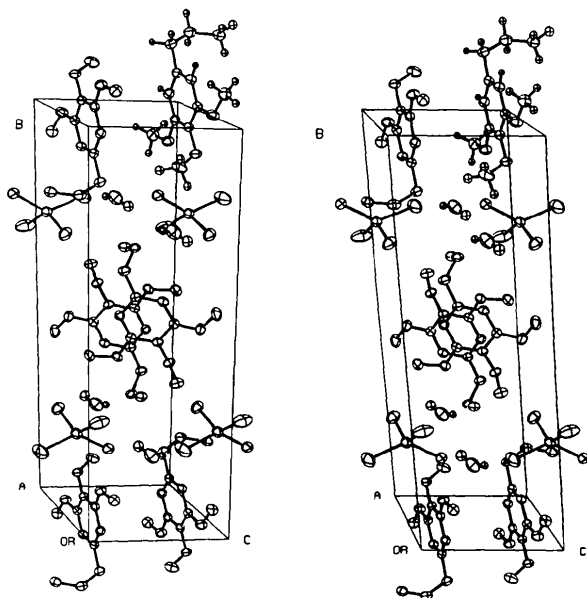


Fig. 2. Stereoscopic view of the packing diagram with 50% probability ellipsoids for non-hydrogen atoms and 10% probability spheres for hydrogen atoms. Some of the hydrogen atoms are omitted for clarity.

involving the amino groups of the mescaline (1) molecules and the water molecules. The resulting two-dimensional network of hydrogen bonds is shown in Fig. 1, also showing the hydrogen-bond distances. From these layers containing the ionic portions of the structure the mescaline molecules extend into the intermediate space (Fig. 2).

#### Chlorocuprate anion and hydrogen bonds

The bond distances and angles in the flattened-tetrahedral CuCl<sub>4</sub><sup>2-</sup> anion are listed in Table 3. They are within the range of values obtained from other tetrachlorocuprates, indicating that the presence of water in the hydrogen-bonding network has no major consequence on the geometry of the CuCl<sub>4</sub><sup>2-</sup> ion. The Cu—Cl(3) bond and, to a lesser extent, the Cu—Cl(1) bond are slightly longer than the two other Cu—Cl bonds, possibly because each of these Cl atoms takes part in two hydrogen bonds.

All but one of the hydrogen-bond distances (*cf.* Fig. 1) are markedly shorter than the van der Waals distance of 3.0 Å between the proton and the acceptor atom (Hamilton & Ibers, 1968), even when an allowance for the low accuracy of the H positions is made. An exception is the pseudo-bifurcated bond of H(8) with a distance of 2.90 Å to Cl(1), indicating a rather weak bond between these atoms, if any. On the whole, hydrogen bonding makes an important contribution to the packing forces in (mesch)<sub>2</sub>CuCl<sub>4</sub>.H<sub>2</sub>O.

#### Mescaline

The atoms of the mesch<sup>+</sup> (2) ion were numbered by adding 20 to the atom numbers of the mesch<sup>+</sup> (1) ion as shown in Fig. 3. All bond distances (*cf.* Table 4) and angles of both protonated mescaline molecules fall into the expected range. They are in good agreement with values obtained from the structure determinations of mescaline hydrochloride (Tsoucaris, de Rango, Tsoucaris, Zelwer, Parthasarathy & Cole, 1973) and mescaline hydrobromide (Ernst & Cagle, 1973). The maximum distance of the six ring C atoms to the mean plane through the ring is 0.009 and 0.017 Å for molecules (1) and (2), respectively.

Of some interest with regard to its neurophysiological potency is the conformation of the mescaline molecule. The dihedral angles between the C—O—C planes and the mean plane through the six ring C atoms (Table 5) indicate that the two *meta*-methoxy groups are nearly coplanar with the ring, whereas the *para*-methoxy group is approximately axial to the ring, in agreement with the findings in mescaline hydrochloride and hydrobromide. Thus the largest mutual distance between the methyl groups is nearly maintained in all cases.

The ethyl group has a nearly axial conformation with respect to the aromatic ring, as can be seen from the dihedral angle between the C(1)—C(7)—C(8) plane and the mean plane through the ring atoms (Table 5). In molecule (2), however, the H bridges of the N deflect the ethyl group by as much as 27° from the axial position. The ethyl and *p*-methoxy groups extend to opposite sides of the ring plane, with the exception of mescaline hydrochloride. Another peculiarity of mescaline hydrochloride is the *anti* conformation of the two substituents of the ethyl groups as expressed by the

Table 3. Bond distances (Å) and angles (°) in the CuCl<sub>4</sub><sup>2-</sup> ion with estimated standard deviations in parentheses

Cu—Cl(1)	2.237 (1)	Cl(1)—Cu—Cl(2)	100.5 (1)
Cu—Cl(2)	2.215 (1)	Cl(1)—Cu—Cl(3)	96.6 (1)
Cu—Cl(3)	2.271 (1)	Cl(1)—Cu—Cl(4)	132.8 (1)
Cu—Cl(4)	2.221 (1)	Cl(2)—Cu—Cl(3)	130.2 (1)
		Cl(2)—Cu—Cl(4)	103.1 (1)
		Cl(3)—Cu—Cl(4)	98.4 (1)

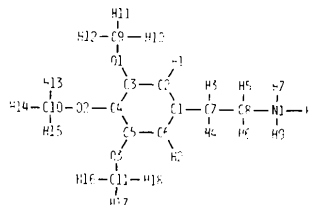


Fig. 3. Atom-numbering scheme for the mesch<sup>+</sup> cation.

Table 4. Bond distances (Å) in the two mesCH<sup>+</sup> cations with e.s.d.'s in parentheses

	(1)	(2)		(1)	(2)
C(1)–C(2)	1.384 (4)	1.387 (3)	C(7)–H(3)	0.98 (3)	0.94 (3)
C(2)–C(3)	1.393 (3)	1.388 (3)	C(7)–H(4)	0.89 (3)	1.03 (3)
C(3)–C(4)	1.393 (3)	1.392 (3)	C(8)–H(5)	0.99 (3)	1.00 (3)
C(4)–C(5)	1.391 (3)	1.388 (3)	C(8)–H(6)	1.00 (3)	0.90 (3)
C(5)–C(6)	1.390 (3)	1.393 (3)	N(1)–H(7)	1.05 (4)	0.91 (3)
C(6)–C(1)	1.384 (3)	1.384 (3)	N(1)–H(8)	0.82 (3)	0.86 (4)
C(1)–C(7)	1.517 (3)	1.513 (3)	N(1)–H(9)	0.90 (3)	0.90 (3)
C(7)–C(8)	1.513 (4)	1.510 (4)	C(9)–H(10)	0.92 (3)	0.96 (3)
C(8)–N(1)	1.490 (4)	1.494 (4)	C(9)–H(11)	0.94 (3)	0.92 (3)
C(3)–O(1)	1.362 (3)	1.363 (3)	C(9)–H(12)	0.93 (3)	1.14 (3)
C(9)–O(1)	1.426 (3)	1.435 (4)	C(10)–H(13)	1.00 (4)	0.94 (3)
C(4)–O(2)	1.377 (3)	1.385 (3)	C(10)–H(14)	1.03 (4)	0.85 (4)
C(10)–O(2)	1.433 (3)	1.430 (3)	C(10)–H(15)	0.93 (4)	1.00 (3)
C(5)–O(3)	1.372 (3)	1.370 (3)	C(11)–H(16)	0.99 (3)	0.96 (3)
C(11)–O(3)	1.437 (3)	1.436 (3)	C(11)–H(17)	1.02 (3)	0.92 (3)
C(2)–H(1)	0.93 (3)	0.93 (3)	C(11)–H(18)	0.95 (3)	1.00 (3)
C(6)–H(2)	0.88 (3)	0.92 (3)			

Table 5. Dihedral angles (°) of the methoxy and ethyl groups to the ring plane and torsion angle (°) between the two ethyl substituents

	mesc.-		mesc.-	
	(1)	(2)	HCl	HBr
C(3),O(1),C(9) -ring	6.4	13.5	10.3	0.9
C(4),O(2),C(10) -ring	75.9	76.1	75.0	81.5
C(5),O(3),C(11) -ring	1.4	10.7	8.6	3.1
C(1),C(7),C(8) -ring	78.5	63.1	89.8	81.8
Torsion angle				
C(1) C(7),C(8) N(1)	-55.6	71.2	176.0	-55.8

torsion angle of nearly 180° (*cf.* Table 5). In the other cases the ethyl group assumes a *gauche* conformation, bringing the protonated amine group much closer to the ring. From molecular-orbital calculations it is known that the two ethyl-group conformations in phenethylamines differ only by a small amount of energy (Pullman, Berthod & Pullman, 1974, and literature cited therein). Therefore minor effects of the packing forces may be responsible for the actual conformation found in the various mescaline salts.

It is noteworthy that the conformation with the maximum extension of the mescaline molecule, *i.e.* the one with an ethyl group in *anti* conformation on the other side of the ring plane to the *para*-methoxy group, is not realized in any of the structures known to date.

We are grateful to Dr R. L. Harlow and Dr S. H. Simonsen for their assistance and helpful suggestions during the course of this work, which was supported by the Robert A. Welch Foundation. The diffractometer

was purchased with funds provided by the National Science Foundation (Grant GP-37028).

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- ERNST, S. R. & CAGLE, F. W. JR (1973). *Acta Cryst.* **B29**, 1543–1546.
- GAŽO, J., BERSUKER, I. B., GARAJ, J., KABEŠOVÁ, M., KOHOUT, J., LANGFELDEROVÁ, H., MELNÍK, M., SERÁTOR, M. & VALACH, F. (1976). *Coord. Chem. Rev.* **19**, 253–297.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- HARLOW, R. L. & SIMONSEN, S. H. (1976). *Cryst. Struct. Commun.* **5**, 265–270.
- HARLOW, R. L., WELLS, W. J., WATT, G. W. & SIMONSEN, S. H. (1974). *Inorg. Chem.* **14**, 2106–2111.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LARSEN, K. P., HAZELL, R. G., TOFTLUND, H., ANDERSEN, P. R., BISGÅRD, P., EDLUND, K., ELIASSEN, M., HERSKIND, C., LAURSEN, T. & PEDERSEN, P. M. (1975). *Acta Chem. Scand. Ser. A*, **29**, 499–504.
- PULLMAN, B., BERTHOD, H. & PULLMAN, A. (1974). *An. Quím.* **70**, 1204–1208.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TSOUCARIS, D., DE RANGO, C., TSOUCARIS, G., ZELWER, C., PARTHASARATHY, R. & COLE, F. E. (1973). *Cryst. Struct. Commun.* **2**, 193–196.
- WANG, P. J. & DRICKAMER, H. G. (1973). *J. Phys. Chem.* **59**, 559–560.
- WILLETT, R. D., HAUGEN, J. A., LEBSACK, J. & MORREY, J. (1974). *Inorg. Chem.* **13**, 2510–2513.