Short Communication

The Crystal Structure of the Tetramethylammonium Salt of Tris(triformylmethane)magnesium(II)

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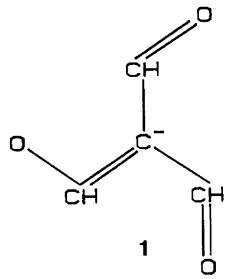
Triformylmethane is a strong acid (pK_a = 2.3) which forms stable salts with alkali metals. It was synthesized for the first time in 1959.[1] There are two possible conformations of the anion:



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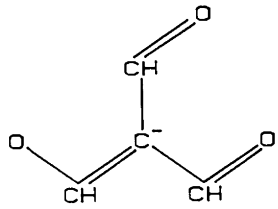

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A synthesis of the tetramethylammonium salt of triformylmethane was carried out with the purpose of establishing the solid-state conformation of the anion by single-crystal X-ray methods.[2] $MgSO_4$ was used as drying agent. The crystal quality was very poor and only small fragments were "extinguished" when the crystals were rotated under crossed Nicol prisms. By cutting away the "bad parts", an acceptable specimen was obtained. It turned out that the drying agent had reacted with the tetramethylammonium salt to give the title compound.

The crystals of $[Mg(C_4H_3O_3)_3][N(CH_3)_4]$ belong to the monoclinic system with cell dimensions a = 9.310(9), b = 25.276(7) and c = 16.831(5) Å; β = 101.97(4)°, space group $C2/c$ and Z = 8 (D_x = 1.23 g cm^{-3}, D_m = 1.20 g cm^{-3}). With $2\theta_{max}$ = 50° and using Mo$K\alpha$ radiation, 1958 independent reflections [$I>2.5\sigma(I)$] were recorded on an automatic diffractometer at ca. −150 °C. No corrections for absorption or secondary extinction were applied (crystal size 0.3×0.5×0.3 mm). The structure was solved by direct methods[3] and refined by the full matrix least-squares technique.[5] Anisotropic temperature factors were introduced for non-hydrogen atoms. Weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02\ C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N the net count. Hydrogen atom positions were calculated and refined with isotropic temperature factors (U = 0.05). The final R-value was R = 5.8 % (R_w = 6.0 %) for 1958 observed reflections. Although the statistics clearly indicated a centre of symmetry, an attempt to solve and refine the structure in space group Cc was made. The refinement converged at ca. 15 %, and high correlations between the corresponding parameters of atoms related by approximate centrosymmetry were observed. Maximum r.m.s. amplitudes ranged from 0.29 to 0.60 Å for the tetramethylammonium carbon atoms. For other atoms, the values lay be-

Table 1. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for non-hydrogen atoms.

Atom	*x*	*y*	*z*	U_{eq} [a]
Mg	0.26247(18)	0.12656(6)	0.49796(10)	0.049
C1	0.3775(5)	0.0084(2)	0.5834(3)	0.050
C2	0.4206(6)	−0.0387(2)	0.6312(4)	0.065
C3	0.2381(6)	0.0106(2)	0.5321(3)	0.058
C4	0.4796(5)	0.0500(2)	0.5882(3)	0.054
O1	0.3426(4)	−0.0765(1)	0.6377(3)	0.083
O2	0.1840(4)	0.0490(1)	0.4902(2)	0.066
O3	0.4596(4)	0.0934(1)	0.5536(2)	0.056
C5	−0.0491(6)	0.1290(2)	0.5698(3)	0.045
C6	−0.1824(6)	0.1208(2)	0.5961(4)	0.056
C7	−0.0567(6)	0.1405(2)	0.4877(4)	0.051
C8	0.0875(6)	0.1295(2)	0.6249(3)	0.052
O4	−0.1931(4)	0.1067(1)	0.6645(3)	0.066
O5	0.0474(4)	0.1480(1)	0.4520(2)	0.053
O6	0.2116(4)	0.1341(1)	0.6114(2)	0.055
C9	0.4903(6)	0.1950(2)	0.4065(3)	0.052
C10	0.6089(8)	0.2182(2)	0.3766(4)	0.076
C11	0.4110(6)	0.1524(2)	0.3636(3)	0.056
C12	0.4562(6)	0.2152(2)	0.4785(4)	0.057
O7A	0.6834(7)	0.2479(3)	0.4112(5)	0.067
O7B	0.6689(7)	0.2089(3)	0.3114(4)	0.055
O8	0.3130(4)	0.1257(1)	0.3857(2)	0.056
O9	0.3621(4)	0.1984(1)	0.5142(2)	0.057
N1	1.00000	0.03595(19)	0.25000	0.045
C13	1.0000	0.0942(3)	0.2500	0.142
C14	1.0708(16)	0.0182(5)	0.3355(8)	0.075
C15	0.8377(12)	0.0218(5)	0.2300(7)	0.074
C16	1.0718(17)	0.0123(8)	0.1855(8)	0.129
N2	0.50000	0.22559(18)	0.75000	0.045
C17	0.5992(6)	0.2595(2)	0.8119(3)	0.061
C18	0.5944(5)	0.1917(2)	0.7079(3)	0.058

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

tween 0.26 and 0.36 Å. Final fractional coordinates and estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Bond distances, bond angles and torsion angles with estimated standard deviations may be found in Table 2. Fig. 1 is a schematic drawing showing the hexacoordinated magnesium cation and the triformylmethane anions. The numbering of atoms is indicated. Fig. 2 is a stereoscopic drawing of the unit cell contents. Fig. 3 shows the two tetramethylammonium cations, situated on two-fold axes of rotation, and the numbering of atoms.

It may be seen in Fig. 1 that the three ligands adopt conformation (II) and that the oxygen atom O7 is disordered. The unreasonable bond distances (Table 2) C10–O7A [1.103(10) Å] and C10–O7B [1.352(10) Å] indicate that C10 is also disordered to some extent. All other C–O bond lengths have an average value within error limits of 1.238 Å. Also, the C–C bond lengths and the lengths of the coordination bonds, Mg^{2+}–O, have mean values within estimated limits of error, of 1.415 Å and 2.058 Å, respectively. Both tetramethylammonium cations are situated on two-fold symmetry axes and one of them is disordered (Fig. 3). Except for N1–C14, the N–C bonds are normal. Apart from those involving C7A and C7B, the values of the bond angles in Table 2 are reasonable. The somewhat large C–C–O angles (ranging from 125.6 to 129.5°) correspond to

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with standard deviations.

Distance		Distance	
Mg – O2	2.086(4)	Mg – O3	2.057(4)
Mg – O5	2.063(4)	Mg – O6	2.068(4)
Mg – O8	2.040(4)	Mg – O9	2.031(4)
C1 – C2	1.446(7)	C1 – C3	1.404(8)
C1 – C4	1.407(7)	C2 – O1	1.218(7)
C3 – O2	1.243(6)	C4 – O3	1.240(6)
C5 – C6	1.416(8)	C5 – C7	1.399(8)
C5 – C8	1.411(8)	C6 – O4	1.229(8)
C7 – O5	1.256(7)	C8 – O6	1.230(7)
C9 – C10	1.430(9)	C9 – C11	1.415(7)
C9 – C12	1.411(8)	C10 – O7A	1.103(10)
C10 – O7B	1.352(10)	C11 – O8	1.252(7)
C12 – O9	1.235(7)	N1 – C13	1.471(10)
N1 – C14	1.380(13)	N1 – C15	1.521(12)
N1 – C16	1.511(16)	N2 – C17	1.508(6)
N2 – C18	1.505(6)		
Angle		**Angle**	
C2 – C1 – C3	119.2(5)	C2 – C1 – C4	118.5(5)
C3 – C1 – C4	122.2(5)	C1 – C2 – O1	126.4(5)
C1 – C3 – O2	126.4(5)	C1 – C4 – O3	126.9(5)
C6 – C5 – C7	118.1(5)	C6 – C5 – C8	121.6(5)
C7 – C5 – C8	120.1(5)	C5 – C6 – O4	125.6(6)
C5 – C7 – O5	128.1(5)	C5 – C8 – O6	129.2(5)
C10 – C9 – C11	119.5(5)	C10 – C9 – C12	118.8(5)
C11 – C9 – C12	121.7(5)	C9 – C10 – O7A	122.8(8)
C9 – C10 – O7B	133.8(6)	O7A – C10 – O7B	103.1(8)
C9 – C11 – O8	126.5(5)	C9 – C12 – O9	127.0(5)
C13 – N1 – C14	109.0(6)	C13 – N1 – C15	103.6(6)
C13 – N1 – C16	113.3(8)	C14 – N1 – C15	113.0(8)
C14 – N1 – C16	109.5(9)	C15 – N1 – C16	108.4(8)
C17 – N2 – C18	108.4(3)	C17 – N2 – C17′	110.7(4)
C17 – N2 – C18′	109.4(3)	C18 – N2 – C18′	110.7(4)
Torsion angle			
C3 – C1 – C2 – O1	−7.1(6)		
C2 – C1 – C3 – O2	177.0(8)		
C4 – C1 – C2 – O1	175.1(9)		
C2 – C1 – C4 – O3	−177.6(8)		
C4 – C1 – C3 – O2	−5.3(5)		
C3 – C1 – C4 – O3	4.6(5)		
C7 – C5 – C6 – O4	174.5(9)		
C6 – C5 – C7 – O5	−178.3(9)		
C8 – C5 – C6 – O4	−10.1(6)		
C6 – C5 – C8 – O6	177.1(9)		
C8 – C5 – C7 – O5	6.2(5)		
C7 – C5 – C8 – O6	−7.6(5)		
C11 – C9 – C10 – O7A	−172.1(11)		
C11 – C9 – C10 – O7B	0.6(7)		
C10 – C9 – C11 – O8	173.9(9)		
C12 – C9 – C10 – O7A	7.5(8)		
C12 – C9 – C10 – O7B	−179.8(11)		
C10 – C9 – C12 – O9	−176.6(9)		
C12 – C9 – C11 – O8	−5.7(5)		
C11 – C9 – C12 – O9	3.0(6)		

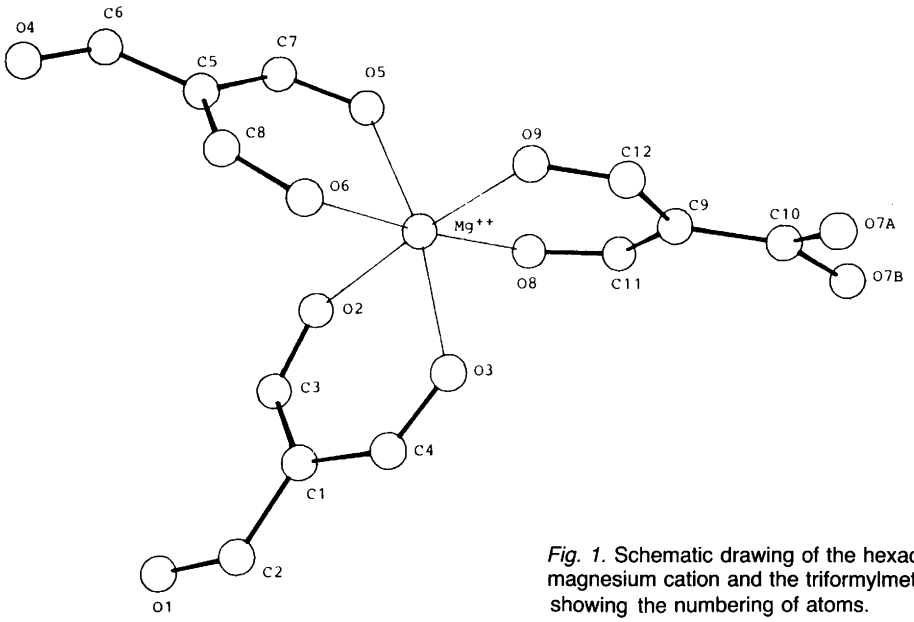

Fig. 1. Schematic drawing of the hexacoordinated magnesium cation and the triformylmethane anions showing the numbering of atoms.

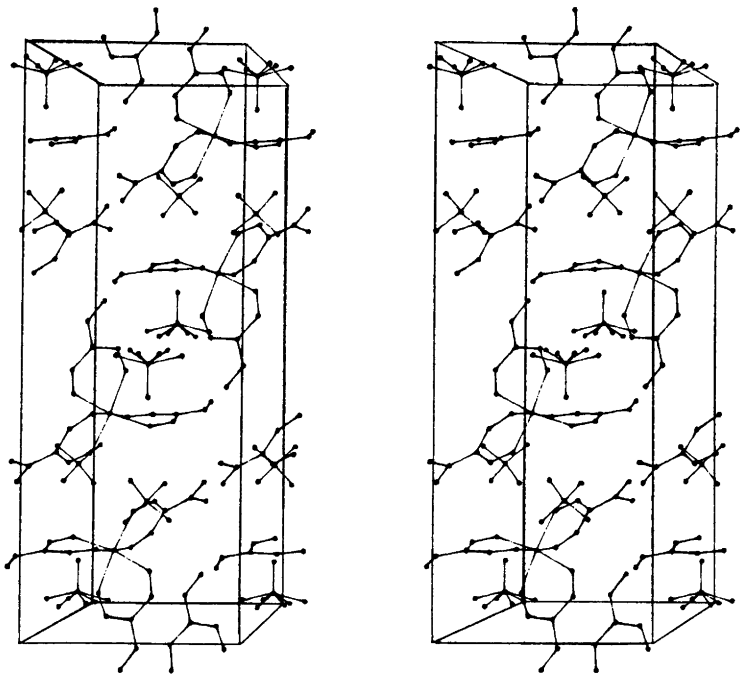

Fig. 2. Stereoscopic view of the unit cell contents.

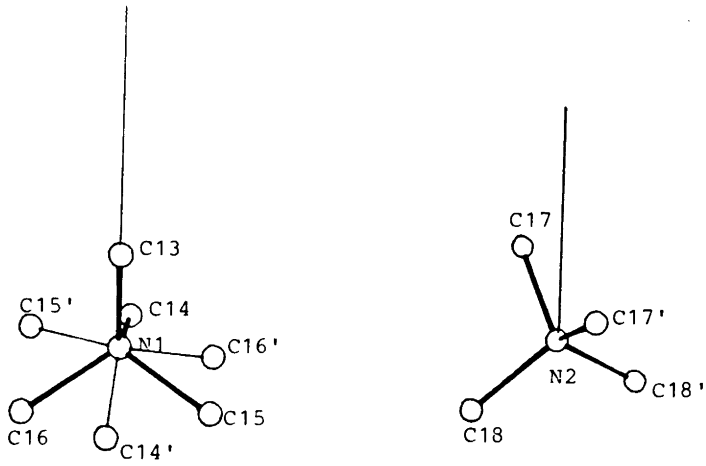

Fig. 3. Schematic drawing of the two tetramethylammonium cations situated on two-fold axes of rotation. The numbering of atoms is shown.

those found in the crystals of the sodium salt of 3-hydroxy-2-propenal.[4] The values of the torsion angles in Table 2 indicate that the ligands are roughly planar (actually, to within 0.06 Å when O7A and O7B are excluded from the calculation of least-squares planes).

Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available from the author on request.

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