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Tris(5-acetyl-3-thienyl)methane–Tetrachloromethane (2/1) Inclusion Compound

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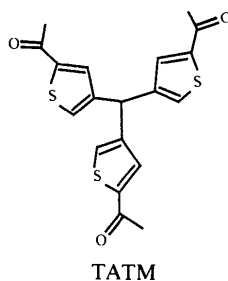
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Abstract

Tris(5-acetyl-3-thienyl)methane forms an inclusion compound with CCl_4 in a host–guest ratio of 2:1, $2\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}_3 \cdot \text{CCl}_4$, which crystallizes in a $P\bar{1}$ triclinic unit cell. Molecular packing in the crystals produces a channel-type cavity in which the CCl_4 molecules are located in two orientationally disordered positions with 65 and 35% occupation.

Comment

The tris(5-acetyl-3-thienyl)methane (TATM) molecule forms 2:1 host–guest inclusion compounds with many solvents (Din & Meth-Cohn, 1977). Several crystal structures have been published recently for inclusion compounds involving ethyl acetate (van Rooyen & Roos, 1991*a*), benzene (van Rooyen & Roos, 1991*b*), *n*-hexane (Roos & Dillen, 1992) and ethanol (Dillen & Roos, 1992). The crystal structure obtained for the CCl_4 inclusion compound (I) is isostructural with the benzene inclusion compound (van Rooyen & Roos, 1991*b*). Four TATM host and two CCl_4 guest molecules are in the unit cell. All TATM host molecules are ordered, whereas the CCl_4 guest molecules have partially disordered structures, in which one Cl atom is ordered but the three remaining Cl atoms are trigonally disordered in two molecular orientations with 65 and 35% occupation.



It can be seen from Fig. 2 that the inclusion compound has channel-type cavities along the *c* axis. By comparing the CCl_4 clathrate with the benzene clathrate (van Rooyen & Roos, 1991*a*), it is found

that the cavity properties are the same in these two clathrates. However, the CCl_4 molecule experiences a disorder effect so that the ordered axial Cl–C bond is nearly perpendicular to the benzene ring. Since the benzene guest molecule is in an ordered site and thus the six C atoms are located at low atom–atom potential minima, the CCl_4 guest molecule would have two possible orientations which produce six disordered equatorial Cl sites in the plane parallel to the benzene ring. Fig. 3 shows the molecular orientations of the CCl_4 and the benzene guests in the same crystal lattice.

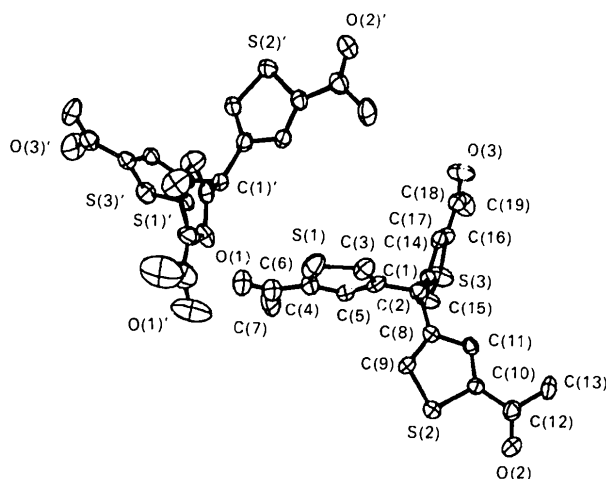


Fig. 1. Labelled ellipsoid plot of both host molecules.

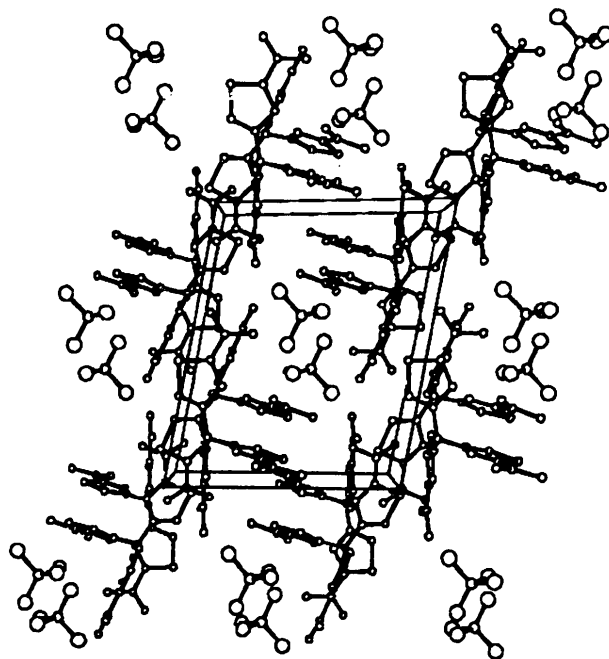


Fig. 2. View of the unit cell of TATM– CCl_4 down the *c* axis. (The minor orientation for CCl_4 has been omitted for clarity.)



Fig. 3. Comparison of the molecular orientations of disordered CCl₄ and ordered benzene in the same crystal lattice.

The disordered structure of the CCl₄ guest molecule has also been confirmed by a ³⁵Cl nuclear quadrupole resonance study (Pang, 1989). Ordered and disordered CCl₄ in other inclusion compounds have been reported in related literature (Pang, Lucken & Bernardinelli, 1990, 1992).

Experimental

The host molecule, TATM, was synthesized using the method of Yakubov, Sudarushkin, Belenki & Gold'farb (1973) and characterized by ¹H NMR. The CCl₄ inclusion compound was formed by recrystallization of the host molecule from the guest solvent. The host-guest ratio of 2:1 was determined by crystal density measurements. A single crystal was selected and removed from the mother liquor, quickly covered with epoxy to prevent deterioration, and mounted on the tip of a glass fibre.

Crystal data

2C₁₉H₁₆O₃S₃.CCl₄

M_r = 930.8

Triclinic

P $\bar{1}$

a = 11.638 (3) Å

b = 13.684 (3) Å

c = 14.235 (5) Å

α = 88.90 (2)°

β = 77.46 (2)°

γ = 78.77 (2)°

V = 2170 (1) Å³

Z = 2

D_x = 1.43 Mg m⁻³

D_m = 1.42 Mg m⁻³

D_m measured by flotation in

KI/H₂O

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 12.5–15°

μ = 0.59 mm⁻¹

T = 295 K

Plate

0.40 × 0.33 × 0.10 mm

Pale yellow

Data collection

Rigaku diffractometer

ω scans (rate 16° min⁻¹, width 1.5°)

Absorption correction: none

6016 measured reflections

5682 independent reflections

3227 observed reflections

[*I* > 2.5σ(*I*)]

R_{int} = 0.021

θ_{\max} = 22.45°

h = -12 → 12

k = 0 → 14

l = -15 → 15

3 standard reflections

monitored every 150

reflections

intensity variation: 0.45%

Refinement

Refinement on *F*

R = 0.058

wR = 0.058

S = 1.81

(Δ/σ)_{max} = 0.098

$\Delta\rho_{\max}$ = 0.510 e Å⁻³

$\Delta\rho_{\min}$ = -0.370 e Å⁻³

Extinction correction: none

3227 reflections
523 parameters
H-atom parameters not refined
w = 1/σ²(*F*)

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

Host molecule (1)	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
S(1)	-0.0533 (2)	0.4386 (2)	0.6826 (2)	5.76 (12)
S(2)	0.1310 (2)	0.0885 (1)	0.3695 (1)	4.52 (11)
S(3)	0.4920 (2)	0.0824 (2)	0.6499 (2)	5.89 (13)
O(1)	0.0487 (6)	0.6132 (4)	0.6079 (4)	7.7 (4)
O(2)	0.1645 (5)	-0.1227 (3)	0.3094 (3)	4.9 (3)
O(3)	0.3797 (5)	0.0706 (4)	0.9281 (3)	6.2 (3)
C(1)	0.1415 (6)	0.1601 (5)	0.6417 (4)	3.4 (3)
C(2)	0.0945 (6)	0.2711 (5)	0.6478 (4)	3.4 (3)
C(3)	-0.0206 (6)	0.3123 (5)	0.6895 (5)	4.3 (4)
C(4)	0.0892 (7)	0.4396 (5)	0.6224 (5)	4.3 (4)
C(5)	0.1603 (7)	0.3455 (5)	0.6087 (4)	3.8 (4)
C(6)	0.1272 (9)	0.5354 (6)	0.5928 (6)	6.4 (5)
C(7)	0.2536 (10)	0.5356 (6)	0.5502 (7)	8.4 (6)
C(8)	0.1412 (6)	0.1147 (5)	0.5452 (4)	3.1 (3)
C(9)	0.1235 (7)	0.1658 (5)	0.4650 (5)	4.1 (4)
C(10)	0.1588 (6)	-0.0152 (4)	0.4369 (4)	2.9 (3)
C(11)	0.1626 (6)	0.0101 (4)	0.5279 (4)	2.9 (3)
C(12)	0.1737 (6)	-0.1137 (5)	0.3917 (5)	3.6 (3)
C(13)	0.2016 (8)	-0.2021 (5)	0.4536 (6)	5.4 (5)
C(14)	0.2653 (6)	0.1315 (4)	0.6644 (4)	3.0 (3)
C(15)	0.3714 (7)	0.1161 (6)	0.5991 (5)	4.7 (4)
C(16)	0.4010 (6)	0.0874 (5)	0.7634 (5)	3.5 (3)
C(17)	0.2818 (6)	0.1147 (4)	0.7615 (5)	3.0 (3)
C(18)	0.4505 (6)	0.0653 (5)	0.8500 (5)	4.1 (4)
C(19)	0.5825 (7)	0.0367 (6)	0.8409 (6)	6.0 (5)
Host molecule (2)				
S(1)'	0.4792 (2)	0.2187 (2)	0.1441 (2)	6.05 (13)
S(2)'	0.1214 (2)	0.3780 (1)	-0.1278 (1)	4.17 (10)
S(3)'	-0.0841 (2)	0.0962 (1)	0.2117 (1)	4.12 (9)
O(1)'	0.3997 (6)	0.2922 (6)	0.4166 (4)	9.1 (5)
O(2)'	0.1878 (3)	0.5681 (3)	-0.1994 (3)	5.9 (3)
O(3)'	-0.0076 (5)	-0.1062 (4)	0.1207 (4)	6.3 (3)
C(1)'	0.1257 (4)	0.3007 (4)	0.1485 (4)	2.9 (3)
C(2)'	0.2520 (6)	0.2777 (4)	0.1682 (5)	3.3 (3)
C(3)'	0.3522 (6)	0.2404 (6)	0.1001 (5)	4.6 (4)
C(4)'	0.3981 (7)	0.2604 (5)	0.2573 (5)	4.1 (4)
C(5)'	0.2749 (6)	0.2921 (5)	0.2630 (5)	3.2 (3)
C(6)'	0.4588 (8)	0.2611 (7)	0.3379 (6)	6.5 (5)
C(7)'	0.5912 (9)	0.2241 (9)	0.3229 (7)	9.7 (8)
C(8)'	0.1273 (6)	0.3474 (4)	0.0498 (4)	3.2 (3)
C(9)'	0.1059 (6)	0.3038 (5)	-0.0292 (5)	3.7 (4)
C(10)'	0.1573 (6)	0.4689 (4)	-0.0638 (4)	3.1 (3)
C(11)'	0.1568 (6)	0.4425 (4)	0.0292 (4)	2.9 (3)
C(12)'	0.1881 (6)	0.5590 (5)	-0.1131 (5)	3.8 (3)
C(13)'	0.2194 (7)	0.6363 (5)	-0.0570 (6)	5.2 (4)
C(14)'	0.0685 (6)	0.2094 (4)	0.1595 (4)	2.9 (3)
C(15)'	-0.0417 (6)	0.2088 (5)	0.2159 (5)	3.5 (3)
C(16)'	0.0495 (6)	0.0468 (5)	0.1330 (4)	3.0 (3)
C(17)'	0.1211 (6)	0.1158 (4)	0.1122 (4)	2.9 (3)
C(18)'	0.0694 (6)	-0.0560 (5)	0.0967 (5)	4.0 (4)
C(19)'	0.1862 (7)	-0.0965 (5)	0.0311 (6)	5.2 (4)
Guest molecule				
C(20)	0.4522 (8)	0.6037 (7)	0.1936 (7)	7.9 (6)
Cl(1)	0.3308 (3)	0.6969 (2)	0.2099 (3)	14.1 (3)
Cl(2)	0.5344 (5)	0.6194 (4)	0.0806 (4)	13.9 (4)
Cl(3)	0.5440 (7)	0.6191 (6)	0.2717 (6)	18.7 (6)
Cl(4)	0.4143 (7)	0.4949 (4)	0.2037 (6)	18.5 (6)
Cl(2)'	0.5685 (9)	0.6545 (7)	0.1955 (9)	13.7 (8)
Cl(3)'	0.4192 (15)	0.5362 (9)	0.2969 (9)	19.1 (12)
Cl(4)'	0.4830 (13)	0.5178 (9)	0.1037 (10)	19.1 (11)

Table 2. Selected geometric parameters (Å, °)

Host molecule			
S(1)—C(3)	1.701 (7)	C(4)—C(5)	1.381 (9)
S(1)—C(4)	1.697 (8)	C(4)—C(6)	1.489 (11)
S(2)—C(9)	1.715 (7)	C(6)—C(7)	1.464 (14)
S(2)—C(10)	1.715 (6)	C(8)—C(9)	1.361 (9)
S(3)—C(15)	1.698 (7)	C(8)—C(11)	1.422 (9)
S(3)—C(16)	1.723 (7)	C(10)—C(11)	1.359 (8)
O(1)—C(6)	1.250 (10)	C(10)—C(12)	1.469 (9)
O(2)—C(12)	1.210 (8)	C(12)—C(13)	1.508 (10)
O(3)—C(18)	1.225 (9)	C(14)—C(15)	1.357 (9)
C(1)—C(2)	1.508 (9)	C(14)—C(17)	1.445 (9)
C(1)—C(8)	1.519 (9)	C(16)—C(17)	1.371 (9)
C(1)—C(14)	1.519 (9)	C(16)—C(18)	1.475 (9)
C(2)—C(3)	1.356 (10)	C(18)—C(19)	1.487 (11)
C(2)—C(5)	1.424 (10)		
Guest molecule			
C(20)—Cl(1)	1.687 (9)	C(20)—Cl(2)'	1.642 (13)
C(20)—Cl(2)	1.719 (11)	C(20)—Cl(3)'	1.733 (14)
C(20)—Cl(3)	1.742 (12)	C(20)—Cl(4)'	1.686 (13)
C(20)—Cl(4)	1.627 (10)		
Host molecule			
C(3)—S(1)—C(4)	90.9 (3)	O(2)—C(12)—C(10)	121.4 (6)
C(9)—S(2)—C(10)	91.5 (3)	O(2)—C(12)—C(13)	122.5 (6)
C(15)—S(3)—C(16)	91.5 (3)	C(10)—C(12)—C(13)	116.0 (6)
C(2)—C(1)—C(8)	112.4 (5)	C(1)—C(14)—C(15)	125.9 (6)
C(2)—C(1)—C(14)	112.9 (5)	C(1)—C(14)—C(17)	122.1 (5)
C(8)—C(1)—C(14)	110.3 (5)	C(15)—C(14)—C(17)	112.0 (6)
C(1)—C(2)—C(3)	122.7 (6)	S(3)—C(15)—C(14)	113.1 (5)
C(1)—C(2)—C(5)	126.0 (6)	S(3)—C(16)—C(17)	112.2 (5)
C(3)—C(2)—C(5)	111.2 (6)	O(1)—C(6)—C(4)	117.4 (8)
S(1)—C(3)—C(2)	113.8 (5)	O(1)—C(6)—C(7)	122.8 (8)
S(1)—C(4)—C(5)	112.7 (5)	C(4)—C(6)—C(7)	119.8 (7)
S(1)—C(4)—C(6)	120.7 (6)	C(1)—C(8)—C(9)	126.1 (6)
C(5)—C(4)—C(6)	126.6 (7)	C(1)—C(8)—C(11)	122.6 (5)
C(2)—C(5)—C(4)	111.5 (6)	C(16)—C(18)—C(19)	120.0 (6)
C(9)—C(8)—C(11)	111.3 (5)	S(3)—C(16)—C(18)	121.9 (5)
S(2)—C(9)—C(8)	112.5 (5)	C(17)—C(16)—C(18)	125.9 (6)
S(2)—C(10)—C(11)	111.3 (5)	C(14)—C(17)—C(16)	111.3 (6)
S(2)—C(10)—C(12)	118.5 (4)	O(3)—C(18)—C(16)	117.8 (6)
C(11)—C(10)—C(12)	130.2 (6)	O(3)—C(18)—C(19)	122.2 (6)
C(8)—C(11)—C(10)	113.4 (5)		
Guest molecule			
Cl(1)—C(20)—Cl(2)	105.3 (6)	Cl(1)—C(20)—Cl(2)'	107.0 (6)
Cl(1)—C(20)—Cl(3)	110.6 (6)	Cl(1)—C(20)—Cl(3)'	101.3 (7)
Cl(1)—C(20)—Cl(4)	111.6 (6)	Cl(1)—C(20)—Cl(4)'	122.2 (8)
Cl(2)—C(20)—Cl(3)	105.1 (6)	Cl(2)'	109.9 (9)
Cl(2)—C(20)—Cl(4)	111.8 (6)	Cl(2)'	111.6 (8)
Cl(3)—C(20)—Cl(4)	112.0 (7)	Cl(3)'	103.8 (9)

The structure was solved by direct methods with the program *SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989) and refined by full-matrix least squares using the *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) system of programs. All the non-H atoms were refined with anisotropic displacement parameters. All positions and displacement parameters of the H atoms were calculated. The CCl_4 solvent is partially disordered. Cl(1) and C(20) are ordered but there are two orientations of the remaining Cl atoms, a major (65%) and a minor (35%).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71621 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1049]

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Structures of the Choline Ion in Different Crystal Surroundings

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Abstract

The crystal structures of four choline salts have been determined: choline (*S*)-*N*-acetylserinate, $\text{C}_5\text{H}_{14}\text{NO}^+ \cdot \text{C}_5\text{H}_8\text{NO}_4^-$, choline (*R,R*)-hydrogentartrate, $\text{C}_5\text{H}_{14}\text{NO}^+ \cdot \text{C}_4\text{H}_5\text{O}_6^-$, choline (\pm)-*N*-acetylphenylalaninate, $\text{C}_5\text{H}_{14}\text{NO}^+ \cdot \text{C}_{11}\text{H}_{12}\text{NO}_3^-$, and dicholine phthalate, $2\text{C}_5\text{H}_{14}\text{NO}^+ \cdot \text{C}_8\text{H}_4\text{O}_4^{2-}$. In these compounds the choline ion adopts two different conformations, extended and folded, both of which are low-energy conformations. In all four crystal structures, the hydroxy group of the choline ion is involved in a hydrogen bond to a carboxylate group. Short contacts between the quaternary ammonium groups and the carboxylate groups are not observed, but there are many weak contacts.

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