

The Crystal Structure of the Cesium Salt of 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione

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The crystal structure of the title compound, $\text{Cs}_2\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S}$, has been determined from 2410 independent, non-zero X-ray reflections collected with a counter diffractometer. The compound crystallizes in the space group $A2/a$ (No. 15) with 8 formula units in a unit cell of dimensions $a=16.55(1)$ Å, $b=4.969(6)$ Å, $c=27.73(9)$ Å and $\beta=108.0(2)^\circ$. The crystal densities are $D_x=2.17$ g cm $^{-3}$ and $D_m=2.17$ g cm $^{-3}$. The structure was solved by the heavy atom method and refined by the full matrix least squares procedure to a final value of $R=0.040$. The structure consists of infinite $(\text{Cs}_2\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_n$ chains running in the direction of the b axis. Within each chain pairs of cesium atoms alternate with pairs of β -diketonate residuals, which roughly may be represented as planes inclined 42, 125 and 70° to the axes of the abc^* reference system. The chains are connected by a 2.73(2) Å F \cdots H contact and two F \cdots Cs contacts of 3.26(2) and 3.43(2) Å. Two of the fluorine atoms involved in these contacts are disordered. The observed bond lengths and angles agree well with those given in the literature for a wide range of acetylacetonates.

The present work is the first of a series of crystal structure studies of metal compounds formed with the unsymmetrical ligand 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (trivial name thenoyltrifluoroacetone), henceforth referred to as HTTA; Fig. 1.

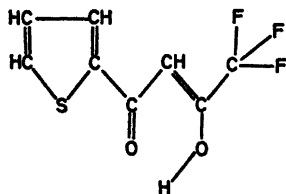


Fig. 1. 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione.

As far as the author is aware, this is the first crystal structure determination of a β -diketonate of an alkali metal. A crystal structure analysis of $\text{NH}_4\text{Pr}(\text{TTA})_4 \cdot \text{H}_2\text{O}$ has been published by Lalancette *et al.*¹

EXPERIMENTAL

Preparation and analysis. 5.00 g of powdered Cs_2CO_3 (Merck) was suspended in 50 ml of ethanol and saturated with CO_2 . 6.80 g of the purified β -diketone (Merck) dissolved in 50 ml of ethanol was added slowly, while a stream of CO_2 was passed through the mixture. The yellowish, impure crystalline residue obtained by evaporation of the solvent was rinsed with benzene and recrystallized from nitromethane. The yield of colourless crystals was 1.1 g. Cs was determined microgravimetrically as Cs_2SO_4 . A few milligrams of the substance were moistened with a mixture of nitric acid and sulfuric acid, taken to fumes by gentle heating and then ignited until constant weight. (Found: Cs 37.36. Calc. for $\text{Cs}_2\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S}$: 37.53).

The thin crystal needles are very easily split along the direction of the needle axis. Only completely transparent crystals showing perfect extinction in polarized light were selected for the structure analysis.

Collection and treatment of intensity data. A nearly cylindrical crystal of 0.01 cm cross section was mounted with the needle axis (b -axis) in the direction of the spindle on a semiautomatic STOE Weissenberg diffractometer, which was run in the ω -scan mode. Monochromatized (LiF) $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å) was applied. Intensities diffracted from all unique planes within a $\sin \theta/\lambda$ range from 0.06 to 0.70 Å $^{-1}$ were measured by means of a scintillation detector provided with a pulse height analysator. The stability of the crystal and the diffractometer system was monitored by frequent remeasurement of a standard reflection of medium strength. The observed intensities

were converted to relative structure factors and standard deviations by the formulas,

$$F_o = (I_o/Lp)^{\frac{1}{2}} \text{ and}$$

$$\sigma(F_o) = \left(\frac{[I + \sigma(I)]^2 - I^2}{Lp} \right)^{\frac{1}{2}},$$

where Lp is the usual Lorentz and polarization correction factor, neglecting prepolarization. The latter calculation, and all other calculations necessary for the solution of the structure, were performed by means of the X-RAY system of crystallographic programs.² Corrections for absorption were omitted ($\mu R = 0.183$). 675 reflections having $F_o < 2\sigma(F_o)$ were rejected as not observable, leaving 2410 reflections for the structure analysis, *i.e.* more than 14 observations per adjustable parameter

CRYSTAL DATA

Formula weight for $Cs_2H_4F_8O_2S$ is 354.1, monoclinic (b axis unique). Unit cell at 22 °C: $a = 16.55(1)$ Å, $b = 4.969(6)$ Å, $c = 27.73(9)$ Å, $\beta = 108.0(2)^\circ$. $V = 2169$ Å³. $F(000) = 1238$. $D_x (Z=8) = 2.17$ g cm⁻³, $D_m(\text{float.}) = 2.17$ g cm⁻³, $\mu(\text{MoK}\alpha) = 36.6$ cm⁻¹.

The unit cell dimensions are average values from several independent precession photographs. The space groups $A2/a$ (No. 15) or Aa (No. 9) were indicated by the systematic absences, hkl for $h+l$ odd and $h0l$ for h odd. The structure analysis was based on space group $A2/a$: $(0,0,0; 0, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; \frac{1}{2} + x, \bar{y}, z)$. The choice of the centrosymmetric space group was confirmed by the solution and successful refinement of the structure.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved for all non-hydrogen atoms by the heavy atom method. Atomic form factors for Cs^+ , given by Cromer and Waber³ were used. The correction for the anomalous dispersion of cesium as well as the form factors for the light atoms were taken from International Tables for X-Ray Crystallography.⁴ The refinement by full matrix least squares calculations proceeded well except for the fluorine atoms F(1) and F(3), Fig. 4. They were substituted by pairs of half atoms F(11), F(12) and F(31), F(32), as suggested by the difference Fourier map, shown in part on Fig. 2.

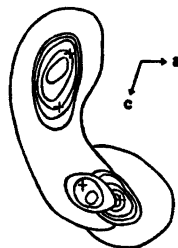


Fig. 2. Composite projection on the ac plane of the difference Fourier map showing the positive electron density in the vicinity of the disordered fluorine atoms. Contours are at 0.5 e Å⁻³ intervals, beginning at 0.5 e Å⁻³. The final half atom sites are shown by +.

Then, the refinement was reassumed and continued until all shifts were less than $1/10$ of the estimated standard deviation. The R value was 0.042. The hydrogen atoms H(1), H(2), and H(6) now showed up clearly on a new difference map. They were assigned an (invariant) isotropic temperature factor corresponding to that of the carrier atom, and refined by two more cycles of least squares calculations. The site of the hydrogen atom H(3), however, remained obscure. During the later stages of refinement an empirical weight function $w^{\frac{1}{2}} = 1/\sigma = [F/(25 + 0.00015F^2)]^{\frac{1}{2}}$ was used. The final R value was 0.040, and the value of the error of fit function, $[\sum w(\Delta F)^2/(n-m)]^{\frac{1}{2}}$, was 1.06. The fractional coordinates of the observed atoms and the thermal parameters are listed in Table 1. A list of the observed and calculated structure factors may be obtained from this institute.

RESULTS AND DISCUSSION

The characteristic feature of the structure is illustrated in Fig. 3. Irregular Cs_2O_4 octahedra sharing two opposite faces form an infinite chain running in the direction of the b axis. The complete chain is made up of pairs of cesium atoms alternating with pairs of the TTA moiety. Roughly, the interleaving TTA pairs (except the fluorine atoms) may be regarded as planes inclined 42 , 125 , and 70° to the axes of the orthogonal reference system abc^* . The six unique $Cs-O$ distances shown on Fig. 3 range from $3.031(6)$ to $3.391(6)$ Å.

Table 1. CsTTA. Fractional atomic coordinates and anisotropic thermal parameters. Standard deviations are in parentheses. The form of the temperature factor is $\exp[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}]$. For labelling of the atoms see Fig. 4. * = half atom sites.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cs ⁺	0.10636(2)	0.21891(6)	0.02515(1)	0.0397(2)	0.0322(2)	0.0492(2)	-0.0037(1)	0.0176(1)	-0.0041(1)
S	0.1591(1)	1.0549(5)	0.1610(1)	0.065(1)	0.070(1)	0.065(1)	-0.014(1)	0.012(1)	-0.011(1)
O(1)	0.0630(3)	0.6980(9)	0.0803(2)	0.061(3)	0.042(3)	0.043(2)	-0.006(2)	-0.028(2)	-0.009(2)
O(2)	-0.0694(3)	0.2796(9)	0.0432(2)	0.054(3)	0.043(2)	0.050(2)	-0.005(2)	0.023(2)	-0.007(2)
C(1)	0.1659(7)	1.2035(19)	0.2162(4)	0.095(7)	0.056(5)	0.068(5)	-0.004(5)	0.024(5)	-0.011(4)
C(2)	0.1045(8)	1.1282(24)	0.2344(4)	0.123(9)	0.082(7)	0.049(4)	0.009(6)	0.017(5)	-0.022(4)
C(3)	0.0464(4)	0.9503(13)	0.2048(2)	0.057(3)	0.051(3)	0.029(2)	-0.005(3)	0.021(2)	-0.006(2)
C(4)	0.0723(4)	0.8798(12)	0.1599(2)	0.054(3)	0.035(2)	0.031(2)	0.006(2)	0.007(2)	-0.017(2)
C(5)	0.0326(4)	0.6987(11)	0.1163(2)	0.044(3)	0.031(2)	0.036(2)	0.004(2)	0.013(2)	0.001(2)
C(6)	-0.0402(4)	0.5479(13)	0.1177(2)	0.051(3)	0.044(3)	0.044(3)	-0.008(2)	0.024(3)	-0.003(2)
C(7)	-0.0840(4)	0.3632(12)	0.0820(2)	0.041(3)	0.036(3)	0.037(3)	0.006(2)	0.014(2)	0.004(2)
C(8)	-0.1654(5)	0.2538(16)	0.0907(2)	0.049(4)	0.065(5)	0.061(4)	-0.013(3)	0.017(3)	-0.012(3)
*F(11)	-0.2281(11)	0.408(4)	0.0808(10)	0.056(9)	0.089(9)	0.209(26)	0.031(7)	0.074(16)	0.024(15)
*F(12)	-0.2302(11)	0.380(6)	0.0528(8)	0.032(6)	0.147(15)	0.125(14)	0.020(7)	0.011(8)	0.011(13)
F(2)	-0.1887(4)	0.0158(13)	0.0685(3)	0.085(4)	0.076(4)	0.182(7)	-0.025(3)	0.064(4)	-0.013(4)
*F(31)	-0.1524(9)	0.140(4)	0.1358(6)	0.071(7)	0.122(12)	0.083(8)	-0.14(7)	0.042(6)	-0.038(9)
*F(32)	-0.1832(12)	0.331(6)	0.1296(7)	0.101(13)	0.268(27)	0.098(12)	-0.107(15)	0.082(11)	-0.075(16)
H(1)	0.209(9)	1.315(19)	0.223(4)	0.090					
H(2)	0.098(8)	1.221(26)	0.226(3)	0.106					
H(6)	-0.052(5)	0.564(13)	0.151(2)	0.058					

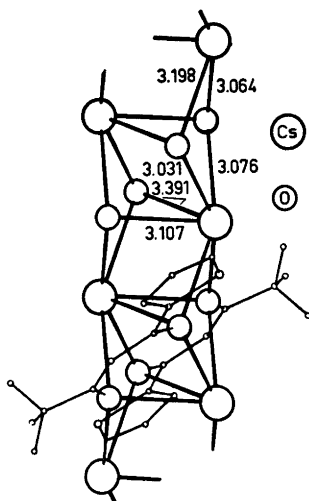


Fig. 3. The Cs—O chain and one centrosymmetric pair of TTA ligands, viewed approximately along the c^* axis. Cs—O distances are given in Å, the estimated standard deviation is 0.006 Å.

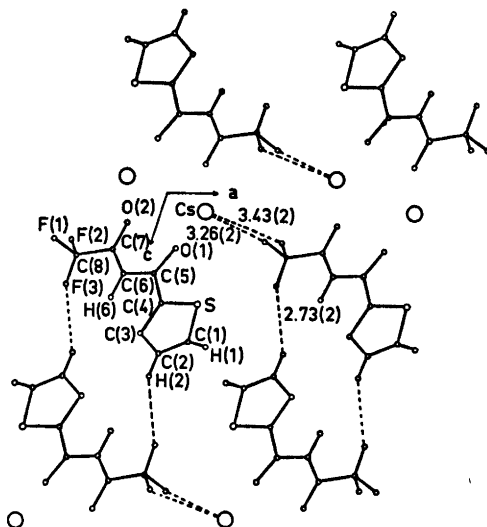


Fig. 4. Projection of the CsTTA structure on the ac plane. Short interchain distances $F\cdots H$ and $F\cdots Cs$ are shown as broken lines.

Fig. 4 shows the packing of the chains. Only three short interchain distances less than 3.5 Å have been found, *viz* the 2.73(2) Å $F(3)\cdots H(2)$ distance, which is approximately equal to the sum of the van der Waals radii, the 3.26(2) Å $F(1)\cdots Cs^+$ distance, and the 3.43(2) Å $F(2)\cdots Cs^+$ distance. They are indicated by broken lines. These contacts provide the weak interchain cohesion which explains the

extreme ease with which the crystals are split along the b direction. Two of the fluorine atoms $F(1)$ and $F(3)$ involved in these contacts are considered to be disordered. Computationally they have been represented by pairs of half atoms. The distances quoted above refer to the center of gravity of the respective half-atom pairs.

Table 2. CsTTA, bond lengths and angles of the ligand with estimated standard deviations.

Bond lengths in Å		Angles in degrees	
S—C(4)	1.679(7)	C(1)—S—C(4)	93.1(5)
S—C(1)	1.676(12)	S—C(1)—C(2)	112.8(8)
C(1)—C(2)	1.318(19)	C(1)—C(2)—C(4)	115.7(9)
C(2)—C(3)	1.375(13)	C(2)—C(3)—C(4)	108.9(8)
C(3)—C(4)	1.480(10)	C(3)—C(4)—S	109.4(4)
C(4)—C(5)	1.487(8)	C(3)—C(4)—C(5)	131.2(6)
C(5)—C(6)	1.427(9)	C(5)—C(4)—S	119.3(5)
C(6)—C(7)	1.380(8)	C(4)—C(5)—O(1)	117.8(6)
C(7)—C(8)	1.538(11)	C(4)—C(5)—C(6)	117.4(6)
C(5)—O(1)	1.247(9)	C(6)—C(5)—O(1)	124.8(5)
C(7)—O(2)	1.243(9)	C(5)—C(6)—C(7)	126.1(6)
C(8)—F(1) ^a	1.268(11)	C(6)—C(7)—O(2)	130.1(6)
C(8)—F(2)	1.334(11)	C(6)—C(7)—C(8)	114.4(6)
C(8)—F(3) ^a	1.182(11)	C(8)—C(7)—O(2)	115.5(5)
C(1)—H(1)	0.88(14)	C(7)—C(8)—F(2)	112.5(7)
C(2)—H(2)	1.04(14)		
C(6)—H(6)	1.00(9)		

^a Distance to the center of gravity of the half atoms.

The observed bond lengths and bond angles of the ligand are listed in Table 2. In general they agree well with those reported in the literature for a wide range of acetylacetonates,⁵ and with those found in the NH₄Pr(TTA)₄·H₂O compound.¹ The C(7)–C(8) bond is a single bond, 1.54(1) Å. The C(1)–C(2), bond, 1.32(2) Å, is a double bond. The remaining C–C bonds are of intermediate order.

The non-hydrogen atoms of the thiophene ring are coplanar ($\chi^2 = 3.0$). The C_{2v} symmetry found in the free thiophene molecule,⁶ however, is destroyed. A similar distortion of the ring has been observed in 2-chloro- and the 2-bromothiophene.⁷

It is noteworthy, that the two C–O bonds are identical, *viz.* 1.247(9) and 1.243(9) Å, in this compound where no benzenoid chelate ring is formed. The C–O bonds are the shortest observed in a β -diketonate, probably due to the ionic character of the Cs–O bond. The intraligand distance O(1) to O(2), 2.962(7) Å, the so-called bite of the ligand, is the longest observed.

The shape of the ligand has been analyzed in terms of several best planes. The dihedral angle between the thiophene plane and the best plane through the atoms C(4) to C(8) is only 2.3°. The O–C–C–O arc is twisted; the dihedral angle between the planar groups O(1)–C(4–6) and O(2)–C(6–8) is 8.1°.

All crystallographic calculations have been performed at the Northern Europe University Computing Center (NEUCC), DK-2800 Lyngby. The drawings, Figs. 3 and 4, have been made by means of the ORTEP II program; of C. K. Johnson.⁸

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