

The Crystal and Molecular Structure of Indium and Iron(III) Complexes with 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione

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Single crystals of the title compounds, $\text{In}(\text{TТА})_3$ and $\text{Fe}(\text{TТА})_3$, have been investigated by X-ray diffractometry. The compounds are isostructural $\text{In}(\text{TТА})_3$: $a = 8.803(15)$ Å, $b = 17.67(3)$ Å, $c = 19.63(4)$ Å, $\beta = 110.2(1)^\circ$. $\text{Fe}(\text{TТА})_3$: $a = 8.865(9)$ Å, $b = 17.46(2)$ Å, $c = 19.69(2)$ Å, $\beta = 110.8(1)^\circ$. Space group $P2_1/c$. The structures were refined to $R = 0.069$ and 0.078 , respectively. The unit cell contains two pairs of *meridional-tris- β -diketonate* complexes centered on the special positions $\frac{1}{2}, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The metal atom is at the center of gravity of the six coordinating oxygen atoms, which form the apices of a slightly deformed octahedron. The average $\text{In}-\text{O}$ distance is $2.13(2)$ Å, the $\text{Fe}-\text{O}$ distance is $1.99(2)$ Å. Contrary to other *tris- β -diketonates* the two $\text{C}-\text{C}$ bonds of the chelate ring are of unequal length, the $\text{C}-\text{C}$ bond closest to the CF_3 group being the shorter. Fluorine atoms apart, each ligand may roughly be represented by a plane pivoted around an edge of the coordination polyhedron.

The crystal structure analysis, reported in this paper, is the second of a current series of structure investigations¹ of metal compounds of 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, (trivial name thenoyltrifluoroacetone). The structure formula of this unsymmetric β -diketone, henceforth designated HTTA, is shown in Fig. 1.

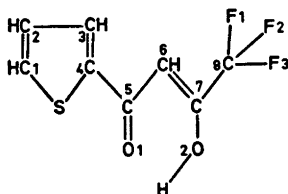


Fig. 1. Structure formula of 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, displaying the labelling scheme.

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The compounds $\text{In}(\text{TТА})_3$ and $\text{Fe}(\text{TТА})_3$, which are the topics of this paper, are isostructural.

EXPERIMENTAL

Preparation and analysis

$\text{In}(\text{TТА})_3$ 6.6 g of InCl_3 (BDH) was dissolved in 130 ml of 50 % ethanol, (v/v). 15.9 g of the β -diketone (Merck), freshly sublimed *in vacuo*, were dissolved in 320 ml of 50 % ethanol and neutralized with ammonia. The former solution was slowly poured into the latter under vigorous stirring. The stirring was continued for half an hour, then the precipitation was completed by addition of 450 ml of water. The white, microcrystalline raw product was washed with water and dried in the air. Colourless, tabular crystals were grown from a solution of the raw product in nitromethane. The melting point, determined on a microscope hot stage (Mettler FP52/5), was 164.6 ± 0.8 °C. After destruction of the complex with concentrated nitric acid, indium was determined by microtitration with EDTA according to Schwarzenbach.² (Found: In 14.68. Calc. for $\text{In}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_3$: 14.75).

$\text{Fe}(\text{TТА})_3$ was prepared as described by Berg and Truemper.³ Single crystals were grown from a solution of the raw material in a 50 % (v/v) mixture of diethylether and cyclohexane. The well-developed, garnet red, prismatic crystals melt at 162.6 ± 0.5 °C on the hot stage microscope; m.p. lit.³ 159–160 °C. Iron was determined by microtitration with EDTA² after appropriate destruction of the complex. (Found: Fe 7.78. Calc. for $\text{Fe}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_3$: 7.76).

Collection and treatment of intensity data

Intensity data were collected by means of a semi-automatic two-circle diffractometer, run in the ω -scan mode. Net intensities were con-

verted to relative structure factors by application of the usual Lorentz and polarization corrections.

In(TTA)₃. Monochromatized (graphite) MoK α radiation ($\lambda=0.71069$ Å) was used to measure the reflections from all unique planes in the $\sin \theta/\lambda$ range from 0.06 to 0.6 Å⁻¹. Two different crystals had to be used. During the scanning of the hkl zone, the first crystal became opaque, and its reflecting power decreased more than 10 % within a few hours. A second crystal sufficed for the remainder of the data collection. For scaling purposes the $h0l$ reflections of the second crystal were also measured. The dimensions of the two crystals were $0.250 \times 0.060 \times 0.375$ mm³ and $0.375 \times 0.070 \times 0.400$ mm³, respectively. Since the platy crystals were mounted with their shortest dimension (the b -axis) along the direction of the Weissenberg spindle, corrections for absorption⁴ were made. A Gaussian grid of 864 sample points was found suitable. Each F_o was assigned a standard deviation based on counting statistics. Reflections with $F_o < 3\sigma(F_o)$ were rejected, leaving 2759 reflections for the structure analysis, i.e. more than 6 observations per adjustable parameter.

Fe(TTA)₃. The $\sin \theta/\lambda$ range was 0.06 to 0.45 Å⁻¹, (LiF-monochromator). No corrections were made for absorption. The yield of $F_o < 3\sigma(F_o)$ was 1178, i.e. approximately 5 observations per refined parameter. (Fe and F atoms only were assigned anisotropic temperature parameters).

CRYSTAL DATA

In(C₆H₄F₃O₃S)₃ (FW=778.3) and *Fe(C₆H₄F₃O₃S)₃* (FW=719.4) both crystallize in the space group $P2_1/c$ (No. 14). Unit cell dimensions were determined from several independent precession photographs.

In(TTA)₃: $a=8.803(15)$ Å, $b=17.67(3)$ Å, $c=19.63(4)$ Å, $\beta=110.2(1)^\circ$, at 22 °C. Volume of the cell = 2867 Å³. $F(000)=1528$. $D_x(Z=4)=1.788$ g cm⁻³, $D_m(\text{float.})=1.788(5)$ g cm⁻³. $\mu(\text{MoK}\alpha)=11.3$ cm⁻¹.

Fe(TTA)₃: $a=8.865(9)$ Å, $b=17.46(2)$ Å, $c=19.69(2)$ Å, $\beta=110.8(1)^\circ$, at 22 °C. Volume of the cell = 2848 Å³. $F(000)=1436$. $D_x(Z=4)=1.678$ g cm⁻³, $D_m(\text{float.})=1.675(5)$ g cm⁻³. $\mu(\text{MoK}\alpha)=8.60$ cm⁻¹.

SOLUTION AND REFINEMENT OF THE STRUCTURES

In(TTA)₃. The structure was solved for all non-hydrogen atoms by application of the heavy atom method. At the later stages of

Table 1. *In(TTA)₃*. Fractional atomic coordinates and anisotropic thermal parameters of the observed atoms. Standard deviations are in parentheses. The form of the temperature factor expression is $\exp[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}]$. See Fig. 1 for labelling of the atoms.

	X	Y	Z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In	0.4544(1)	0.21043(5)	0.08363(2)	0.050(1)	0.028(1)	0.033(1)	0.000(5)	0.020(5)	0.001(5)
S(1)	0.2994(6)	0.1463(2)	0.2933(2)	0.096(4)	0.056(2)	0.055(2)	0.003(2)	0.028(2)	0.008(2)
F(11)	0.119(2)	0.4577(7)	0.0940(7)	0.27(2)	0.082(9)	0.12(1)	0.10(1)	0.131(15)	0.057(8)
F(12)	0.074(2)	0.4137(2)	-	0.168(15)	0.076(9)	0.10(1)	0.038(9)	-	0.030(8)
F(13)	0.2970(15)	0.4560(5)	0.0507(8)	0.12(1)	0.062(8)	0.198(15)	0.005(7)	0.05(1)	0.060(9)
O(11)	0.338(1)	0.1982(4)	0.1630(4)	0.083(8)	0.029(5)	0.044(6)	0.010(5)	0.043(6)	0.002(4)
O(12)	0.287(1)	0.3000(5)	0.0446(4)	0.078(8)	0.040(6)	0.030(5)	0.017(5)	0.021(5)	0.001(4)
C(11)	0.236(2)	0.168(1)	0.3683(8)	0.090(15)	0.07(1)	0.05(1)	-	0.04(1)	0.009(1)
C(12)	0.171(2)	0.236(1)	0.357(1)	0.06(1)	0.08(1)	0.09(1)	0.00(1)	0.04(1)	-
C(13)	0.1576(15)	0.2774(5)	0.2955(6)	0.038(8)	0.033(7)	0.035(7)	-	0.023(6)	0.006(5)
C(14)	0.2367(15)	0.2314(8)	0.2532(6)	0.036(9)	0.048(9)	0.032(7)	-	0.005(6)	0.000(6)
C(15)	0.2665(15)	0.2493(7)	0.1863(6)	0.044(9)	0.045(8)	0.016(6)	-	0.017(6)	0.002(5)

Table 1. Continued.

C(16)	0.218(2)	0.3195(7)	0.1512(6)	0.06(1)	0.0933(7)	0.034(8)	0.009(7)	0.020(7)	-0.002(6)
C(17)	0.2313(15)	0.3374(7)	0.0868(7)	0.036(9)	0.043(8)	0.033(7)	-0.001(6)	0.005(6)	-0.019(6)
C(18)	0.180(2)	0.4158(8)	0.0581(8)	0.07(1)	0.048(9)	0.047(9)	0.024(9)	0.019(9)	-0.003(8)
S(2)	0.6329(6)	0.2040(2)	-0.1275(2)	0.100(4)	0.067(3)	0.049(2)	0.007(3)	0.028(3)	-0.008(2)
O(21)	0.571(1)	0.2229(4)	0.0048(4)	0.075(7)	0.030(5)	0.034(5)	-0.006(5)	0.025(5)	-0.010(4)
O(22)	0.624(1)	0.2947(6)	0.1409(4)	0.059(7)	0.042(6)	0.043(5)	-0.009(5)	0.017(5)	-0.014(5)
F(21)	0.768(3)	0.4718(7)	0.1205(7)	0.034(2)	0.070(8)	0.114(9)	-0.10(1)	0.113(8)	-0.040(6)
F(22)	0.867(2)	0.4015(8)	0.2066(8)	0.138(15)	0.12(1)	0.14(1)	0.00(1)	-0.05(1)	-0.07(1)
F(23)	0.637(2)	0.4391(7)	0.1815(8)	0.15(1)	0.11(1)	0.18(1)	-0.044(9)	0.11(1)	-0.11(1)
C(21)	0.704(3)	0.2443(15)	-0.1887(9)	0.091(15)	0.14(2)	0.030(9)	0.022(15)	0.010(9)	0.02(1)
C(22)	0.754(3)	0.3132(15)	-0.172(1)	0.095(15)	0.14(2)	0.081(15)	0.00(2)	0.05(1)	0.048(15)
C(23)	0.750(2)	0.3396(7)	-0.1062(6)	0.045(9)	0.050(8)	0.023(7)	-0.021(7)	0.008(6)	0.013(6)
C(24)	0.677(2)	0.2821(8)	-0.0740(7)	0.063(9)	0.056(9)	0.028(7)	0.005(8)	0.015(7)	0.008(7)
C(25)	0.639(2)	0.2807(7)	-0.0082(6)	0.053(9)	0.043(8)	0.035(7)	0.003(7)	0.016(7)	0.000(6)
C(26)	0.686(2)	0.3442(8)	0.0403(7)	0.08(1)	0.043(8)	0.034(8)	-0.008(8)	0.029(8)	-0.006(6)
C(27)	0.674(2)	0.3459(7)	0.1059(6)	0.05(1)	0.042(8)	0.027(7)	-0.007(7)	0.018(7)	-0.020(6)
C(28)	0.737(3)	0.4150(9)	0.1527(9)	0.105(15)	0.05(1)	0.06(1)	-0.02(1)	0.03(1)	-0.016(8)
S(3)	0.0260(6)	0.0640(2)	-0.0977(2)	0.056(3)	0.077(3)	0.048(2)	-0.008(2)	0.010(2)	0.004(2)
F(31)	0.642(2)	0.08(1)	0.1785(9)	0.178(15)	0.046(7)	0.170(15)	0.013(8)	-0.07(1)	0.028(8)
F(32)	0.588(2)	0.0198(7)	0.2475(8)	0.065(7)	0.24(2)	0.12(1)	0.093(15)	0.08(1)	0.136(15)
F(33)	0.7945(15)	0.1287(6)	0.0118(4)	0.065(7)	0.033(5)	0.079(8)	0.019(7)	0.001(6)	0.037(7)
O(31)	0.597(1)	0.119(5)	0.1385(4)	0.060(7)	0.038(5)	0.032(5)	-0.009(5)	0.009(5)	0.003(4)
C(31)	-0.066(2)	-0.016(1)	-0.1363(6)	0.059(15)	0.105(16)	0.030(5)	0.003(5)	0.012(5)	-0.005(4)
C(32)	0.161(2)	-0.077(1)	-0.1014(9)	0.080(15)	0.084(15)	0.05(1)	-0.03(1)	0.02(1)	0.02(1)
C(33)	0.179(2)	-0.0620(8)	-0.0426(8)	0.07(1)	0.06(1)	0.065(15)	-0.05(1)	0.02(1)	-0.02(1)
C(34)	0.3030(15)	0.0154(7)	0.0218(6)	0.09(1)	0.03(8)	0.054(9)	-0.016(9)	0.045(9)	-0.025(8)
C(35)	0.4172(15)	0.0570(5)	0.0773(7)	0.037(9)	0.03(8)	0.050(9)	-0.005(7)	0.019(8)	-0.001(7)
C(36)	0.5455(15)	0.0191(8)	0.0773(7)	0.05(1)	0.030(15)	0.037(7)	-0.001(6)	0.027(7)	-0.010(6)
C(37)	0.641(2)	0.0520(8)	0.1314(8)	0.026(8)	0.043(8)	0.047(9)	0.008(7)	0.013(8)	-0.014(7)
C(38)	0.641(2)	0.0015(9)	0.1947(9)	0.058(15)	0.040(8)	0.07(1)	0.010(7)	0.013(7)	0.002(7)
H(11)	0.24(2)	0.14(1)	0.40(1)	0.059	0.05(1)	0.07(1)	0.011(9)	0.02(1)	0.015(8)
H(12)	0.12(3)	0.26(1)	0.39(1)	0.078	0.06(1)	0.06(1)	0.016(9)	0.045(9)	-0.025(8)
H(16)	0.17(2)	0.354(9)	0.175(8)	0.039	0.06(1)	0.054(9)	-0.016(9)	0.045(9)	-0.025(8)
H(21)	0.65(2)	0.24(1)	-0.24(1)	0.101	0.03(8)	0.050(9)	-0.005(7)	0.019(8)	-0.001(7)
H(22)	0.80(3)	0.36(1)	-0.20(1)	0.089	0.03(8)	0.037(7)	-0.001(6)	0.027(7)	-0.010(6)
H(26)	0.73(2)	0.39(1)	0.022(9)	0.049	0.043(8)	0.047(9)	0.008(7)	0.013(8)	-0.014(7)
H(31)	-0.17(2)	-0.021(1)	-0.17(1)	0.065	0.040(8)	0.07(1)	0.010(7)	0.013(7)	0.002(7)
H(32)	0.00(2)	-0.12(1)	-0.12(1)	0.062	0.05(1)	0.07(1)	0.011(9)	0.02(1)	0.015(8)
H(36)	0.41(2)	-0.04(1)	0.076(9)	0.049	0.05(1)	0.07(1)	0.011(9)	0.02(1)	0.015(8)

refinement an empirical weight function, $w^{\frac{1}{2}} = (5.0 + 0.0140 F_o)^{-\frac{1}{2}}$, was used. When the refinement was nearly completed, the sites of the hydrogen atoms, except those attached to the C(3) atoms, could be localized on a Fourier difference map. Each hydrogen atom was assigned an (invariant) isotropic temperature factor corresponding to that of the carrier atom. A few more cycles of least squares calculations brought the refinement to a conclusion, where all shifts were less than 1/10 of the estimated standard deviation. The final R value was 0.069, and the error of fit quotient was 1.15.

$Fe(TTA)_3$. The structure was solved and refined for all non-hydrogen atoms, the indium compound being used as a starting model. $w^{\frac{1}{2}} = 14.1/F_o$, maximum allowed $w = 0.1$. The refinement terminated at $R = 0.078$. The error of fit quotient was 1.09.

Atomic form factors for the neutral atoms were used throughout. For indium the form factors were those given by Cromer and Waber.⁵ The other form factors, as well as corrections for the anomalous dispersion of In and Fe, were taken from *International Tables for X-Ray Crystallography*.⁶ Fractional coordinates and thermal parameters of the observed atoms are listed in Tables 1 and 2. Lists of observed and calculated structure factors may be obtained from this institute.

All crystallographic calculations have been performed with the X-RAY program system edited by Stewart.⁷ The stereo drawing Fig. 2 has been made by means of the ORTEP II program of Johnson.⁸

RESULTS AND DISCUSSION

Both structures consist of pairs of *meridional tris- β -diketonate* molecules, centered around the special positions $\frac{1}{2}, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (Fig. 2). The separation of the two enantiomorphous molecules in terms of the metal to metal distance is 8.28 Å for $In(TTA)_3$ and 8.22 Å for $Fe(TTA)_3$. The next shortest metal to metal distance is the a translation.

The metal atom is almost exactly at the common center of gravity of the six coordinating oxygen atoms, which form the apices of a slightly deformed octahedron. Metal to oxygen distances, oxygen to oxygen distances and some

Table 2. $Fe(TTA)_3$. Fractional atomic coordinates and thermal parameters of the observed atoms. Standard deviations are in parentheses. The form of the temperature factor expression is $\exp[-2\pi^2 \sum h_i^2 a_i^2 \sigma_i^2 U_{ij}]$. See Fig. 1 for labelling of the atoms.

	X	Y	Z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.460(3)	0.2117(1)	0.0830(1)	0.065(2)	0.040(2)	0.036(2)	0.003(2)	0.192(1)	0.004(1)
S(1)	0.3132(8)	0.1436(4)	0.2859(3)	0.086(2)					
F(11)	0.112(3)	0.456(1)	0.079(1)	0.27(2)	0.102(15)	0.196(15)	0.127(15)	0.144(15)	0.087(1)
F(12)	0.100(2)	0.412(1)	-0.0209(8)	0.150(15)	0.130(15)	0.09(1)	0.05(1)	-0.016(9)	0.024(9)
F(13)	0.305(2)	0.459(1)	0.047(1)	0.13(1)	0.09(1)	0.192(15)	0.00(1)	0.05(1)	0.06(1)
O(11)	0.3548(15)	0.2000(7)	0.1578(6)	0.049(3)					
O(12)	0.3069(15)	0.2986(7)	0.0445(6)	0.059(3)					
C(11)	0.253(3)	0.1618(15)	0.357(1)	0.075(6)					
C(12)	0.179(3)	0.2308(15)	0.350(1)	0.084(7)					
C(13)	0.161(2)	0.2761(9)	0.2851(8)	0.025(4)					
C(14)	0.247(2)	0.229(1)	0.2464(9)	0.048(5)					
C(15)	0.277(2)	0.247(1)	0.1812(9)	0.042(5)					
C(16)	0.228(2)	0.320(1)	0.147(1)	0.055(6)					

Table 2. Continued.

C(17)	0.245(2)	0.338(1)	0.082(1)	0.046(5)					
C(18)	0.187(3)	0.413(1)	0.048(1)	0.071(6)					
S(2)	0.6194(9)	0.2018(4)	-0.1260(4)	0.096(2)					
F(21)	0.800(3)	0.464(1)	0.1308(9)	0.40(3)					-0.07(1)
F(22)	0.860(2)	0.393(1)	0.2160(9)	0.165(15)				0.11(2)	-0.06(1)
F(23)	0.640(2)	0.440(1)	0.183(1)	0.124(13)				-0.05(1)	-0.12(1)
O(21)	0.5624(15)	0.2237(7)	0.0070(6)	0.049(3)			0.120(5)		
O(22)	0.6182(14)	0.2898(7)	0.1393(6)	0.053(3)			0.13(1)		
C(21)	0.691(3)	0.2358(15)	-0.189(1)	0.080(7)			0.189(15)		
C(22)	0.754(3)	0.3029(15)	-0.1681(15)	0.106(8)			0.02(1)		
C(23)	0.762(2)	0.331(2)	-0.1029(8)	0.023(4)			-0.02(1)		
C(24)	0.671(2)	0.276(1)	-0.070(1)	0.057(5)					
C(25)	0.641(2)	0.278(1)	-0.003(9)	0.044(5)					
C(26)	0.693(2)	0.343(1)	0.042(1)	0.056(5)					
C(27)	0.682(2)	0.340(1)	0.111(1)	0.051(5)					
C(28)	0.735(3)	0.4114(15)	0.1587(15)	0.081(7)					
S(3)	0.0293(8)	0.0718(4)	-0.0946(3)	0.077(2)					
F(31)	0.682(2)	0.063(1)	0.180(1)	0.20(2)			0.157(15)		0.021(9)
F(32)	0.805(2)	0.012(1)	0.2476(8)	0.15(1)			0.09(1)		0.12(1)
F(33)	0.802(2)	0.0288(9)	0.2226(7)	0.09(1)			0.01(1)		0.059(6)
O(31)	0.3157(15)	0.1347(7)	0.0172(6)	0.047(3)					
O(32)	0.5959(15)	0.1268(7)	0.1351(6)	0.049(3)					
C(31)	-0.069(3)	-0.0103(15)	-0.135(1)	0.084(7)			0.04(1)		
C(32)	0.013(3)	-0.0740(15)	-0.1018(15)	0.099(8)			0.103(15)		
C(33)	0.163(3)	0.058(1)	-0.040(1)	0.064(6)			0.01(1)		
C(34)	0.181(2)	0.023(1)	-0.0309(9)	0.050(5)					
C(35)	0.310(2)	0.062(1)	0.022(1)	0.053(5)					
C(36)	0.424(2)	0.021(1)	0.080(1)	0.055(5)					
C(37)	0.550(2)	0.058(1)	0.1315(9)	0.056(5)					
C(38)	0.652(3)	0.092(1)	0.196(1)	0.068(6)					
					0.07(1)	0.157(15)	0.04(1)	0.05(1)	
					0.27(2)	0.09(1)	0.103(15)	0.06(1)	
					0.127(15)	0.01(1)	0.01(1)	0.01(1)	

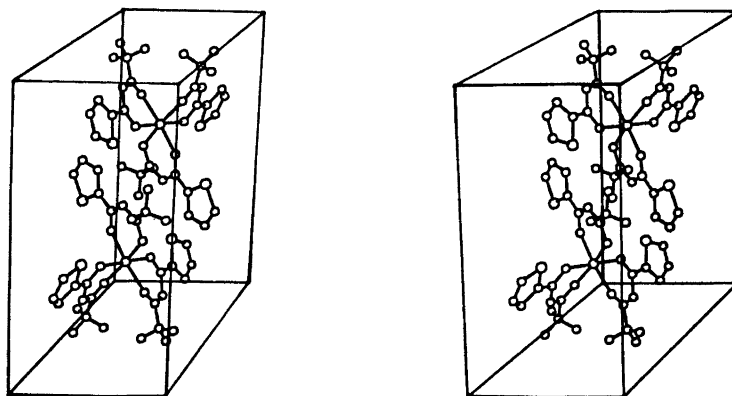


Fig. 2. Stereo drawing of one enantiomorphous pair of $\text{In}(\text{TTA})_3$ molecules centered around $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The b axis is pointing upward.

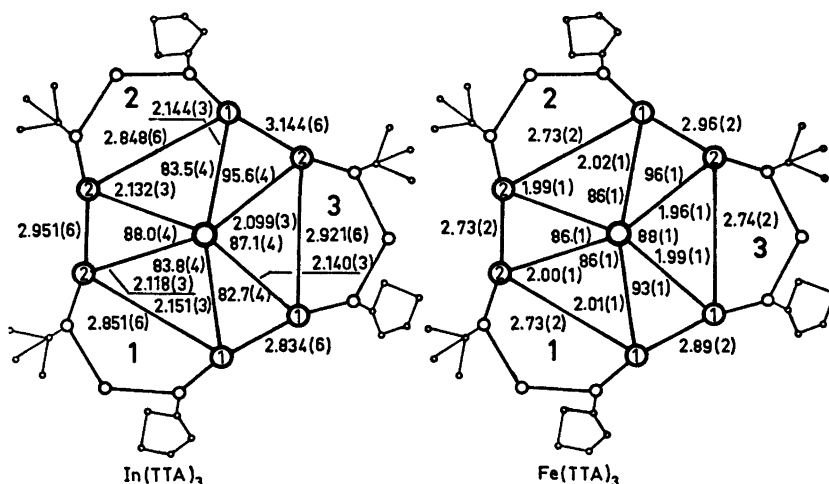


Fig. 3. Schematic representation of the complexes showing distances and (some) angles of the octahedron of coordination. Standard deviations are in parentheses.

oxygen-metal-oxygen bond angles are shown in Fig. 3.

The average $\text{Fe}-\text{O}$ distance is $1.99(2)$ Å*. The same average distance $1.992(6)$ Å, has been found in ferric *tris*-acetylacetonate.⁹ Also the average oxygen to oxygen "bite" distances of the chelate rings are virtually the same in the two ferric compounds, *viz.* $2.740(15)$ Å in the present compound and $2.732(2)$ Å in the acetylacetonate. The average $\text{In}-\text{O}$ distance is $2.13(2)$ Å. No structure determinations of

* Standard deviations of averages quoted in this section are sample deviations.

β -diketonates or similar compounds have been reported as yet. $\text{In}-\text{O}$ distances ranging from ~ 2.1 to ~ 2.2 Å have been found in some purely inorganic compounds, *e.g.* $2.171(8)$ Å in $\text{In}(\text{OH})_3$ ¹⁰.

As far as bond lengths and bond angles of the ligand are concerned the compounds investigated resemble each other closely. Average values for each compound are listed in Tables 3 and 4. The results compare well with those found for the Cs salt¹ and with those reported for $\text{NH}_4\text{Pr}(\text{TTA})_4 \cdot 2\text{H}_2\text{O}$.¹¹

A certain lack of regularity of the chelate ring is expected, due to the electronegative

Table 3. $\text{In}(\text{TТА})_3$ and $\text{Fe}(\text{TТА})_3$. Average lengths, in Å, of chemically equivalent bonds. The standard deviations (in parentheses) have been calculated from the formula $\sigma_l = [\sum_i (l_i - \bar{l})^2 / (n-1)]^{1/2}$. The typical standard deviation of individual bonds as estimated from the least squares refinement is 0.02 Å for $\text{In}(\text{TТА})_3$ and 0.03 Å for $\text{Fe}(\text{TТА})_3$.

Atoms	$\text{In}(\text{TТА})_3$ Average	Range	$\text{Fe}(\text{TТА})_3$ Average	Range
S—C(1)	1.688(9)	0.015	1.70(2)	0.04
S—C(4)	1.709(15)	0.032	1.68(3)	0.05
C(1)—C(2)	1.32(2)	0.04	1.34(4)	0.07
C(2)—C(3)	1.41(2)	0.03	1.43(7)	0.12
C(3)—C(4)	1.44(2)	0.08	1.49(5)	0.09
C(4)—C(5)	1.45(1)	0.02	1.43(1)	0.03
C(5)—C(6)	1.41(3)	0.06	1.430(5)	0.01
C(6)—C(7)	1.35(3)	0.05	1.38(1)	0.03
C(7)—C(8)	1.52(1)	0.02	1.51(3)	0.05
C(8)—F	1.29(2)	0.05	1.28(4)	0.11
C(5)—O(1)	1.27(1)	0.03	1.26(2)	0.05
C(7)—O(2)	1.28(2)	0.04	1.269(5)	0.009
C(1)—H(1)	0.93(6)	0.10		
C(2)—H(2)	0.93(15)	0.32		
C(6)—H(6)	0.99(4)	0.11		

Table 4. $\text{In}(\text{TТА})_3$ and $\text{Fe}(\text{TТА})_3$. Average bond angles, in degrees. The standard deviations (in parentheses) have been calculated from the formula $\sigma_a = [\sum_i (a_i - \bar{a})^2 / (n-1)]^{1/2}$. In most cases the standard deviation of the individual angles as estimated from the least squares refinement is 1 or 2 degrees.

Atoms	$\text{In}(\text{TТА})_3$ Average	Range	$\text{Fe}(\text{TТА})_3$ Average	Range
C(1)—S—C(4)	92.2(3)	0.6	95(2)	3.9
S—C(1)—C(2)	112(1)	2.7	110(2)	2.3
C(1)—C(2)—C(3)	115.9(7)	2.3	118(3)	5.0
C(2)—C(3)—C(4)	108(1)	2.4	107(3)	5.2
C(3)—C(4)—S	111(1)	2.4	111(4)	6.9
S—C(4)—C(5)	119(1)	1.7	120(3)	4.2
C(3)—C(4)—C(5)	130(2)	3.1	129(3)	6.1
C(4)—C(5)—C(6)	120(1)	2.1	120(2)	2.8
C(5)—C(6)—C(7)	125(1)	2.0	120(2)	2.5
C(6)—C(7)—C(8)	117.4(4)	0.8	117(2)	3.7
O(1)—C(5)—C(4)	116(2)	3.0	118(1)	2.3
O(1)—C(5)—C(6)	123.7(9)	1.6	123(2)	3.9
O(2)—C(7)—C(8)	118.8(7)	1.4	114(2)	3.1
O(2)—C(7)—C(6)	130.9(6)	1.1	133(6)	9.8
F—C(8)—C(7)	113(2)	6.9	114(3)	8.0
F—C(8)—F	105(2)	5.3	104(4)	10.9

Table 5. Comparison of chelate C—C bond lengths (Å) in some TTA compounds.

Compound	C(5)—C(6)	C(6)—C(7)	Ref.
CsTTA	1.427(9)	1.380(8)	1
<i>mer</i> -Fe(TTA) ₃	1.430(5)	1.38(1)	present work
<i>mer</i> -In(TTA) ₃	1.41(3)	1.35(3)	present work
<i>fac</i> -Cr(TTA) ₃	1.406(6)	1.363(8)	unpubl.
Average ^a	1.418(7)	1.367(8)	
Weighted			
Average ^a	1.414(4)	1.370(5)	

^a Based on individual observations and standard deviations from the least squares refinement.

character of the terminal CF₃ group. The data collected in Table 5 suggest, that the C(6)—C(7) bond is shorter than the C(5)—C(6) bond. This is supported by statistical tests.¹² The pooled set of observed C(5)—C(6) distances show no significant differences, (5 % level). The same is true for the set of C(6)—C(7) distances. The difference between the averages of the sets, however, is highly significant, (0.5 % level).

The essential features of the molecular conformation are visible on the stereo drawing Fig. 2. The non-hydrogen atoms of each thiophene group are coplanar (5 % level). Roughly, each ligand may be represented by a plane defined by the five atoms C(4) through C(8). The standard deviation from the plane of the atoms defining it is ~0.04 Å. The pivoting of the ligand plane around the O(1)—O(2) line is a well-known characteristic of β-diketonate complexes.

The conformation of the two ligands, facing each other in Fig. 2, deviates slightly from that of the other four. The rotation (~25°) of the CF₃ group around the C(7)—C(8) bond is distinct.

In keeping with the high volatility of the β-diketonates,¹³ intermolecular distances less than 0.2 Å + sum of van der Waals radii are scarce. No obvious pattern of contacts can be disentangled.

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