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Molecular Structure of Tris(acetylacetonato)technetium(III)

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The molecular structure of tris(acetylacetonato)technetium-(III) was determined by means of the single crystal X-ray diffraction method. The complex has a typical octahedral coordination and the average ∠O-Tc-O is 90.2°. The average Tc-O distance is 2.025 Å.

Several reports concerning syntheses of tris(β-diketonato)technetium(III) complexes have appeared recently.[1-4] However, there is no known crystal structure with respect to the tris(β-diketonato)technetium(III) complexes; only one structure of $Tc^{III}Cl(acac)_2(P(C_6H_5)_3)$[5] has been referred to in our investigation. Consequently, we report the crystal structure of tris(acetylacetonato)-technetium(III) 1 by means of the X-ray diffraction method.

1 was prepared by the method proposed by Abrams et al.[2] and recrystallized from ethanol. A small needle-like crystal of 0.13×0.03×0.20 mm^3 was obtained. A graphite monochromated Cu-K_α radiation (λ=1.5418 Å) was used for the data collection on a Rigaku automated four-circle diffractometer, equipped with a rotating anode (40 kV, 200 mA). Crystal data are as follows: M.F.=$C_{15}H_{21}O_6Tc$, M.W.=396.33, monoclinic space group $P2_1/c$, a=14.050(3), b=7.497(2), c=16.509(3) Å, β=99.02(2)°, V=1717.4(7) $Å^3$, Z=4, D_{calcd} = 1.53 g/cm^3, μ(Cu-K_α)=71.28 cm^{-1}. A total of 1852 reflections within 2θ=126° were collected with ω-2θ scan mode at a ω scan speed of 4° min^{-1}. The structure was solved by the direct method, and then the successive Fourier syntheses[6]. Finally all 43 atoms were refined with a final R factor 0.04 (R_w=0.039) for 1504 reflections with $|F_o|>3\sigma(|F_o|)$.

Figure 1 shows a perspective view of 1 with the atom numbering scheme. Selected bond distances and angles are listed in Table 1. There are no significant differences of the distances and angles in the chemically equivalent bonds. Therefore, discussion can be made in terms of the average values as shown in Fig. 2. In the present results, it is worthwhile to note that the coordination geometry involves no distortion, showing closely a regular octahedron. The intra- and inter-chelate (O⋯O) distances (av. 2.870 and 2.861 Å) are almost equal. The [O⋯O(interachelate)]/[M-O] value of 1.417 is very close to 1.414 in a regular octahedron.

Compared with isomorphous complexes of the same type[7,8] the M-O distance of technetium is the longest one: Tc>Ru>Rh>Mn>Cr>Co>Al. A nearly regular octahedral

structure is also seen in the corresponding manganese(III) complex.

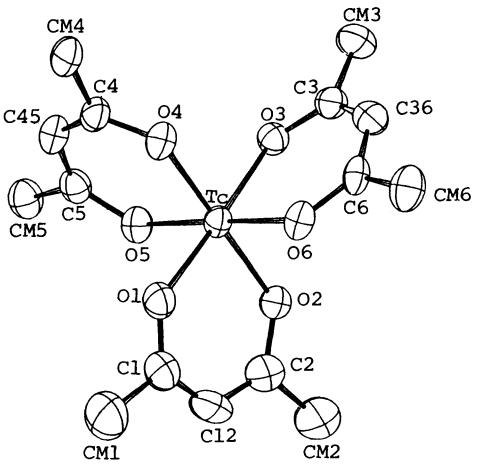

Fig. 1. ORTEP thermal ellipsoid view (30% probability level).

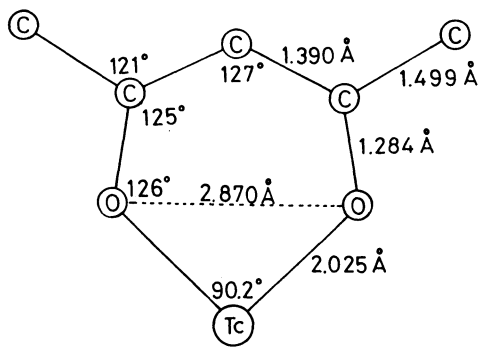

Fig. 2. Average intramolecular bond lengths and angles for $Tc(acac)_3$.

Table 1. Selected bond lengths(in Å) and angles(in degree)

Tc - O1	2.013(6)	C1 - O1	1.271(14)
Tc - O2	2.026(6)	C2 - O2	1.277(15)
Tc - O3	2.028(5)	C3 - O3	1.285(10)
Tc - O4	2.026(5)	C4 - O4	1.297(11)
Tc - O5	2.026(5)	C5 - O5	1.288(9)
Tc - O6	2.030(6)	C6 - O6	1.283(10)
O1 - Tc - O2	89.9(2)	O1 - Tc - O3	177.3(2)
O3 - Tc - O6	89.8(2)	O2 - Tc - O4	179.5(2)
O4 - Tc - O5	91.0(2)	O5 - Tc - O6	178.8(2)

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