

Crystal and Molecular Structure of Binuclear Technetium Carbonyl Chloride Complexes $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{C}_5\text{H}_8\text{O}_2)]_2$ ($\text{C}_5\text{H}_8\text{O}_2 = \text{Acetylacetonate}$) and $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$

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Abstract—The crystal and molecular structures of the complex $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{C}_5\text{H}_8\text{O}_2)]_2$ ($\text{C}_5\text{H}_8\text{O}_2 = \text{Hacac} = \text{acetylacetonate}$) formed in the course of prolonged standing of a $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ solution in $\text{CCl}_4/\text{CDCl}_3$ and of its analog containing no organic ligand, $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$, were determined. Both complexes contain a $[\text{Tc}_2(\mu\text{-Cl})_2]$ four-membered ring. The remaining sites in the coordination sphere of the Tc atom are occupied by carbonyl ligands, and in the case of $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$, also by the neutral acetylacetonate molecule in the enol form. The Hacac molecules in the binuclear complex are in the cis position to the Cl atoms in the octahedral surrounding of the Tc atoms and in the trans position to each other relative to the $[\text{Tc}_2(\mu\text{-Cl})_2]$ ring. A comparative analysis of the geometries of the complexes and their known analogs was performed.

Keywords: technetium, carbonyl complexes, bridging halide complexes, acetylacetonate, crystal and molecular structure

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INTRODUCTION

Technetium carbonyl β -diketonates were prepared for the first time in our early study [1]. We have determined the crystal and molecular structure of two representatives of this class, $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_3]_2$ and $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_3(\text{Et}_2\text{NH})]$ (acac is acetylacetonate anion) [2]. Later a series of papers concerning the possible use of technetium carbonyl β -diketonates in nuclear medicine were published [3–6]. In this connection, it is important to study the formation conditions and reactivity of technetium carbonyl β -diketonates. In particular, they not always behave as “innocent” coordination cores to which various ligands can be linked and can undergo various transformations [5].

Therefore, we have resumed studies of technetium carbonyl β -diketonates to examine their reactivity more

comprehensively. In the course of the studies, we have found that prolonged standing of a $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ solution in CCl_4 with the addition of CDCl_3 led to the formation of a small amount of crystals identified by X-ray diffraction analysis as $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ (Hacac is acetylacetonate in the enol form). This paper deals with a comparative structural analysis of this complex, the compound $[\text{}^{99}\text{TcCl}(\text{CO})_4]$ with a similar structural motif, and related manganese, technetium, and rhenium compounds for which structural data are available.

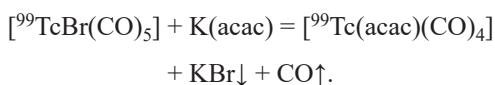
EXPERIMENTAL

The complexes $[\text{}^{99}\text{TcX}(\text{CO})_5]$ ($X = \text{Cl}, \text{Br}$) were prepared by carbonylation of $\text{K}^{99}\text{TcO}_4$ with a mixture of formic and the corresponding hydrohalic acid in

an autoclave as described previously [7]. Prior to use, the pentacarbonyl complexes were additionally purified by sublimation in a rough vacuum. Potassium acetylacetonate (Kacac) was prepared by the reaction of KOH with excess acetylacetone. Excess diketone was removed by heating in a vacuum. The solvents CH_2Cl_2 and CCl_4 were purified by distillation from P_2O_5 . The other chemicals were chemically pure (Fluka and Sigma–Aldrich) and were used without additional purification.

The IR spectra of the solutions were recorded with a Simex FT-801 spectrometer in the range 1700–2400 cm^{-1} using cells with CaF_2 windows. The ^{99}Tc NMR spectrum was recorded at 296 K with a Bruker Avance III 400 spectrometer operating at a frequency of 90.06 MHz for ^{99}Tc ; CCl_4 with the addition of CDCl_3 was used as a solvent. The ^{99}Tc content of the samples was determined by the spectrophotometric procedure with thiourea [8] with a Mettler Toledo UV5 spectrometer. The spectrophotometric analysis was performed using quartz cells of the highest quality with the optical path length of 10 mm (Hellma Analytics, QS type).

A solution of $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ in CCl_4 was prepared by stirring solid $[\text{}^{99}\text{TcBr}(\text{CO})_5]$ with a threefold excess of the potassium salt of acetylacetone under a solvent layer at room temperature for 2 h similarly to the procedure described in [1]. The reaction progress was monitored by IR spectroscopy using the characteristic $\nu(\text{CO})$ bands. IR spectrum of $[\text{}^{99}\text{TcBr}(\text{CO})_5]$ (CCl_4 , ν , cm^{-1}): 2152.4 w, 2059.8 s, 1998.1 m. IR spectrum of $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ (CCl_4 , ν , cm^{-1}): 2113.8 w, 2025.1 s, 1998.1 s, 1951.8 s; published data [1] (CCl_4 , ν , cm^{-1}): 2115 w, 2026 s, 1998 s, 1950 s. The yield of $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ was evaluated from the ^{99}Tc content of the solution according to [8] and was found to be 87%.



The solution of the tetracarbonyl acetylacetonate complex was separated from the KBr precipitate by filtration in an inert atmosphere. $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ is relatively unstable [1], and we failed to isolate it in the solid state. It was identified in the solution, along with IR spectroscopy, also by ^{99}Tc NMR ($\text{CCl}_4/\text{CDCl}_3$, δ , ppm): –1068.8.

After recording the ^{99}Tc NMR spectrum of the $[\text{}^{99}\text{Tc}(\text{acac})(\text{CO})_4]$ solution, the contents of the ampule

were transferred into a penicillin vial which, in turn, was placed in a large vessel containing P_2O_5 . The vessel was purged with argon, hermetically stoppered, and placed in a refrigerator at 8°C. On standing for 1.5 weeks, crystals suitable for X-ray diffraction analysis were formed in the penicillin vial.

Crystals of $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ for comparative analysis were prepared by short (5 min) heating of a $[\text{}^{99}\text{TcCl}(\text{CO})_5]$ solution in toluene at 100°C as described in [9]. A crystal for X-ray diffraction analysis was selected from the $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ precipitate formed on cooling (yield 37.5%).

To perform an X-ray diffraction experiment, crystals of $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ (1) and $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ (2) were fixed on a microholder and placed into a Rigaku XtaLAB Synergy-S single crystal diffractometer equipped with a HyPix-6000HE planar semiconductor high-rate direct-action detector of reflected X-ray beams. Measurements were performed using microfocused monochromatic MoK_α radiation. The unit cell parameters (Table 1) were refined by the least-squares method. The data were integrated with the background, Lorentz, and polarization effect corrections in the CrysAlisPro program complex [10]. The absorption correction was introduced in the CrysAlisPro program complex empirically using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm. The structures were solved using the dual-space algorithm and were refined using SHELX programs [11, 12] built in the OLEX2 complex [13]. The positions of the hydrogen atoms were calculated by the algorithms included in the SHELX program complex, with $U_{\text{iso}}(\text{H})$ set as $1.5U_{\text{eq}}(\text{C})$ at C–H 0.98 Å for CH_3 groups and as $1.2U_{\text{eq}}(\text{C})$ at C–H 0.95 Å for CH groups. The CCDC 2376839 (1) and 2376840 (2) files contain additional crystallographic data for this study and can be obtained free of charge from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/structures/.

RESULTS AND DISCUSSION

Although the binuclear complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ is known for more than 60 years [14], its X-ray diffraction analysis has not been performed. Previously we determined the structure of $[\text{}^{99}\text{TcI}(\text{CO})_4]_2$ [15] and found from the powder diffraction data that the compounds $[\text{}^{99}\text{TcX}(\text{CO})_4]$ (X = Cl, Br, I) are

Table 1. Crystallographic data and structure refinement parameters for 1 and 2^a

Parameter	[⁹⁹ TcCl(CO) ₄] ₂ (1)	[⁹⁹ TcCl(CO) ₃ (Hacac)] ₂ (2)
Formula	C ₈ Cl ₂ O ₈ Tc ₂	C ₁₆ H ₁₆ Cl ₂ O ₁₀ Tc ₂
Molecular mass	490.98	635.19
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> , Å	9.7377(3)	10.1883(4)
<i>b</i> , Å	11.6572(4)	10.7757(3)
<i>c</i> , Å	12.9476(4)	12.6288(4)
α, deg	90	88.746(2)
β, deg	108.991(3)	66.390(3)
γ, deg	90	62.648(4)
<i>V</i> , Å ³	1389.74(8)	1105.76(8)
<i>Z</i>	4	2
Crystal size, mm ³	0.08 × 0.02 × 0.002	0.07 × 0.05 × 0.03
μ, mm ⁻¹	2.403	1.540
<i>D</i> _{calc} , g/cm ³	2.347	1.908
Temperature, K	293(2)	150(2)
Radiation	MoK _α	MoK _α
2θ measurement range, deg	6.57–60.00	6.72–60.00
Total number of reflections	23653	12155
Number of unique reflections	4043	5855
Number of reflections with $ F_o \geq 4\sigma_F$	3224	4956
<i>R</i> _{int}	0.0649	0.0243
<i>R</i> _σ	0.0384	0.0361
<i>R</i> ₁ ($ F_o \geq 4\sigma_F$)	0.0274	0.0341
<i>wR</i> ₂ ($ F_o \geq 4\sigma_F$)	0.0661	0.0848
<i>R</i> ₁ (all data)	0.0384	0.0432
<i>wR</i> ₂ (all data)	0.0724	0.0911
<i>S</i>	1.022	1.041
ρ _{min} , ρ _{max} , e/Å ³	−0.493, 0.792	−0.890, 1.699
CCDC	2376839	2376840

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2) / 3$; $s = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

isostructural [9]. The single crystal X-ray diffraction analysis of [⁹⁹TcCl(CO)₄]₂, performed in this study, confirmed the conclusions made in our early paper [9]. Like other structurally studied compounds [MX(CO)₄]₂ (M = Mn, X = Cl, Br, I; M = Tc, X = I; M = Re, X = Cl, I)

[15–25], the complex [⁹⁹TcCl(CO)₄]₂ crystallizes in the monoclinic system (space group *P*2₁/*c*). All the above complexes have close (taking into account differences in the size of the metal and halogen atoms) unit cell parameters.

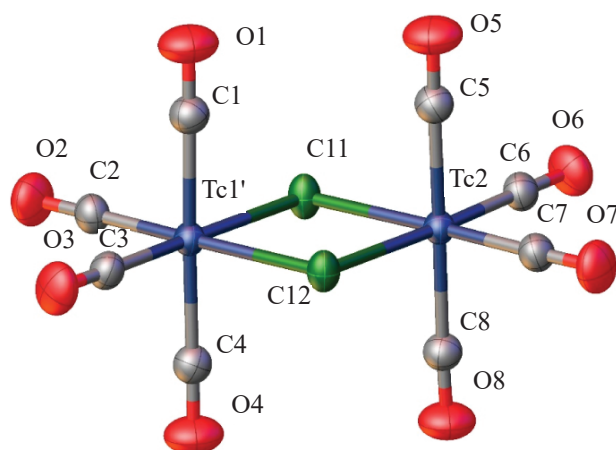


Fig. 1. Molecular structure of the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$.

Figure 1 shows the molecular structure of the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ (1). The bond lengths and angles in the coordination sphere of the complex are given in Table 2. The packing of $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ molecules in the crystal lattice is shown in Fig. 2.

The structural units of 1 are the dimeric complexes $[\text{TcCl}(\text{CO})_4]_2$, which can be described as two Tc-centered $\text{TcCl}_2(\text{CO})_4$ octahedra sharing a common edge of Cl atoms with the formation of a practically

planar $[\text{Tc}_2(\mu\text{-Cl})_2]$ four-membered ring (Fig. 1). The ClTcClTc torsion angle is 0.47° . In the other previously studied compounds $[\text{MX}(\text{CO})_4]_2$, the XMXM torsion angle is also close to zero. The dimeric complex is a symmetrically independent part of the crystal structure, and all its atoms occupy general positions. The symmetry elements of monoclinic space group $P2_1/c$ relate the adjacent equivalent complexes to each other. The dimeric complexes are packed in chains oriented along $[1\ 0\ 0]$ (Fig. 2a). The chains, in turn, form a layered motif perpendicularly to $[0\ 0\ 1]$ (Fig. 2b). The equatorial planes of the dimers in the adjacent chains are oriented approximately parallel to the $(-1\ -3\ 5)$ and $(-1\ 3\ 5)$ planes. The Tc-containing complexes are linked to each other by van der Waals interactions.

A characteristic feature of the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$, as well as of the other compounds $[\text{MX}(\text{CO})_4]_2$, is significant nonequivalence of the Tc–C bonds: The bonds located in the *trans* position to each other are, on the average, approximately 0.1 Å longer than the Tc–C bonds in the *trans* position to the halogen atoms. This trend, which we also noted previously for the compounds $[\text{}^{99}\text{TcX}(\text{CO})_5]$ ($X = \text{Cl}, \text{Br}, \text{I}$) [26, 27], is apparently due to the mutual *trans* effect of two π -acceptor ligands. Correspondingly, the C=O bonds in

Table 2. Selected bond lengths d and bond angles ω in the molecule of $[\text{TcCl}(\text{CO})_4]_2$ (1)

Bond	d , Å	Angle	ω , deg	Angle	ω , deg
Tc1–C11	2.5187(6)	Tc1–Cl1–Tc2	97.09(2)	C4–Tc1–Cl2	89.08(8)
Tc1–Cl2	2.5215(6)	Tc1–Cl2–Tc2	96.93(2)	C11–Tc2–Cl2	82.87(2)
Tc1–Cl1	1.994(3)	C11–Tc1–Cl2	83.11(2)	C5–Tc2–Cl1	89.97(8)
Tc1–C2	1.901(3)	C1–Tc1–Cl1	88.84(8)	C5–Tc2–Cl2	88.60(8)
Tc1–C3	1.907(3)	C1–Tc1–Cl2	90.02(9)	C5–Tc2–C8	179.28(11)
Tc1–C4	2.018(3)	C1–Tc1–C4	178.60(12)	C6–Tc2–Cl1	93.59(8)
Tc2–Cl1	2.5246(6)	C2–Tc1–Cl1	93.94(8)	C6–Tc2–Cl2	176.42(8)
Tc2–Cl2	2.5279(6)	C2–Tc1–Cl2	177.00(8)	C6–Tc2–C5	90.86(11)
Tc2–C5	2.011(3)	C2–Tc1–C1	90.47(12)	C6–Tc2–C8	89.78(11)
Tc2–C6	1.913(3)	C2–Tc1–C3	89.02(12)	C7–Tc2–Cl1	176.98(8)
Tc2–C7	1.899(3)	C2–Tc1–C4	90.38(11)	C7–Tc2–Cl2	94.11(8)
Tc2–C8	2.019(3)	C3–Tc1–Cl1	176.93(9)	C7–Tc2–C5	89.96(11)
		C3–Tc1–Cl2	93.93(8)	C7–Tc2–C6	89.43(12)
		C3–Tc1–C1	90.33(11)	C7–Tc2–C8	90.38(11)
		C3–Tc1–C4	90.81(11)	C8–Tc2–Cl1	89.66(8)
		C4–Tc1–Cl1	89.98(8)	C8–Tc2–Cl2	90.73(8)

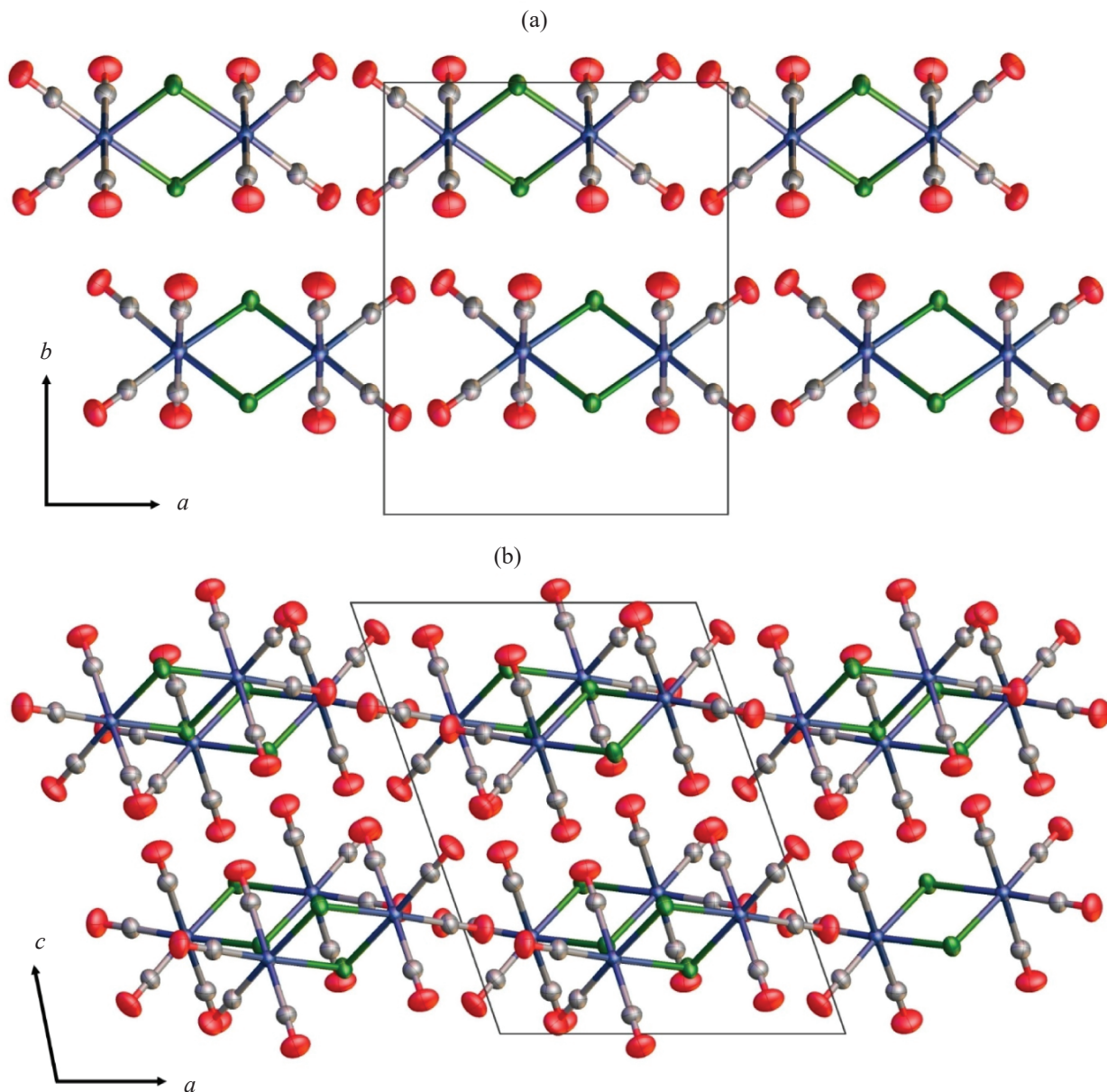


Fig. 2. Packing of $[\text{TcCl}(\text{CO})_4]_2$ molecules in the crystal lattice, projection onto (a) ab and (b) ac . The unit cell contours are shown.

the *trans* position to each other are somewhat shorter (1.126 Å on the average) than the C=O bonds in the *trans* position to the Cl atoms (1.145 Å on the average). The Tc–Cl bond (mean length 2.523 Å) is longer than the terminal Tc–Cl bond in the complex $[\text{TcCl}(\text{CO})_5]$ (2.4815 Å [26]) but shorter than the Tc– μ_3 -Cl bond in the tetrameric complex $[\text{TcCl}(\text{CO})_3]_4$ (2.5590 Å [28]). However, as in the case of the iodide analogs [15], the Tc–Cl bond length increases upon bridge formation to a relatively small extent; i.e., the Cl atom on coordination

to the Tc atom largely preserves its donor power. This fact accounts for high stability of bridging technetium halide complexes.

The binuclear complex $[\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ is the first structurally characterized example of technetium compounds of the type $[\text{TcX}(\text{CO})_3\text{L}]_2$ (X is halide ion, L is a monodentate neutral ligand). A number of such compounds (L = THF, acetonitrile, pyridine) were prepared in our early study [29], but conclusions on their structure were based only on the IR spectra

and results of chemical analysis. Figure 3 shows the molecular structure of the complex. The bond lengths and angles in the coordination sphere of the complex are given in Table 3. The packing of $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ molecules in the crystal lattice is shown in Fig. 4.

The structural units in 2 are also dimeric complexes consisting of two Tc-centered octahedra sharing a common edge of Cl atoms (Fig. 3). As in the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$, the structural core of this complex is the $[\text{Tc}_2(\mu\text{-Cl})_2]$ four-membered ring. It is planar, and the mean Tc–Cl bond length is 2.519 Å, differing only slightly from the mean Tc–Cl bond length in the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$. In the crystal structure of 2, there are two crystallographically nonequivalent dimers. The differences in their geometries are insignificant. The dimeric complex is centrosymmetrical with the symmetry center in the middle of the TcClTcCl parallelogram. Thus, only a half of atoms forming each dimer are crystallographically nonequivalent.

The Tc–C bond lengths (mean value 1.900 Å) are practically equal for the bonds located in the *trans* position to the Cl and O atoms and are close to the lengths of the Tc–C bonds in the *trans* position to the Cl atoms in the complex $[\text{}^{99}\text{TcCl}(\text{CO})_4]_2$ (mean value 1.905 Å).

The Hacac molecules are coordinated in the monodentate fashion via carbonyl oxygen atom (O4) of the ketoenol form of acetylacetonate. The Tc–O

bond (mean length 2.176 Å) is approximately 0.05 Å longer than those in the complex with the acac anion coordinated in the bidentate fashion (2.128 Å [2]). The Hacac molecules are located in the apical positions of the Tc octahedra in the *trans* position to each other relative to the $[\text{Tc}_2(\mu\text{-Cl})_2]$ ring. The enol hydroxy group O5H forms an H-bond with the carbonyl oxygen atom of the same Hacac molecule ($\text{O4}\cdots\text{O5} = 2.561(4)$ Å; Table 4, Fig. 3). The planes of the acetylacetonate ligands of the adjacent dimers are located parallel to each other. In the case of the first dimer, the planes are located at the normal distance between the incomplete rings (O4–C4–C7–C5–O5) of the molecules of 3.512(4) Å with the parallel shift of 1.70(1) Å. In the case of the second dimer, the normal contact between the incomplete rings of the molecules (O4A–C4A–C7A–C5A–O5A) is longer, 3.647(4) Å, but the shift is smaller, 0.67(1) Å. Thus, these contacts can be identified as stacking interaction. In the first case, the system of the contacts is organized approximately along $[1\ -4\ 2]$, and in the second case, approximately along $[2\ 2\ 1]$. The dimeric complexes in 2 form chains oriented along $[1\ 0\ 0]$. The chains, in turn, are packed in layers oriented parallel to $(0\ 1\ 0)$ (Fig. 4). The dimers are linked with each other by weak hydrogen bonds C–H \cdots O and van der Waals interactions (Table 4). The second dimer forms a denser H-bond system, with all its H atoms involved in bonding, whereas in the first dimer only one CH₃ group forms weak H-bonds (Table 4).

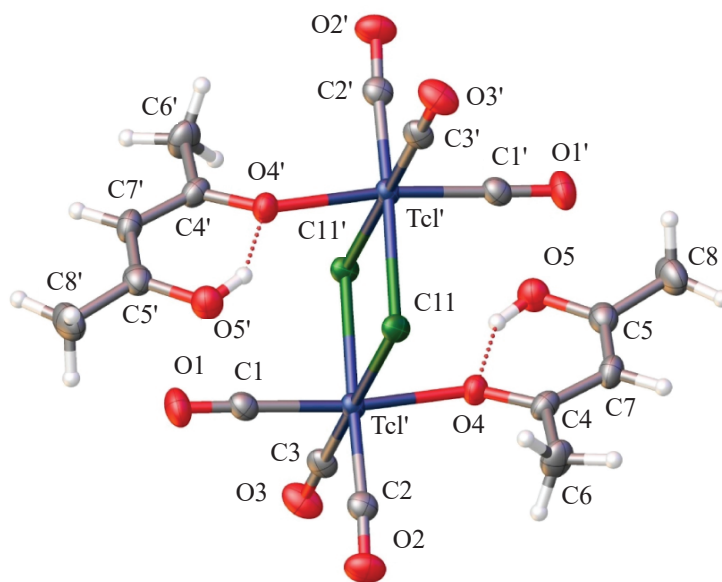


Fig. 3. Molecular structure of the complex $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$.

Table 3. Selected bond lengths d and bond angles ω in the molecules of $[\text{}^{99}\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ (2)

Bond	d , Å	Angle	ω , deg	Angle	ω , deg
Tc1–Cl1	2.5165(8)	Tc1–Cl1–Tc1'	97.85(3)	Tc1A–Cl1A–Tc1A'	97.64(2)
Tc1–Cl1'	2.5212(8)	Cl1–Tc1–Cl1'	82.15(3)	Cl1A–Tc1A–Cl1A'	82.36(2)
Tc1–O4	2.180(2)	O4–Tc1–Cl1	79.08(6)	O4A–Tc1A–Cl1A	81.37(6)
Tc1–C1	1.901(3)	O4–Tc1–Cl1'	85.51(6)	O4A–Tc1A–Cl1A'	85.67(6)
Tc1–C2	1.898(3)	C1–Tc1–Cl1	93.80(10)	C1A–Tc1A–Cl1A	93.69(10)
Tc1–C3	1.901(3)	C1–Tc1–Cl1'	93.18(10)	C1A–Tc1A–Cl1A'	91.46(10)
Tc1A–Cl1A	2.5192(8)	C1–Tc1–O4	172.26(11)	C1A–Tc1A–O4A	172.82(11)
Tc1A–Cl1A'	2.5098(7)	C1–Tc1–C3	87.19(14)	C1A–Tc1A–C2A	89.44(13)
Tc1A–O4A	2.172(2)	C2–Tc1–Cl1	94.82(10)	C2A–Tc1A–Cl1A'	176.09(10)
Tc1A–C1A	1.899(3)	C2–Tc1–Cl1'	176.84(10)	C2A–Tc1A–Cl1A	95.24(10)
Tc1A–C2A	1.904(3)	C2–Tc1–O4	99.82(11)	C2A–Tc1A–O4A	90.93(11)
Tc1A–C3A	1.892(3)	C2–Tc1–C1	87.92(14)	C3A–Tc1A–Cl1A	176.42(9)
		C2–Tc1–C3	86.08(13)	C3A–Tc1A–Cl1A'	94.09(10)
		C3–Tc1–Cl1	178.68(9)	C3A–Tc1A–O4A	98.87(11)
		C3–Tc1–Cl1'	96.93(10)	C3A–Tc1A–C1A	88.31(14)
		C3–Tc1–O4	93.40(11)	C3A–Tc1A–C2A	88.32(13)

Table 4. Hydrogen bonds in the structure of $[\text{Tc}(\text{CO})_3(\text{Hacac})\text{Cl}]_2$ (2)

D–H \cdots A	D–H, Å	H \cdots A, Å	D \cdots A, Å	DHA angle, deg
O5–H5 \cdots O4	0.84	1.84	2.562(3)	142.8
O5–H5 \cdots Cl1	0.84	2.91	3.495(3)	128.6
O5A–H5A \cdots O4A	0.84	1.84	2.560(3)	143.1
O5A–H5A \cdots Cl1A	0.84	3.06	3.644(3)	128.7
C6–H6A \cdots O1A	0.98	2.70	3.585(5)	150.0
C6–H6B \cdots O3A	0.98	3.01	3.873(5)	147.3
C6–H6C \cdots Cl1	0.98	2.89	3.662(4)	136.2
C6–H6C \cdots O5A	0.98	2.54	3.370(5)	142.8
C6A–H6AA \cdots O1	0.98	2.65	3.450(5)	139.5
C6A–H6AA \cdots Cl1A	0.98	2.95	3.681(4)	132.5
C6A–H6AB \cdots O5	0.98	2.69	3.590(4)	153.5
C6A–H6AA \cdots O2	0.98	2.68	3.509(5)	142.8
C7A–H7A \cdots O5	0.95	2.68	3.525(4)	148.0
C8A–H8AA \cdots O2	0.98	2.67	3.391(5)	130.9
C8A–H8AB \cdots O2A	0.98	2.67	3.553(5)	149.5

The ligands L are in the *trans* position relative to the $[\text{M}_2\text{X}_2]$ ring in the overwhelming majority of the structurally studied related complexes $[\text{MX}(\text{CO})_3\text{L}]_2$ (M = Mn, Re; X = Cl, Br). The *trans* position of ligands L is noted in the Mn and Re complexes with L = tetra-

hydrofuran [30, 31], acetonitrile [32, 33], pivalonitrile [34], pyridine [35], benzimidazole derivative [36], tris(cyclohexyl)phosphine [37], and 3,3-dimethylthietane [38]. We have found only two examples of complexes with the *cis* location of monodentate ligands L

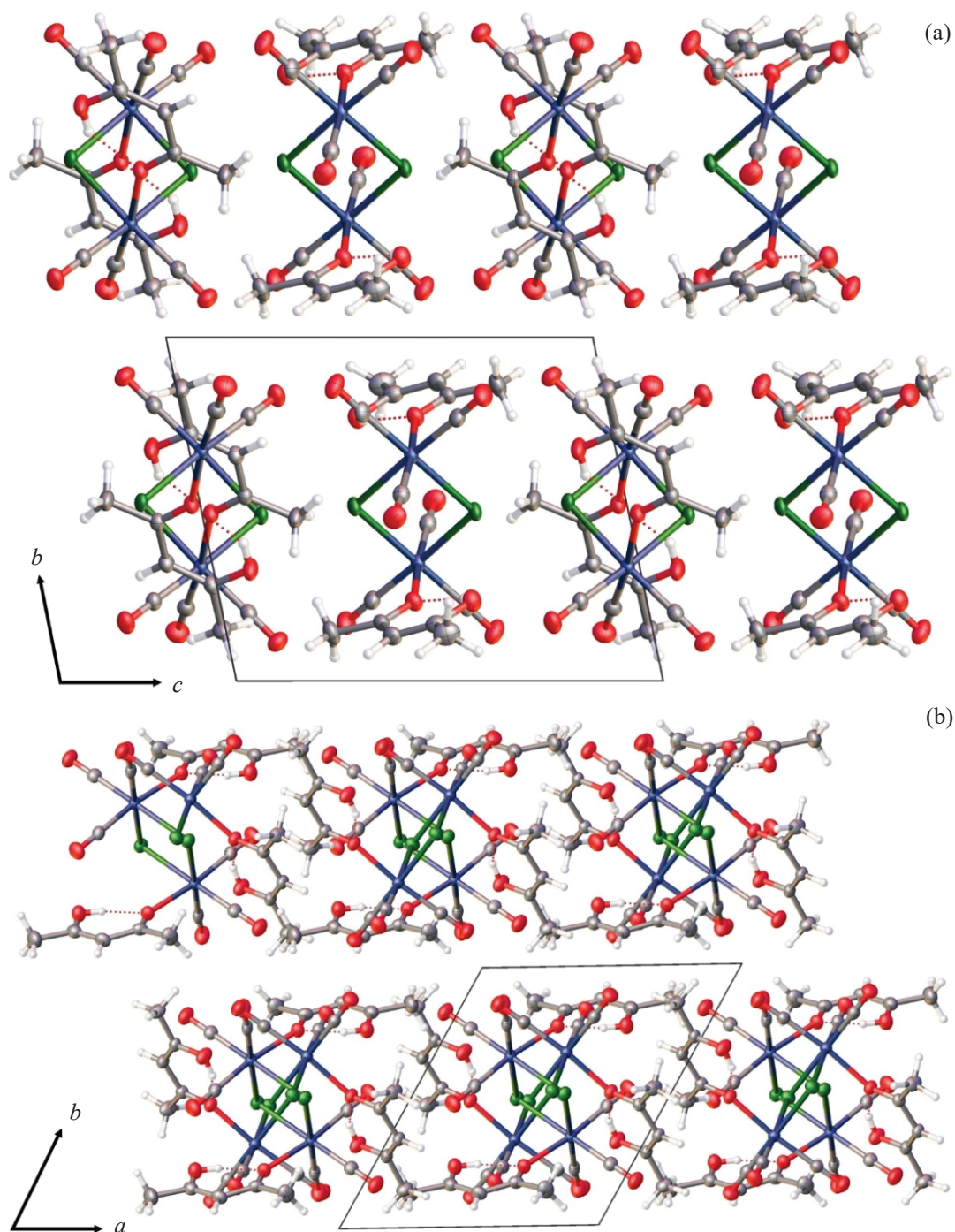


Fig. 4. Packing of $[\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$ molecules in the crystal lattice, projection onto (a) bc and (b) ab . Contours of the unit cell are shown.

relative to the $[\text{M}_2\text{X}_2]$ ring [39, 40]. Interestingly, one of them is also a complex with a neutral β -diketone molecule, $[\text{ReCl}(\text{CO})_3(\text{benzoylacetone})]_2$. In this complex, as in our complex $[\text{TcCl}(\text{CO})_3(\text{Hacac})]_2$, the diketone is

coordinated in the monodentate fashion in the ketoenol form via acetyl oxygen atom, but a different stereoisomer is realized. Stabilization of the complex with the *cis* location of the diketone molecules may be associated

with the π - π interactions between the ketoenol and phenyl groups. In this structure [40], there is intramolecular stacking between the incomplete rings of the ketoenol fragment (normal distance 3.311(5) Å, shift 0.09(1) Å). The benzene ring of one dimer and the incomplete ring of the ketoenol fragment of the adjacent dimer are involved in the intermolecular stacking (normal distance 3.531(5) Å, shift 1.69(1) Å). Thus, in the structure of [40], there is a helical system of stacking interactions of the complexes along [0 0 1]. It should also be noted that the ClReClRe torsion angle in this complex is abnormally large (9.46°), whereas in the complexes with the *trans* location of ligands L the MXMX ring is planar.

In the complexes [MX(CO)₃L]₂ with O-donor ligands L (tetrahydrofuran, β -diketone), the difference between the lengths of the M-C bonds with the CO groups located in the *trans* position to the halogen atom and to the organic ligand is insignificant. It becomes appreciable in going to complexes [ReCl(CO)₃L] with ligands L exhibiting certain π -acceptor properties: phosphine [37] and carbene [39] (the Tc-C bond in the *trans* position to the organic ligand is 0.05–0.07 Å longer), approaching the level characteristic of [ReCl(CO)₄] (about 0.08 Å).

To conclude, let us briefly discuss the probable pathway of the [⁹⁹TcCl(CO)₃(Hacac)]₂ formation. Apparently, the source of chlorine and hydrogen (X-ray diffraction analysis does not allow distinguishing isotopes of atoms) is deuteriochloroform added to a solution of a substance in CCl₄ for recording the NMR spectrum. Unfortunately, the attempted purposeful synthesis of this complex by the reaction of [⁹⁹TcCl(CO)₅] or [⁹⁹TcCl(CO)₄]₂ with pure acetylacetone or its solution in CCl₄ or CH₂Cl₂ with the variation of the reactant ratio, temperature, and reaction time or by the reaction of [⁹⁹Tc(acac)(CO)₄] in CCl₄ with dry HCl failed. We were unable to isolate the individual crystalline complex from the reaction mixtures.

CONCLUSIONS

We have determined the structures of the previously unknown complex [⁹⁹TcCl(CO)₃(Hacac)]₂ and of the complex [⁹⁹TcCl(CO)₄]₂, which is well known but was not studied by single crystal X-ray diffraction previously. We have performed a comparative analysis using available data for the related manganese, technetium, and rhenium complexes and discussed the manifestations of the *trans* effect in their structures. The

complex [⁹⁹TcCl(CO)₃(Hacac)]₂ is the first structurally studied example of binuclear technetium complexes [⁹⁹TcX(CO)₃L] with the [Tc₂(μ -X)₂] four-membered core, where X is a halogen and L is an organic ligand. The very fact of formation of this complex shows that technetium(I) carbonyl β -diketonate complexes exhibit limited stability.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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