

ELECTRONIC, CRYSTAL, AND MOLECULAR STRUCTURE OF TETRA(μ -ACETATO)DITECHNETIUM(III) DIPERTECHNETATE(VII)

N. A. Baturin, K. É. German, M. S. Grigofev,
and S. V. Kryuchkov

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The compound $[Tc_2(\mu-CH_3COO)_4][TcO_4]_2$ (I) has been synthesized in the form of an admixture of several single crystals in a host phase of $[Tc_2(CH_3COO)_4]Cl_2$, which can be obtained in the form of a finely crystalline powder when the mother solutions are slowly oxidized by atmospheric oxygen in the second stage of the synthesis of $K\{[Tc_2(CH_3COO)_4]Cl_2\}$ and $[Tc_2(CH_3COO)_4]Cl$ from $K_3[Tc_2Cl_8] \cdot nH_2O$ according to a previously described procedure. An x-ray structural investigation of compound I has been performed: space group $P2_1/n$, $a = 8.324(1)$, $b = 7.826(1)$, $c = 14.644(4)$ Å, $\beta = 101.81(2)^\circ$, $V = 934$ Å³, $Z = 2$. Compound I is built up from binuclear $[Tc_2(CH_3COO)_4]^{2+}$ cations with a Tc-Tc quadruple bond [$2.149(1)$ Å] and two pertechnetate anions, which are axially coordinated to the cations by means of bridging oxygen atoms. Calculations of the electronic structure of compound I have been performed by the extended Hückel method.

Pertechnetates and cluster compounds of technetium are two classes of technetium coordination compounds that have been studied intensively [1, 2]. The interest of investigators in the former class is due, first of all, to the fact that its members are the most stable compounds of technetium under oxidative conditions and practically any synthesis of its coordination compounds begins from just this class of technetium complexes. The interest of theoreticians and experimentalists in technetium cluster compounds is due mainly to the general interest of modern inorganic chemistry in compounds with metal-metal bonds (M-M) [3] and to the discovery of the special cluster-forming properties of this element [4].

In this communication we shall present the experimental and theoretical results of investigations of the structure of the first example of a technetium complex compound which simultaneously belongs to the two classes of compounds mentioned above $[Tc_2(\mu-CH_3COO)_4][TcO_4]_2$ (I).

The synthesis of $[Tc_2(\mu-CH_3COO)_4]Cl_2$ (II) was reported in [1, 5, 6], but the exact structure of this complex was not established. The problem of the abnormal strengthening of Tc-Tc bonds in binuclear d^4-d^5 complexes (with a formal order of the M-M bonds equal to 3.5) in comparison to d^4-d^4 complexes of similar composition and structure (with classical fourfold M-M bonds), which has been widely debated in the literature [1-4, 7-10], created a need to structurally characterize compound II, since the literature already contained analogous data for three acetato d^4-d^5 complexes of technetium (Table I) [11-13].

Synthesis of $[Tc_2(\mu-CH_3COO)_4][TcO_4]_2$. Compound I was obtained in the form of several tiny single crystals during an attempt to synthesize single crystals of $[Tc_2(\mu-CH_3COO)_4]Cl_2$ that would be suitable for an x-ray structural investigation. The acetic acid mother solutions formed in the second stage of the autoclave synthesis of $K\{[Tc_2(\mu-CH_3COO)_4]Cl_2\}$ (III) and $[Tc_2(CH_3COO)_4]Cl$ (IV) as a result of the replacement of the chloride ligands in $K_3[Tc_2Cl_8] \cdot nH_2O$ by acetate ions in a medium of glacial acetic acid at a temperature of $120-200^\circ C$ [27] were placed in a closed conical flask with a limited content of air. After -1 month, a powdery red deposit and tiny red crystals started to form on the bottom and the walls of the flask. After nearly six months they ceased to grow, and the compound formed was flushed from the walls of the flask by ethyl alcohol, washed with diethyl ether, and dried. It had the form of a fine powder with a few transparent single crystals of cubic habit disseminated in it.

The mixture of substances obtained was mechanically separated into two phases: a coarsely crystalline phase and a finely crystalline phase. Single crystals were selected for the x-ray structural investigation. The finely crystalline fraction (-200 mg) was identified on the basis of the data in [5] with the aid of IR spectroscopy, x-ray powder diffraction analysis,

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TABLE 1. Principal Interatomic Distances (*d*, Å) in Technetium and Rhenium Complexes

Compound	<i>d</i> (M—M)	<i>d</i> (M—X _{ax})	<i>d</i> (M—X _{eq})	Literature
[Tc ₂ (CH ₃ COO) ₄]Cl	2,117 (1)	2,656 (1)	2,065 (5)	[11]
K{Tc ₂ (CH ₃ COO) ₄]Cl ₂	2,1260 (5)	2,589 (1)	2,07 (1)	[12]
[Tc ₂ (CH ₃ COO) ₄]Br	2,112 (1)	2,843 (1)	2,060 (4)	[13]
{Tc ₂ [(CH ₃) ₃ CCOO] ₄ }Cl ₂	2,192 (1)	2,408 (4)	2,032 (4)	[14]
(C ₅ H ₅ NH) ₃ [Tc ₂ Cl ₈]	2,1185 (5)		2,364 (15)	[15]
[(C ₄ H ₉) ₄ N] ₂ [Tc ₂ Cl ₈]	2,147 (4)		2,33 (1)	[16]
[Re ₂ (CH ₃ COO) ₄]Cl ₂	2,2240 (5)	2,521 (1)	2,018 (12)	[17]
[Re ₂ (<i>n</i> -C ₃ H ₇ COO) ₄](ReO ₄) ₂	2,251 (2)	2,18 (3)	2,015 (27)	[18]
[Re ₂ Cl ₂ (<i>i</i> -C ₃ H ₇ COO) ₃]ReO ₄	2,259 (3)	2,28 (4)	2,026 (29)	[19]
[(C ₄ H ₉) ₄ N] ₂ [Re ₂ Cl ₈]	2,222 (2)		2,33 (2)	[20]
	<i>d</i> (Tc—O) _{min}	<i>d</i> (Tc—O) _{max}	<i>d</i> (Tc—O) _{av}	
K[TcO ₄]	1,71 (1)	1,71 (1)	1,71 (1)	[21]
NH ₄ [TcO ₄]	1,711 (2)	1,711 (2)	1,711 (2)	[22]
Cs[TcO ₄]	1,685 (5)	1,704 (5)	1,699 (42)	[23]
[(CH ₃) ₄ N][TcO ₄]	1,589 (11)	1,719 (9)	1,676 (56)	24, 25]
[(C ₄ H ₉) ₄ N][TcO ₄]	1,57 (3)	1,69 (3)	1,605 (52)	25, 26]

and chemical analysis as [Tc₂(μ-CH₃COO)₄]Cl₂. The *Kα* x-ray emission spectra of technetium were subsequently recorded from this material.

X-Ray Structural Investigation. One of the single crystals (-0.05 X 0.05 X 0.05 mm) appeared to be suitable for an x-ray investigation, which was performed on a CAD-4 automatic x-ray diffractometer (from Enraf-Nonius) with a graphite monochromator (Mo *Kα* radiation, *w*-2θ scan technique). The unit-cell parameters were determined from 16 reflections with *h* > 14. The experimental set consisted of 1817 independent reflections with *I* > 3σ(*I*).

Compound I belongs to space group *P*2₁/*n* and has the following unit-cell parameters: *a* = 8.324(1), *b* = 7.826(1), *c* = 14.644(4) Å, β = 101.81(2)°, *V* = 934 Å³, *Z* = 2. The structure was solved by the direct method with the aid of the SHELX-86 program.

Two high peaks of approximately equal intensity were initially revealed in the *E* synthesis. After attempts to interpret these peaks as Tc (the Tc-Tc distance through the inversion center was -2.16 Å) and Cl atoms did not yield positive results, it was postulated that the second intense peak (at a distance of more than 3 Å from the first peak) also belongs to a Tc atom. Several successive Fourier syntheses of the electron density made it possible to reveal the entire structure. After refinement of all the nonhydrogen atoms with the aid of a Fourier synthesis in an approximation employing anisotropic temperature parameters, some of the H atoms in the acetate ions were located on the difference Fourier synthesis. The final refinement of the structure by the full-matrix least-squares method (SHELX-76) with fixed coordinates for the H atoms, whose positions were calculated geometrically [*d*(C-H) = 1.05 Å] with consideration of the orientation of the objectively located H atoms and a refined isotropic temperature parameter shared by all the H atoms gave *R*₁ = 0.037 and *R*_w = 0.043. All the calculations were performed on an IBM PC AT computer.

Investigation of the Electronic Structure. The electronic structure of compound I was studied by the extended Hückel method with the parametrization presented Table 2. The parameters for Tc were taken from [28], but in a single-zeta approximation for the *d* AO's. Calculations of {[Tc₂(CH₃COO)₄]Cl₂}⁻ and [TcO₄]⁻ were previously performed in [31] with the use of a double-zeta parametrization for the *d* AO's of the technetium atoms. The results of the calculations of the electronic structure of these ions performed in the present work turned out to practically coincide with the results in [31], allowing us to use the single-zeta parametrization for the *d* AO's of the technetium atoms in all further calculations.

All the calculations of the electronic structure were performed on an IBM PC AT 287 computer by the Hoffmann method [32-35] according to a program adapted for this type of computer by Yu. V. Plekhanov. The real geometries of

TABLE 2. Parameters of the Extended Hückel Method Used in the Calculations.

Element, orbital	<i>H</i> _{ii} , eV	ξ ₁ (C ₁)	ξ ₁ (C ₂)	Literature
Tc 4 <i>d</i>	-12,82	4,90 (0,5715)	2,094 (0,6012)	[28]
5 <i>s</i>	-10,07	2,018		
5 <i>p</i>	-5,40	1,984		
Cl 3 <i>s</i>	-30,0	2,033		[28]
3 <i>p</i>	-15,0	2,033		
O 2 <i>s</i>	-32,3	2,275		[29]
2 <i>p</i>	-14,8	2,275		
C 2 <i>s</i>	-21,4	1,625		[29]
2 <i>p</i>	-11,4	1,625		
H 1 <i>s</i>	-13,6	1,30		[30]

TABLE 3. Coordinates of the Atoms and Isotropic (Equivalent) Temperature Factors in the Structure of $[\text{Tc}_2(\text{CH}_3\text{COO})_4][\text{TcO}_4]_2$

Atom	x	y	z	$B_{\text{iso}} (B_{\text{eq}}), \text{\AA}^2$
Tc(1)	0,5255 (1)	0,0669 (1)	0,44050 (5)	1,54
Tc(2)	0,6478 (1)	0,4244 (1)	0,29400 (5)	2,81
O(1)	0,7371 (5)	-0,0607 (5)	0,4498 (3)	2,3
O(2)	0,6849 (5)	-0,2018 (5)	0,5712 (2)	2,3
O(3)	0,6492 (5)	0,2463 (5)	0,5277 (3)	2,2
O(4)	0,5946 (5)	0,1045 (5)	0,6495 (2)	2,0
O(5)	0,8409 (8)	0,416 (1)	0,2786 (6)	9,1
O(6)	0,5928 (7)	0,2312 (6)	0,3365 (3)	3,6
O(7)	0,634 (1)	0,5764 (7)	0,3730 (5)	8,1
O(8)	0,5167 (7)	0,4660 (7)	0,1918 (4)	4,3
C(1)	0,7791 (7)	-0,1718 (7)	0,5142 (4)	2,3
C(2)	0,9361 (9)	-0,263 (1)	0,5220 (5)	4,0
C(3)	0,6597 (7)	0,2326 (7)	0,6159 (3)	2,0
C(4)	0,7514 (8)	0,3616 (9)	0,6797 (4)	2,8
H(2.1)	0,9364	-0,3809	0,5576	10(1)
H(2.2)	1,0309	-0,1854	0,5576	10(1)
H(2.3)	0,9552	-0,2871	0,4541	10(1)
H(4.1)	0,7278	0,3545	0,7463	10(1)
H(4.2)	0,7074	0,4860	0,6559	10(1)
H(4.3)	0,8754	0,3545	0,6804	10(1)

TABLE 4. Principal Interatomic Distances and Bond Angles in the Structure of $[\text{Tc}_2(\text{CH}_3\text{COO})_4][\text{TcO}_4]_2$

Bond	d, \AA	Bond	d, \AA
Tc(1)-Tc(1)'	2,149 (1)	Tc(1)-Tc(2)	3,790 (1)
Tc(1)-O(1)	2,005 (4)	Tc(1)-O(2)'	2,022 (4)
Tc(1)-O(3)	2,031 (4)	Tc(1)-O(4)'	1,999 (4)
Tc(1)-O(6)	2,153 (5)	Tc(2)-O(5)	1,670 (7)
Tc(2)-O(6)	1,732 (5)	Tc(2)-O(7)	1,679 (7)
Tc(2)-O(8)	1,694 (6)	O(1)-C(1)	1,278 (7)
O(2)-C(1)	1,279 (7)	O(3)-C(3)	1,281 (6)
O(4)-C(3)	1,284 (7)	C(1)-C(2)	1,47 (1)
C(3)-C(4)	1,477 (8)		
Angle	ω , deg	Angle	ω , deg
Tc(1)'Tc(1)Tc(2)	159,88 (3)	Tc(1)'Tc(1)O(1)	91,1 (1)
Tc(1)'Tc(1)O(2)'	90,7 (1)	Tc(1)'Tc(1)O(3)	89,2 (1)
Tc(1)'Tc(1)O(4)'	93,0 (1)	Tc(1)'Tc(1)O(6)	171,1 (1)
O(1)Tc(1)O(2)	178,1 (2)	O(1)Tc(1)O(3)	88,6 (2)
O(1)Tc(1)O(4)	114 (2)	O(1)Tc(1)O(6)	89,6 (2)
O(2)'Tc(1)O(3)	90,6 (2)	O(2)'Tc(1)O(4)'	89,2 (2)
O(2)'Tc(1)O(6)	58,5 (2)	O(3)Tc(1)O(4)'	177,8 (2)
O(3)Tc(1)O(6)	82,0 (2)	O(4)'Tc(1)O(6)	95,8 (2)
O(5)Tc(2)O(6)	110,2 (3)	O(5)Tc(2)O(7)	108,9 (4)
O(5)Tc(2)O(8)	110,7 (4)	O(6)Tc(2)O(7)	108,1 (3)
O(6)Tc(2)O(8)	108,4 (3)	O(7)Tc(2)O(8)	110,6 (3)
Tc(1)O(1)C(1)	119,5 (4)	Tc(1)O(2)'C(1)'	119,0 (4)
Tc(1)O(4)'C(3)'	117,7 (3)	Tc(1)O(6)Tc(2)	154,4 (3)
O(1)C(1)O(2)	119,7 (5)	O(1)C(1)C(2)	119,5 (5)
O(2)C(1)C(2)	120,9 (5)	O(3)C(3)O(4)	120,3 (5)
O(3)C(3)C(4)	120,0 (5)	O(4)C(3)C(4)	119,7 (5)

complexes 1 and 111, which were taken from the results of the x-ray structural investigations in the present work and [12], respectively, were used in all calculations. The calculations of the electronic structure of $[\text{Tc}_2(\text{CH}_3\text{COO})_4]\text{Cl}_2$ were performed for the compound with the structure of the ditechneium cation in compound I having the geometry taken directly from the present work. The Cl atoms were placed along the Tc-Tc bond at distances which can be varied in the range from 2.0 to 2.7 \AA. The calculation of the electronic structure of the pertechnetate ions was performed for $[\text{TcO}_4]^-$ with the geometry taken from the structure of $[(\text{CH}_3)_4\text{N}][\text{TcO}_4]$ [24, 25] and from the structure of compound I. Model calculations of oxidized and reduced carboxylato complexes of technetium with the geometries of the starting compounds were performed.

RESULTS AND DISCUSSION

Table 3 presents the coordinates of the atoms in the structure of compound I. Crystals of I (Fig. 1) are built up from neutral molecules of $[\text{Tc}_2(\mu\text{-CH}_3\text{COO})_4][\text{TcO}_4]_2$, which in turn consist of: 1) a binuclear $[\text{Tc}_2(\mu\text{-CH}_3\text{COO})_4]^{2+}$ fragment with a

TABLE 5. Averaged Values of Bonds Orders and Effective Atomic Charges (Z_{eff}) in Pertechnetates and Binuclear Technetium Acetates Calculated by the Extended Hückel Method

Compo	gm	Bond order†				$Z_{eff}†$				
		Tc=Tc	Tc-X	Tc-O (TcO ₄ ⁻)	Tc-O (Acet)	Tc (Acet)	Tc (TcO ₄ ⁻)	O (Acet)	O (TcO ₄ ⁻)	Cl
[Tc ₂ Acet ₄][TcO ₄] ₂		0,254		0,606 (0,537)	0,296 (0,197)	1,60	4,02	-0,89	-1,21 (-1,20)	
{[Tc ₂ Acet ₄][TcO ₄] ₂ }-		0,251		0,606 (0,537)	0,294 (0,197)	1,12	4,02	-0,89	-1,21 (-1,20)	
{[Tc ₂ Acet ₄][TcO ₄] ₂ } ²⁻		0,248		0,606 (0,537)	0,291 (0,197)	0,64	4,01	-0,90	-1,21 (-1,20)	
{[Tc ₂ Acet ₄][TcO ₄] ₂ } ⁴⁻		0,204		0,606 (0,538)	0,289 (0,196)	0,33	4,00	-0,90	-1,21 (-1,20)	
[TcO ₄] ⁻ (compound I)				0,604			4,03		-1,26 (-1,36)	
[(CH ₃) ₄ N][TcO ₄]		0,243		0,617	0,305	1,72	3,9	-0,88	-1,24	
[Tc ₂ Acet ₄] ²⁺		0,240			0,303	1,24		-0,88		
[Tc ₂ Acet ₄] ⁺		0,253	0,19		0,295	1,61		-0,89		-0,85
[Tc ₂ Acet ₄] ₂ Cl ₂	2,7	0,250	0,19		0,293	1,43		-0,89		-0,85
{[Tc ₂ Acet ₄] ₂ Cl ₂ }-		0,258	0,27		0,290	1,56		-0,89		-0,78
[Tc ₂ Acet ₄] ₂ Cl ₂	2,5	0,255	0,27		0,287	1,08		-0,90		-0,78
{[Tc ₂ Acet ₄] ₂ Cl ₂ }-		0,284	0,37		0,283	1,49		-0,90		-0,70
[Tc ₂ Acet ₄] ₂ Cl ₂	2,3	0,261	0,37		0,281	1,01		-0,90		-0,70
{[Tc ₂ Acet ₄] ₂ Cl ₂ }-		0,266	0,42		0,280	1,45		-0,91		-0,64
[Tc ₂ Acet ₄] ₂ Cl ₂	2,2	0,263	0,42		0,277	0,97		-0,91		-0,64
{[Tc ₂ Acet ₄] ₂ Cl ₂ }-		0,056	0,51		0,277	1,22		-0,90		-0,45
[Tc ₂ Acet ₄] ₂ Cl ₂	2,1	0,155	0,50		0,274	0,82		-0,91		-0,52
{[Tc ₂ Acet ₄] ₂ Cl ₂ }-		0,054	0,56		0,273	1,44		-0,90		-0,36
[Tc ₂ Acet ₄] ₂ Cl ₂	2,0	0,439	0,56		0,272	0,67		-0,90		-0,39

*The Tc-Cl distances (Å) are given alongside the large curly brackets.

†The values for the bridging and axial oxygen atoms of the pertechnetate groups are indicated in round brackets.

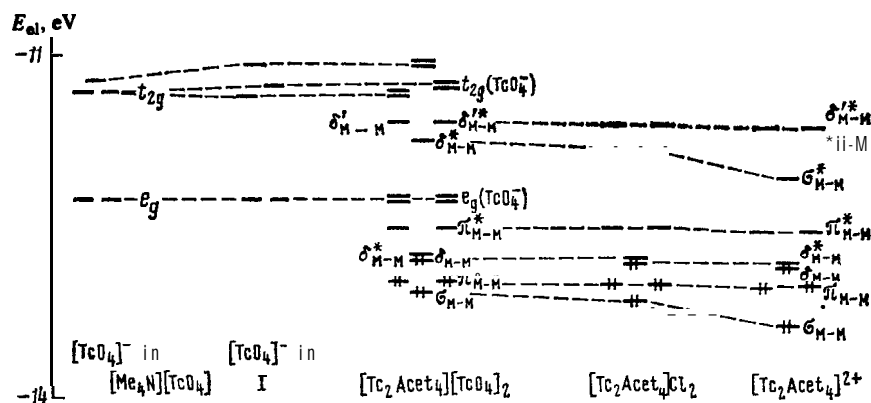


Fig.2. Schemes of MO's for compounds according to results of the extended Hückel calculations.

Tc-Cl distance equal to -2.6 \AA with respect to the effective charges of the atoms and the bonds orders. In other words, the axial coordination of the pertechnetate ions has the same influence on the **tetra(acetato)ditechnetium** cation as do the chloride ions in ordinary chlorotetraacetato complexes with Tc-Cl, distances equal to -2.6 \AA . It is seen from Table I that small M-Cl, distances are observed in the case of similar d^4-d^4 rhenium complexes, as well as in the case of d^4-d^5 chloroacetato technetium complexes. However, in the technetium d^4-d^4 complex $\text{Tc}_2[(\text{CH}_3)_3\text{CCOO}]_4\text{Cl}_2$ the Tc-Cl, distances are considerably smaller (Table 1), and, as a result, there is considerable elongation of the **Tc=Tc** bonds in comparison to compound I.

We note that a Tc-Cl, distance equal to -2.6 \AA seems to be the optimal distance when there is no significant *trans* influence on the **Tc=Tc** bond. In fact, it is enough to compare the M-M interatomic distances in I and other d^4-d^5 and d^4-d^4 complexes [1-4] to be convinced of this. Thus, the slight elongation of the Tc-Tc distance in compound I in comparison to d^4-d^5 acetato complexes of technetium is directly attributable to effects which have been widely discussed in the literature [1-4, 7-10, 36, 37]. According to the latest experimental and theoretical results [I, 4, IO. 36], this elongation of the Tc-Tc distances in d^4-d^4 complexes with M-M quadruple bonds in comparison to the analogous d^4-d^5 complexes with formal bond orders equal to 3.5 is attributable to configuration-interaction (CI) effects.

As has been noted, the binding of the pertechnetate ions to the two-dimensional acetato fragment in compound I is of special interest. We have already shown that the binding of the pertechnetate ions in compound I has the same overall influence as axial chloride ligands at a Tc-Cl, distance equal to -2.6 \AA . It can be seen from Table 5 that this case corresponds to an effective charge (Z_{eff}) of the pertechnetate ions equal to about -0.8 and that the principal effect accompanying the binding of the pertechnetate ions is caused by the pumping of the electron density from the bridging oxygen atoms in the pertechnetate groups to the technetium atoms in the acetato dimers. We note that this causes a decrease in the value of Z_{eff} for the technetium atoms in the carboxylato dimer, an increase in the order of the Tc-Tc bonds, and consequent strengthening of these bonds and the entire molecular system as a whole. At the same time, there is a **decrease** in the order of the **(Tc- μ -O)_{TcO₄]}** bonds in comparison to **[TcO₄]** in the tetramethylammonium salt, but there is almost no decrease in comparison to isolated pertechnetate ions with the geometry taken from the structure of compound I. This finding attests to the fact that the coordination of pertechnetate ions to the **dimeric** cluster is not accompanied by a significant change in the character of the bonding within the pertechnetate ions themselves. Additional confirmation may be provided by the fact that the order of the **Tc-O_{ax}** bonds is 0.197 ($\sim 2/3$ of the value for the **Tc-O_{acet}** bonds), which is close to the order of the Tc-Cl, bonds in chloroacetato complexes with an analogous distance equal to -2.6 \AA , **where the charge Z_{eff} on the Cl atoms is equal to about -0.8 .**

All these facts are evidence that both a covalent component and an ionic component make contributions to the binding of the pertechnetate ions to the binuclear fragment in the structure of compound I. According to the values of the mean **Tc-O** distances (Tables 1 and 4), the overall influence of the **dimeric** acetato cations on the pertechnetate ions is intermediate between the cases of pertechnetates with very small alkali-metal cations and large tetrabutylammonium cations, i.e., it is **closer** to the case of **[(CH₃)₄N][TcO₄]**. For this reason, it would be interesting to compare the structure of the pertechnetate ions in compound I and in **[(CH₃)₄N][TcO₄]**. It is seen from Table 5 that the small differences in the **electronic** structure of these anions are manifested in the values of Z_{eff} for the technetium and oxygen atoms, and in the order of the **Tc-O** bonds. However, these **small** differences cause **considerable** deviations in **character of the distortion of the pertechnetate ions**. In fact, **while [(CH₃)₄N][TcO₄]** contains one short [$1.589(11) \text{ \AA}$] and three long [$1.719(9) \text{ \AA}$] **Tc-O** bonds, compound I contains one long [$1.732(5) \text{ \AA}$] (**Tc- μ -O**) and three short ($1.670-1.694 \text{ \AA}$) **Tc-O** bonds. We note that compound I is more **similar** to **[(C₄H₉)₄N][TcO₄]** with respect to the character of the distortion of the pertechnetate ions (Table 1).

An hypothesis which attributed such distortions in pertechnetate ions to the pseudo-Jahn-Teller effect was previously advanced in [2, 38]. According to this hypothesis, there are two energetically equivalent variants of C_{3v} distortions for pertechnetate ions, and initiation of a particular variant is specified by finer crystal effects. Thus, the coordination of one of the oxygen atoms of each pertechnetate ion to the binuclear cluster fragment in compound I causes initiation of the distortion of $[TcO_4]^-$ of the one long $Tc-O$ bond and three short $Tc-O$ bonds type. At the same time, in the case of $[(CH_3)_4N][TcO_4]$ the diametrically opposed phenomenon occurs, but these two distortion variants are energetically virtually identical, as can be seen from Table 5 and Fig. 2.

Thus, this investigation has demonstrated that compound I completely combines the properties of two classes of technetium complexes: pertechnetates and binuclear carboxylates with a high-order M-M bond. At the same time, the anionic and **cationic** fragments composing this compound have considerable effects on each other, and this influences their electronic and molecular structure.

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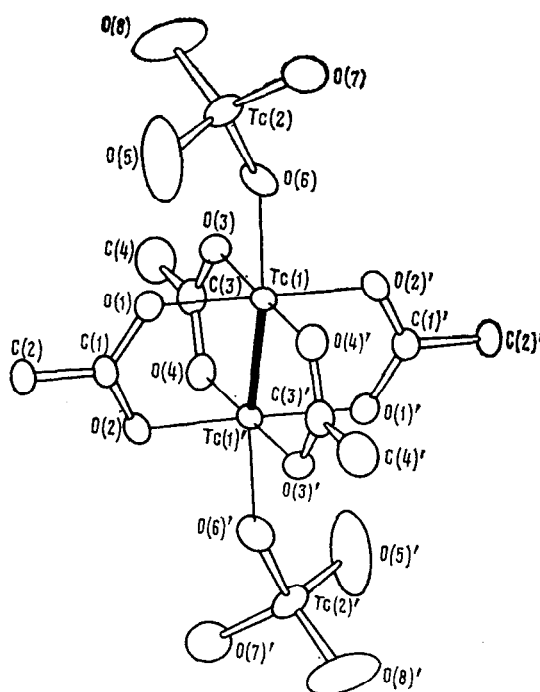


Fig. 1. Molecular structure of $[\text{Tc}_2(\mu\text{-CH}_3\text{COO})_4][\text{TcO}_4]_2$.

lantern structure, a short Tc-Tc distance, and four bridging acetato ligands, which additionally bind the technetium atoms together; 2) two pertechnetate ligands coordinated approximately axially to the $[\text{Tc}_2(\text{CH}_3\text{COO})_4]^{2+}$ fragment by means of one of their oxygen atoms. Table 4 presents the principle interatomic distances and bond angles in structure I.

It is seen from the results presented that the structure of compound I is rather unusual, although similar compounds of rhenium have previously been reported [18, 19]. Compound I probably formed during the slow oxidation of the dilute acetic acid solutions of III and IV by atmospheric oxygen to $[\text{TcO}_4]^-$ followed by the formation of mixed **tetraacetatoditechnetium(III)** pertechnetates due to the lack of other ligands capable of axial coordination in the solution. In fact, H_2O molecules or chloride ions might have served as such ligands. Since the mother solutions obtained in the second stage of the synthesis of III and IV were used only for the synthesis of I and II, the solutions consisted mainly of CH_3COOH and $[\text{Tc}_2(\text{CH}_3\text{COO})_4]\text{Cl}$. Since the small quantity of chloride ions present in these solutions was utilized in the formation of II, it is not surprising that $[\text{TcO}_4]^-$ ions which gradually formed in the solution as a result of the oxidation of the acetato complexes by atmospheric oxygen were coordinated specifically to the $[\text{Tc}_2(\text{CH}_3\text{COO})_4]^{2+}$ cation.

Table 1 presents the most important interatomic distances for all the ditechneium pertechnetates and carboxylates with known structures and for some similar rhenium compounds. The results presented reveal that the mean interatomic distances $d(\text{Tc}-\text{O}_{\text{eq}})$ and $d(\text{Tc}-\text{O})_{[\text{TcO}_4]^-}$ in compound I are close to the analogous distances in other carboxylates of Tc and Re and in pertechnetates. At the same time, the $\text{Tc}=\text{Tc}$ and $(\text{Tc}-\text{O})_{[\text{TcO}_4]^-}$ distances are smaller than the $\text{Re}=\text{Re}$ and $(\text{Re}-\text{O})_{[\text{ReO}_4]^-}$ distances, in agreement with the general laws of the crystal chemistry of Tc and Re. The fact that the values of $d(\text{M}-\text{O})_{[\text{MO}_4]^-}$ in **tetra(μ -carboxylato)dimetal(III) permethylates(VII)** corresponding to the distances between the M atoms and the bridging oxygen atoms scarcely differ from the other $(\text{M}-\text{O})_{[\text{MO}_4]^-}$ distances is noteworthy. We also note that the values of $d(\text{M}-\text{O}_{\text{ax}})$ in the structures of **carboxylatodimetal(III) permethylates(VII)** are considerably longer than ordinary M-O coordinate bonds. Nevertheless, Calvo et al. [18, 19] considered these bonds to be ordinary ones. For this reason it would be interesting to examine this type of binding in greater detail.

Figure 2 shows schemes of the MO's for compounds I and II, as well as for $[\text{TcO}_4]^-$ ions with the Tc-O distances taken from the results of the x-ray structural investigations of $[(\text{CH}_3)_4\text{N}][\text{TcO}_4]$ [24, 25] and compound I. It is seen that in the HOMO-LUMO region of compound I there are no MO's belonging to pertechnetate ions over a large energy range. This is evidence of the significantly higher stability of pertechnetate ions toward oxidation-reduction than of carboxylate cations, whose oxidation-reduction activity is specified mainly by the high-energy $\delta_{\text{M}-\text{M}}$, $\delta_{\text{M}-\text{M}}^*$, $\pi_{\text{M}-\text{M}}$, and $\pi_{\text{M}-\text{M}}^*$ MO's.

Table 5 presents the results of the extended Hückel calculations of compound I, pertechnetate ions and hypothetical ditechneium acetates and chloroacetates with interatomic distances corresponding to the $[\text{Tc}_2(\text{CH}_3\text{COO})_4]^{2+}$ fragment from structure I. The $\text{Tc}-\text{Cl}_{\text{ax}}$ distance was varied in 2.0-2.7 Å range and up to ∞ in the calculations. These calculations were performed due to the need to assess the type of binding of the **perpertechnetate ions to the tetra(μ -acetato) cation in structure I. A comparison of the results presented in Table 5 and Fig. 2 reveals that compound I is the most similar to compound II with a**