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The Chemistry of the Cluster Compounds of Technetium

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The results of studies published up to 1983 inclusive and devoted to the synthesis and the molecular and electronic structure as well as the chemical and physicochemical properties of dinuclear and polynuclear cluster compounds of technetium are examined. It is shown that the majority of the chemical and physicochemical properties of such cluster compounds are analogous to those of the similar compounds of other *d* transition elements. However, a number of properties of the technetium cluster differ from those of other transition elements, which is explained from the standpoint of modern theoretical concepts. The bibliography includes 106 references.

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I. INTRODUCTION

Technetium,[1] which is a typical representative of *d* transition elements of the second transition series, has properties most of which are similar to those of rhenium and in certain cases molybdenum. Since it is known[2-4] that the maximum capacity of transition elements for cluster formation with weak-field ligands is manifested by Group VI and VII elements, technetium is included among the most powerful cluster-forming elements. However, only the one anion $[Tc_2Cl_8]^{3-}$, in which a powerful metal–metal bond (M–M) is manifested, was known for technetium for a long time. The absence of data for this field of the chemistry of cluster compounds was due primarily to the low availability of technetium and its radioactivity.

Complexes of technetium in the lowest oxidation states are unstable and are formed as a rule with strong-field ligands, while complexes with weak-field ligands exist only in the presence of metal–metal bonds.[1] Thus the chemistry of complexes of technetium in oxidation states below 3+ with weak-field ligands can be regarded in essence as the chemistry of the cluster compounds of this element.

The studies on the chemistry of cluster compounds of technetium in the USSR were initiated at the beginning of the 1970's at the Institute of Physical Chemistry of the USSR Academy of Sciences after weighable amounts of this element had been obtained from the waste in the processing of nuclear fuel from atomic reactors.[1] This review deals with the present state of the chemistry of the cluster compounds of technetium and surveys and analyses the results of studies of the molecular and electronic structures of dinuclear and polynuclear technetium complexes with metal–metal bonds. Much attention is devoted to questions of the synthesis of cluster compounds of technetium and the investigation of their chemical and physicochemical properties.

II. SYNTHESIS AND MOLECULAR AND ELECTRONIC STRUCTURE

It is possible to differentiate two methods of synthesis of cluster compounds of technetium with weak-field ligands. The first[5] consists in the reduction of pertechnetate ions in concentrated hydrochloric acid by metallic zinc. The other method of synthesis, which has been used by the authors of this review,[6-8] is based on the reduction of pertechnetate ions by molecular hydrogen under pressure in an autoclave. This method has the advantage that the crystals produced are well formed and contain no extraneous impurities. The autoclave method had been developed initially for the synthesis of dinuclear technetium clusters with the $[Tc_2Cl_8]^{3-}$ anions and inorganic and organic cations.[6-8] Subsequently the autoclave method for the synthesis of clusters proved convenient also for the synthesis of more complex technetium clusters, including polynuclear clusters.[9-13] All the technetium clusters known at present can be divided arbitrarily into groups characterised by similar molecular and electronic structures.

1. Dinuclear Cluster Compounds of Technetium with the d^4–d^5 Electronic Configuration of the Central Atoms

These compounds constitute the most numerous groups of technetium clusters which have been investigated (Table 1, compounds 8–22). In our view this is due to the greater stability of the d^4–d^5 clusters compared with the d^4–d^4 clusters and also the fact that compounds with the $[Tc_2Cl_8]^{3-}$ anions had been obtained initially for technetium[5-8,14-16] and were subsequently employed to synthesise new technetium clusters.[9-13,17,18]

(a) *The Octachloroditechnetates* $M_3[Tc_2Cl_8].nH_2O$

Compounds of this type were first obtained by the reduction of pertechnetate ions by metallic zinc in concentrated hydrochloric acid at approximately 100 °C.[5] Later this method was used with some modifications in other studies also for the preparation of salts of octachloroditechnetate ions.[17-22] The reduction of pertechnetate ions under the given conditions is as a rule accompanied by the formation of brown solutions, which are rapidly oxidised in air to greenish-blue solutions with $\lambda_{max} \cong 615$ nm,[5] which corresponds to the absorption of light by the $[Tc_2Cl_8]^{3-}$ ions. When salts with the cations $M^+ = K^+$, NH_4^+, $^1/_3Y^{3+}$, or

Table 1. The physicochemical properties of technetium cluster compounds.

No.	Compound [references to method of synthesis]	m, (n)	Magnetic properties: μ_{eff}, 300 K; μ_{eff}, 80 K; θ	Refs.	$\epsilon(Tc3d_{5/2})$, eV; $\epsilon(X)$, eV; References	Structural data: sp. gr.; (Z)	a, Å; b, Å; c, Å	α, deg; β, deg; γ, deg	$R(Tc_2-Tc)$, Å	$R(Tc-L_{eq})$, Å; $R(Tc-L_{ax})$, Å	Refs.
1	$K_3[Tc_2Cl_8O_2]$, [11, 13]	4.5; (2.0)	4.15; 3.69; —40	[13]	256.8; 268.9; [13.57]	—	—	—	—	—	—
2	TcO_2, [66]	4.0; (1.0)	1.5; 1.0; —200	[13]	255.2; —; [57]	—	5.53 (1); 4.79 (1); 5.53 (1)	90; 120; 90	~2.5	—	[66]
3	$[Tc_2(H_2EDTA)_2\mu\text{-}O_2]\cdot 5H_2O$, [65]	4.0; (~2.0)	D	[65]	—	$Pna2_1$; (4)	18.41 (1); 10.96 (1); 16.25 (1)	90; 90; 90	2.331 (1)	μ=O —1.913 (8); O—2.011 (7); N—2.207 (16)	[65]
4	$[(C_4H_9)_4N]_2[Tc_2Cl_8]$, [13, 22, 27, 51]	3.0; (4.0)	D	[13,22]	255.8; 268.5; [57]	$P2_1/c$; (4)	10.915 (3); 15.382 (3); 16.469 (2)	90; 122.37; 90	2.147 (4)	2.33 (1)	[27]
5	$[(C_4H_9)_4N]_2[Tc_2Br_8]$, [13, 22]	3.0; (4.0)	D	[13,22]	—	—	—	—	—	—	—
6	$Tc_2[(CH_3)_3CCOO]_4Cl_2$, [17]	3.0; (4.0)	D	[17]	—	$I4/m$; (2)	11.515 (2) 11.515 (2) 10.625 (3)	90; 90; 90	2.192 (1)	2.032 (4); 2.408 (4)	[17]
7	$Tc_2(ClH_3COO)_4Cl_2$, [49]	3.0; (4.0)	D	[49]	—	—	—	—	—	—	—
	$K_8(H_3O)[Tc_2Cl_8]_3\cdot 3H_2O$, [6]						12.80 (5); 12.80 (5); 8.30 (4)	90; 90; 120	2.144 (17)	2.38 (13) 3.53 (1)	[25,26]
8	$K_3[Tc_2Cl_8]\cdot 2H_2O$, [16]	2.5; (3.5)	1.74; 1.74; 0	[13,47]	255.5; 269.0; [57]	$P3_121$; (3)	12.838 (3); 12.838 (3); 8.197 (2)	90; 90; 120	2.117 (2)	2.364 (16); 3.579 (3)	[16]
	$K_6'K_{3-x}''(H_3O)_x[Tc_2Cl_8]\cdot nH_2O$ *)						12.817 (3); 12.817 (3); 8.185 (2)	90; 90; 120	2.119 (1)	2.363 (14); 3.578 (1)	
9	$Cs_3[Tc_2Cl_8]\cdot 2H_2O$, [6]	2.5; (3.5)	2.17; —; —	[6]	—	$P3_121$; (3)	12.90 (5); 12.90 (5); 8.70 (4)	90; 90; 120	—	—	[25,26]
10	$(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$, [5, 6]	2.5; (3.5)	1.74; 1.74; 0	[13]	255.5; 269.0; [13.57]	$P3_121$ (3)	13.04 (2); 13.04 (2); 8.40 (1)	90; 90; 120	2.13 (1)	2.36 (3); —	[14,15]
11	$Y[Tc_2Cl_8]\cdot 2H_2O$, [5, 21]	2.5; (3.5)	~1.74; —; —	[21]	—	$P42_12$; (4)	11.712 (2) 11.712 (2) 7.661 (2)	90; 90; 90	2.105 (1)	2.363 (4); —	[21]
12	$(C_5H_5NH)_3\cdot[Tc_2Cl_8]\cdot 2H_2O$, [7]	2.5; (3.5)	~1.8; —	[7]	—	—	—	—	—	—	—
13	$(C_9H_7NH)_3[Tc_2Cl_8]\cdot 2H_2O$, [8]	2.5; (3.5)	2.08; 1.84; —	[8]	—	—	—	—	—	—	—
14	$[(C_4H_9)_4N]_3[Tc_2Cl_8]$, [13, 22]	2.5; (3.5)	1.73; 1.74; 0	[13]	—	—	—	—	—	—	—
15	$K_3[Tc_2Br_8]\cdot 2H_2O$, [13]	2.5; (3.5)	1.73; 1.73; 0	[13]	—	$P3_121$; (3)	13.63 (1); 13.63 (1); 8.46 (1)	90; 90; 120	—	—	[13]
16	$(NH_4)_3[Tc_2Br_8]\cdot 2H_2O$, [13]	2.5; (3.5)	1.73; 1.73; 0	[13]	—	—	—	—	—	—	—
17	$[Tc_2(C_5H_5N)_2Cl_5]$, [39]	2.5; (3.5)	1.8; —; —	[39]	255.3; 268.8; [57]	—	—	—	—	—	—
18	$[Tc_2(CH_3COO)_4Cl]$, [9]	2.5; (3.5)	1.73; 1.75; 0	[13,47]	255.8; 268.3; [57]	$C2/c$; (1)	15.035 (3); 7.801 (1); 12.894 (4)	90; 109.65; 90	2.117 (1)	2.065 (5); 2.656 (1)	[36]
19	$K[Tc_2(CH_3COO)_4Cl_2]$, [9]	2.5; (3.5)	1.73; 1.74; 0	[13,47]	255.8; 268.2; [57]	$P4_2/n$; (4)	11.9885 (3); 11.9885 (3); 11.4443 (2)	90; 90; 90	2.1260 (5)	2.07 (1); 2.589 (1)	[38]
20	$[Tc_2(o\text{-}C_5H_4ON)_4Cl]$, [18]	2.5; (3.5)	1.7; — —	[18]	—	$I4/m$; (2)	11.793 (3); 11.793 (3); 7.454 (1)	90; 90; 90	2.095 (1)	2.087 (3); 2.679 (1)	[18]
21	$[Tc_2(CH_3COO)_4Br]$, [10]	2.5; (3.5)	1.74; 1.74; 0	[13,47]	255.7; 181.4; [57]	$C2/m$; (1)	7.102 (3); 14.772 (4); 7.095 (2)	90; 113.36; 90	2.112 (1)	2.060 (4); 2.843 (1)	[37]

Table 1 (contd)

No.	Compound [references to method of synthesis]	m, (n)	Magnetic properties: μ_{eff}, 300 K; μ_{eff}, 80 K; θ	Refs.	$\varepsilon(Tc3d_{5/2})$, eV; $\varepsilon(X)$, eV References	Structural data: sp. gr.; (Z)	a, Å; b, Å; c, Å	α, deg; β, deg; γ, deg	R(Tc–Tc), Å	R(Tc–L_{eq}), Å; R(Tc–L_{ax}), Å	Refs.
22	$Tc_4O_5 \cdot nH_2O$, [13, 23]	2.5; (3.5)	1.75; 1.74; 0	[13]	255.9; —; [57]	—	—	—	—	—	—
23	$M_2[Tc_2Cl_6] \cdot nH_2O$, M=$NH_4$, K, [10, 13]	2.0; (5.0)	D	[10]	254.9; 268.9; [57]	—	—	—	—	—	—
24	$M_2[Tc_2Br_6] \cdot nH_2O$, M=$NH_4$, K, [10, 13]	2.0; (5.0)	D	[10]	254.6; 181.4; [57]	—	—	—	—	—	—
25	$[(R)_4N]_2[Tc_2X_6]$; R=C_2H_5, C_4H_9; X=Cl, Br, [13]	2.0; (5.0)	D	[13]	—	—	—	—	—	—	—
26	$[(CH_3)_4N]_3 \cdot [Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$, [12, 13]	1.83; (4.0); (0.5)	~1.7; ~1.6; 0	[12,13]	254.6; 268.9; 270.5; [13]	*Pcmn*; (4)	11.583 (2); 13.527 (3); 24.387 (3)	80; 90; 90	2.16 (1) 2.69 (1)	2.38 (1); μ-Cl—2.38 (2); ~3.0	[79]
27	$[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$, [12]	1.67; (3.0); (1.0)	~1.1; ~0.8; —	[12]	—	$P\bar{1}$; (2)	11.644 (4); 11.633 (4); 14.017 (6)	69.66; 65.89; 60.13	2.22 (1); 2.57 (1)	2.40 (1); μ-Cl—2.45 (1); ~3.2	[76]
28	$[H_3O(H_2O)_3]_2 \cdot [Tc_6Br_6\mu\text{-}(Br, OH)_6]$ *, [10, 13]	1.67; (1.0)	~0.7; ~0.7; —	[13]	—	$P2_1/c$; (2)	9.258 (4); 9.211 (3); 17.437 (7)	90; 101.09; 90	2.59 (1)	2.55 (1); μ-Br—2.46 (2);	[79]
29	$[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ *, [10, 13]	1.5; (4.0); (1.0); (0.5)	~1.0; ~0.6; —	[13]	254.7; 181.1; 182.8; [57]	$P2_1/n$; (2)	7.561 (2); 13.553 (5); 12.620 (3)	90; 102.62; 90	2.155 (3); 2.531 (2); 2.70 (2)	2.53 (2); μ-Br—2.51 (2); ~3.0	[78]
30	$[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$*, [12]	1.5; (4.0); (1.0); (0.5)	~1.1; ~0.7; —	[12]	—	$P2_1/a$; (2)	22.151 (9); 9.026 (3); 9.396 (4)	90; 105.94; 90	2.152 (9); 2.520 (9); 2.69 (1)	2.52 (1); μ-Br—2.52 (1); ~2.9	[76]
31	$[Tc_2(CO)_{10}]$, [67]	0; (1.0)	D	[67]	—	—	14.65 (1); 7.18 (1); 14.93 (1)	90; 105.6; 90	3.04 (1)	2.00 (1); 1.90 (1)	[67]
32	$[MTc(CO)_{10}]$, M=Mn, Re, [71]	0; (1.0)	D	[71]	—	—	—	—	—	—	—

Notation: $\varepsilon(X)$ is the energy of the electrons in the Cl_{2s} or $Br_{2p_{3/2}}$ skeleton, θ the Weiss constant, m the formal oxidation state of technetium, n the formal multiplicity of the Tc–Tc bonds, D a diamagnetic compound, and sp.gr. the space group.

*In these compounds there is a possibility that OH^- or H_3O^+ ions are present instead of H_2O molecules (or conversely).

**The results of a study by the authors of the review together with M.S.Grigor'ev and P.A.Koz'min.

$(C_4H_9)_4N^+$ are added to these solutions, crystals of complexes with the overall general formula $M_3[Tc_2Cl_8] \cdot nH_2O$ are formed[17–22] (Table 1).

Another method of synthesis of the octachloroditechnetate consists in the reduction of complexes of technetium(IV)–technetium(VII) in concentrated hydrochloric acid with molecular hydrogen under pressure in an autoclave at 120–180 °C.[6–8,11–13] As in the reduction with metallic zinc, the autoclave reduction is accompanied by the formation of brown solutions (λ_{max} = 465 nm), which are rapidly oxidised in air to greenish-blue solutions (λ_{max} = 645 nm). The reduction in autoclave proceeds at an initial hydrogen pressure of ~3 MPa. When technetium(IV) complexes are used as the initial compounds in the synthesis, the working temperature of the autoclave must be higher by 20–40 °C than in the case of pertechnetates, since the hexahalogenotechnetates(IV) are as a rule less soluble than the corresponding pertechnetates. Compounds having the composition $M_3[Tc_2Cl_8] \cdot nH_2O$, where $M^+ = K^+$, Cs^+, NH_4^+, PyH^+, or $QuinH^+$ are formed when salts with the cations $M^+ = K^+$, NH_4^+, $^1/_3Y^+$, or $(CuHg)_4N^+$ are added to these solutions[17–22] (Table 1).

All the octachloroditechnetates are substances which crystallise in the form of dark hexahedral needles, which give rise to a pale-grey powder on being ground. The complexes dissolve in hydrochloric acid with formation of turquoise solutions, which rapidly oxidise in air or disproportionate in its absence at low concentrations of the $[Tc_2Cl_8]^{3-}$ ions (~10^{-4} M) and are comparatively stable at high concentrations of such ions (~10^{-1} M). These compounds are sparingly soluble in polar organic solvents (clusters with organic cations are dissolved more effectively). In non-polar solvents the octachloroditechnetates do not dissolve, while in water and alkalies they rapidly hydrolyse with formation of brown colloidal solutions of the hydrated oxide $Tc_4O_5 \cdot nH_2O$.[23,24]

The autoclave method of synthesis of clusters with the $[Tc_2Cl_8]^{3-}$ anions[6-8] made it possible to observe an interesting phenomenon, which had not been noted by other workers[5,14-16,19-21] and which involves a non-stoichiometric variable content of certain singly-charged cations (M^+ = K^+, NH_4^+, or Cs^+) in octachloroditechnetate salts having the general formula $M_3[Tc_2Cl_8].nH_2O$. It was found that the composition of these clusters depends greatly on the hydrochloric acid concentration in the mother liquor from which they crystallise. For example, at an HCl concentration of 4–5 M, the K : Tc : Cl ratios in the potassium octachloroditechnetate formed are ~3 : 2 : 8, while in concentrated HCl solutions the ratios approach 2 : 2 : 8. A decrease of the content of K^+ ions in the complexes is accompanied by a decrease of the content of their water of crystallisation.

We may also note that the composition of these compounds depends on other factors as well, in particular on the rate of crystallisation. However, analysis of the diffractometer traces for the potassium octachloroditechnetate powders, obtained under different conditions, showed that the complex undergoes no appreciable crystal-chemical changes: the positions of all the lines on the diffractometer traces remain unchanged and correspond to the dimensions of the trigonal unit cell (a = 12.80 ± 0.05 Å; c = 8.30 ± 0.04 Å[25]), while the slight alteration of the intensities of the individual lines is mainly associated with the presence of a texture in the specimens.

One can assume *a priori* that the cause of the variable composition of the octachloroditechnetates may be either a variable oxidation state of technetium or the substitution of some of the cations by the H_3O^+ ions. The first version was proposed initially,[6] since the accuracy (±0.017 Å) of the X-ray diffraction study by a photomethod[25] precluded the determination of fine differences between the Tc–Tc distances in the $[Tc_2Cl_8]^{3-}$ and $[Tc_2Cl_8]^{2-}$ anions, which amount to ~0.03 Å according to the latest X-ray diffraction data[16,26,27] (Table 1). After revised X-ray diffraction data had been obtained,[16,21,26,27] an attempt was made to determine the H_3O^+ ions in potassium octachloroditechnetate, which led to their detection from the weak characteristic absorption lines in the infrared spectra [ν(OH) = 2965, 2930, and 2865 cm^{-1}; $\delta(OH)_2$ = 1610 cm^{-1} [28,29]]. The results did not conflict with the revised X-ray diffraction data,[26] according to which the K^+ ions in the unit cell of potassium octachloroditechnetate (+2.5) are present in two non-equivalent positions: sixfold (K′) and threefold (K″) (Fig.1); under these conditions, the sixfold positions were fully occupied by K^+ ions, while the threefold positions were half-occupied.

Summarising all that has been said above concerning the structure of the octachloroditechnetates(+2.5), one may conclude that their true composition is described by a formula with variable coefficients, namely $M'_6M''_{3-x}(H_3O)_x \cdot [Tc_2Cl_8]_3.nH_2O$, where x and n vary from 0 to 3. The

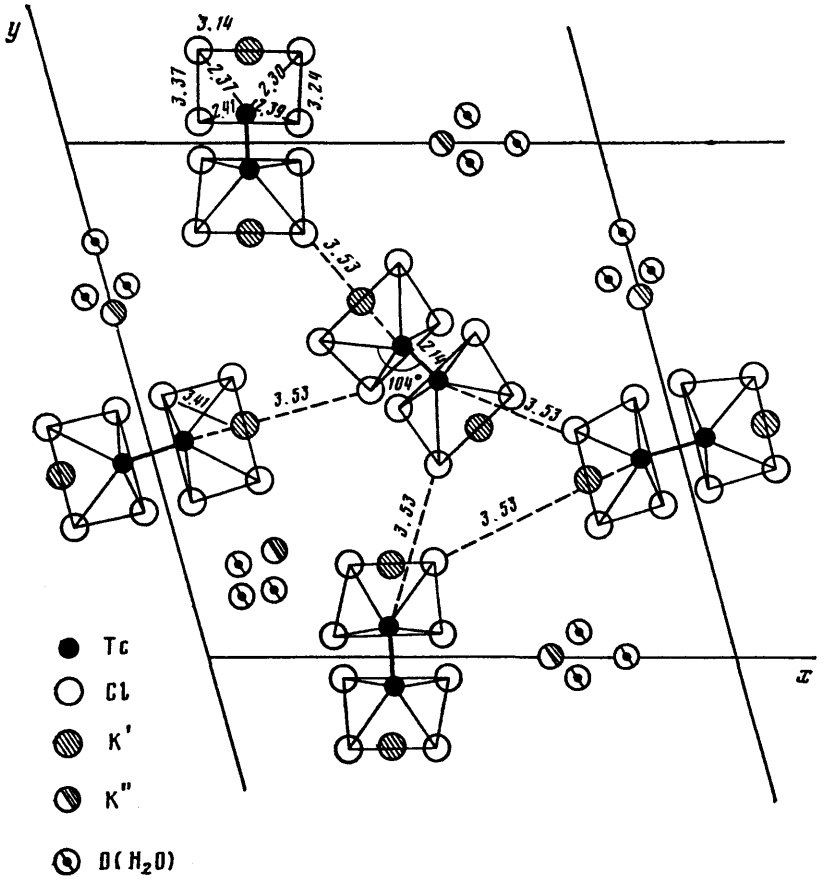


Figure 1. Projection of the unit cell of $K_6(H_3O)[Tc_2Cl_8]_3.3H_2O$ onto the xy plane.[25,26]

substitution of some of the M^+ ions by H_3O^+ ions is possible by virtue of the similarity of the properties of the hydronium cation and the alkali metal cations both in solutions and in the crystalline state.[30,31] The knowledge of such fine differences between the compositions of the octachlorodi-technetates(+2.5) is useful mainly for the study of certain solid-phase reactions, since the dissolution of these compounds leads to their dissociation into the M^+, H_3O^+, and $[Tc_2Cl_8]^{3-}$ ions and the properties of the solutions are then determined by the concentration of the octachloroditechnetate ions. The simplified formula of these complexes $M^3[Tc_2Cl_8].nH_2O$ was therefore used in subsequent studies.[7-13]

The structure of the ammonium,[14,15] potassium,[16,25,26] and yttrium[21] salts of the anion $[Tc_2Cl_8]^{3-}$ (Figs.1 and 2; Table 1) has been investigated by X-ray diffraction. The characteristic features of the molecular structure of this anion are its eclipsed conformation (D_{4h} symmetry) and a short Tc–Tc distance, much shorter than the analogous distance in metallic technetium (~2.70 Å[1]). It is striking that the change of the cation leads to an alteration of the Tc–Tc distance by ~0.04 Å (Table 1). We may note that the influence of the nature of the cation on the metal–metal distance in the rhenium and molybdenum complexes of the type $[M_2X_8]^{n-}$ (where M = Re or Mo and X = Cl or Br) with a quadruple M–M bond is weaker (the distance changes by ~0.02 Å[4,32-34]). In the case of technetium the true change in the M–M bond length on replacing the cations in the octachloroditechnetates is apparently somewhat smaller than the unduly high experimental value owing to the low accuracy of the X-ray diffraction study.[25,26]

(b) The Octabromoditechnetates $M_3[Tc_2Br_8].nH_2O$

When the potassium and ammonium halide complexes of technetium(VII)–technetium(IV) are reduced with molecular hydrogen under pressure (~3 MPa) in an autoclave in concentrated hydrobromic acid at 120–140 °C, the corresponding octabromoditechnetates(+2.5) of the type $M_3[Tc_2Br_8].2H_2O$ (where M = NH_4 or K), which are isostructural with the analogous cluster technetium chlorides,[12,13] are formed. Since the $[Tc_2Br_8]^{3-}$ ions are much less stable than $[Tc_2Cl_8]^{3-}$,[10-13,24] the formation of the octabromoditechnetates is observed only in a mixture with technetium(II) and technetium(IV) bromide complexes. This mixture can be conveniently resolved under the microscope using the distinctive characteristics of the octabromoditechnetates(+2.5) (large hexahedral needles or conglomerates of the latter, whose comminution yields a pale-brown powder). The octabromoditechnetates(+2.5) are sparingly soluble in polar and non-polar organic solvents, hydrolyse rapidly in water and alkalies, and dissolve in concentrated hydrogen halide acid solutions with formation of the $[Tc_2Br_8]^{3-}$ ions, which rapidly oxidise to $[TcBr_6]^{2-}$ or, in the absence of oxidants, disproportionate to $[Tc_2Br_6]^{2-}$ and $[TcBr_6]^{2-}$.[13,24]

(c) Dinuclear Cluster Compounds with a Structure of the "Lantern" Type

$Tc_2(o\text{-}C_5H_4ON)_4Cl$. Green crystals of $[Tc_2(o\text{-}C_5H_4ON)_4]Cl$, with sublime *in vacuo* (~10^{-9} Pa) at 350 °C without decomposition, have been obtained by the reaction of ammonium octachloroditechnetate with o-hydroxypyridine in nitrogen at 150 °C.[18] The compound is sparingly soluble in organic and inorganic solvents. Fig.3 illustrates the molecular structure of this cluster, which has the D_{2h} symmetry.

In contrast to $[Tc_2Cl_8]^{3-}$, the Tc–Tc bond in the oxopyridine cluster is additionally strengthened by four $o\text{-}C_5H_4ON$ bridging ligands, which have a contracting effect and lead to structures of the "lantern" type. The shortening of the Tc–Tc bond in the oxopyridine dinuclear cluster relative to the octachloroditechnetates(+2.5) amounts to ~0.015 and is close to the analogous value for dinuclear rhenium(III) clusters.[35]

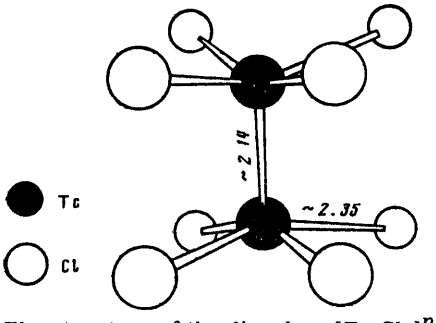


Figure 2. The structure of the dinuclear $[Tc_2Cl_8]^{n-}$ (n = 2 or 3) ions (according to a number of investigations[14,15,21,25-27]).

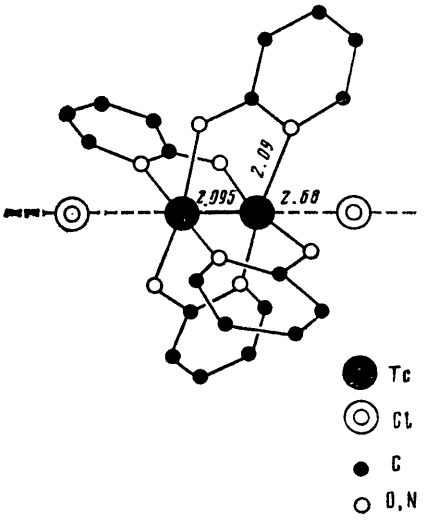


Figure 3. Fragment of the $[Tc_2(o\text{-}C_5H_4NO)_4Cl]$ structure.[18]

Acetate complexes. When $K_3[Tc_2X_8].2H_2O$ or $K_2[Tc_2X_6].2H_2O$ (where X = Cl or Br) interacts with glacial acetic acid in an autoclave at 120–200 °C in an argon or molecular hydrogen atmosphere (3–5 MPa), green crystals of the acetate dinuclear complexes having a structure of the "lantern" type are formed: $K[Tc_2(CH_3COO)_4]Cl_2$ and $[Tc_2(CH_3COO)_4]X$ (where X = Cl or Br)[9-11] (Table 1, Figs.4–6). The compounds are readily soluble in polar organic solvents and water and give rise to pale-green solutions, which gradually darken in air. On dissolution in concentrated hydrogen halide acid solutions, the corresponding octahalogenoditechnetates(+2.5) are formed.

Technetium acetate complexes without inorganic cations are volatile at ~400 °C like the oxopyridine complex which has a similar structure.

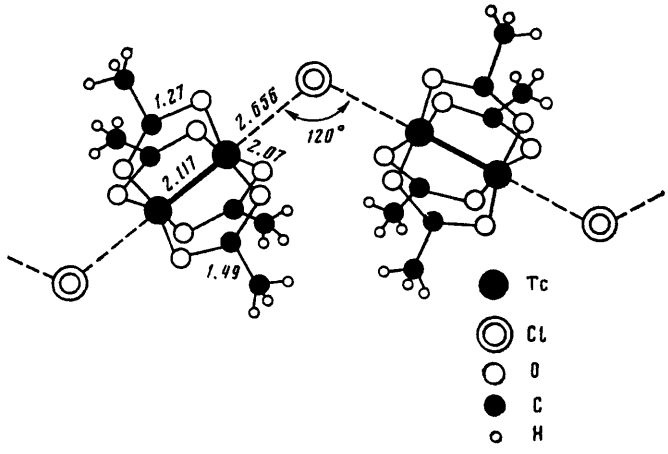


Figure 4. Fragment of the $[Tc_2(CH_3COO)_4Cl]$ structure.[36]

(d) Compounds Which Have Not Been Investigated by X-ray Diffraction

$Tc_4O_5.nH_2O$. A black powder, whose composition can be expressed by the overall formula $Tc_4O_5.14H_2O$, has been obtained by the hydrolysis of $K_3[Tc_2Cl_8].2H_2O$ in argon.[13] The freshly prepared hydrated oxide dissolves in concentrated hydrochloric acid with formation of $[Tc_2Cl_8]^{3-}$ ions. This demonstrates the retention of M–M bonds of high multiplicity in the hydrated oxide. The structure of $Tc_4O_5.14H_2O$ or its thermal degradation are accompanied, according to ESCA, infrared spectroscopic, and X-ray diffraction data[13] by irreversible structural changes. The final dehydration product is the black oxide Tc_4O_5.

The X-ray electronic and infrared spectra of Tc_4O_5 indicate the non-equivalence of technetium atoms as well as the oxygen atoms in its structure but this is not associated with the formation of a metallic technetium phase, TcO_2, or other known technetium oxides on dehydration of $Tc_4O_5.14H_2O$. According to magnetic measurements (Table 1), on the hydrated and anhydrous oxides, there is approximately one unpaired electron for each two technetium atoms, as in all the dinuclear d^4–d^5 clusters. The exact structure of the two compounds is unknown, but the set of chemical and physicochemical properties suggests the presence of Tc–Tc bonds with a high multiplicity in their structure.

$[Tc_2(C_5H_5N)_2Cl_5]$. The thermal decomposition of pyridinium octachloroditechnetate(+2.5) in argon at 250–280 °C yielded the compound $[Tc_2(C_5H_5N)_2Cl_5]$, the chemical analysis of which as well as optical and X-ray electronic spectra (Table 1) made it possible to ascribe to it a dinuclear structure with a Tc–Tc bond having a high multiplicity and with pyridine and chloride ligands.[39] The molecular structure of the compound is so far unknown. It has been isolated in the form of a dark-brown powder soluble in pyridine and unstable on dissolution in inorganic acids and alkalies. Treatment with nitric acid or a peroxide–alkali mixture as well as prolonged storage in air lead to its oxidation to technetium(IV) in the form of the stable compound $[Tc(C_5H_5N)_2Cl_4]$. In water the complex $[Tc_2(C_5H_5N)_2Cl_5]$ rapidly hydrolyses, while in alkalies it dissolves with decomposition.

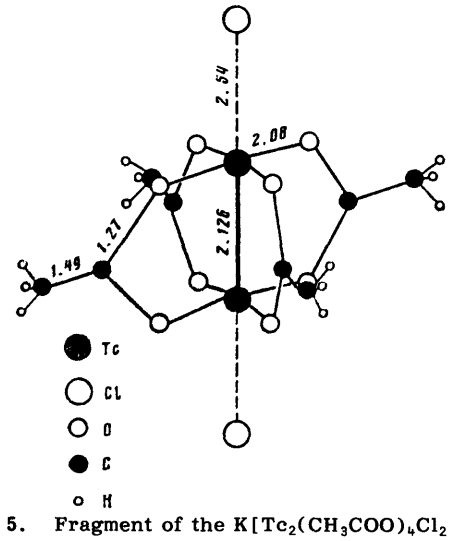


Figure 5. Fragment of the $K[Tc_2(CH_3COO)_4Cl_2]$ structure.[38]

(e) The Electronic Structure of Dinuclear d^4–d^5 Clusters

The d^4–d^5 clusters are of considerable experimental and theoretical interest, because they constitute so far the only representatives of dinuclear clusters of *d* transition elements with multiple M–M bonds having this electronic structure†. Attempts have been frequently made to examine the electronic structure of these compounds. According to the MO scheme for the quadruple M–M bond in dinuclear clusters with D_{4h} symmetry (Fig.7), the "superfluous" ninth electron in $[Tc_2Cl_8]^{3-}$ in isoelectronic clusters can be in one of the following MO: $b_{1u}(\delta^*_{M-M})$;[19,20,40,41] $a_{2u}(\sigma'_{n,\,M-M})$;[14,15,42,43] $a_{1g}(\sigma''_{M-M})$.[44] There exist indirect data confirming each of these versions but none of the confirmations constitute direct and well founded experimental results.

The claim by Cotton and co-workers[19,20,40] that the unpaired electron in the $[Tc_2Cl_8]^{3-}$ anion is in the $b_{1u}(\delta^*_{M-M})$ orbital has received somewhat more justification than others. This conclusion was reached on the basis of quantum-chemical calculations,[40] optical spectroscopic experiments,[1] and EPR of frozen solutions.[20] However, the accuracy of the quantum-mechanical calculations of the highest MO is not high and more reliable results, which are in no way directly dependent on these calculations, are provided in this instance by the EPR method. However, the EPR spectra

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†The synthesis and electronic structure of the dinuclear d^4–d^5 rhenium cluster $\{Re_2Cl_4[P(n\text{-}C_3H_7)_3]_4\}PF_6$ have been described,[45,46] but its molecular structure has not so far been confirmed by X-ray diffraction.

(and hence also their interpretation) quoted by Cotton and Pedersen[20] arouse certain doubts. Indeed, Cotton and Pedersen[20] recorded the EPR spectra of frozen solutions of $Y[Tc_2Cl_8].9H_2O$ in a mixture of 10 vol.% of concentrated hydrochloric acid and 90 vol.% of ethanol and later it became known[13,23] that the $[Tc_2Cl_8]^{3-}$ ions undergo solvolytic reactions in such a mixture. This affects the charge of the dinuclear anions and their optical spectra, so that the EPR spectra obtained under these conditions refer to a mixture of species of the type $[Tc_2Cl_{8-n}.(Solv)_n]^{(3-n)-}$. As a result of this, the resolution of the $[Tc_2Cl_8]^{3-}$ spectrum is low, particularly that of parallel orientation lines, which might have been the cause of the inaccuracy in the determination of the parameters of the EPR spectra.

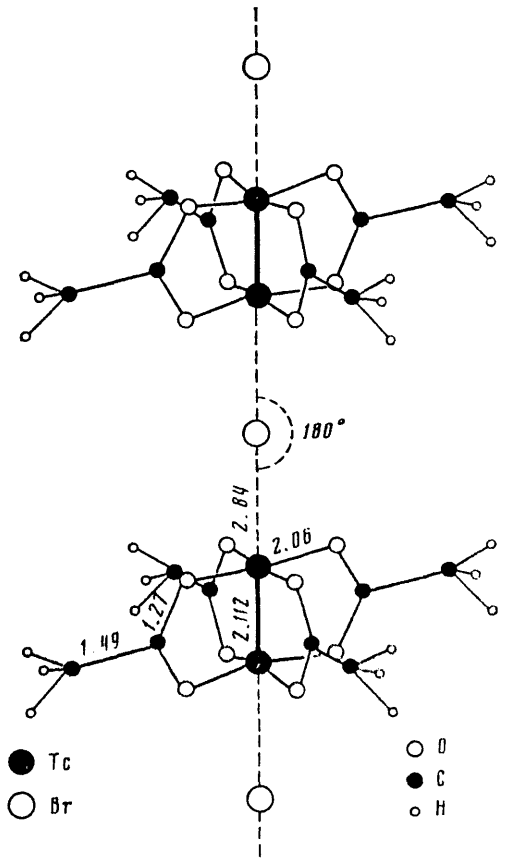


Figure 6. Fragment of the $[Tc_2(CH_3COO)_4Br]$ structure.[37]

A combined magnetochemical study of a whole series of paramagnetic dinuclear technetium clusters with a d^4–d^5 configuration of the central atoms has been carried out recently.[13,47,48] It was shown that a single broad signal with an effective g-factor of 2.09 ± 0.02 is observed in the EPR spectra of polycrystalline clusters. Their effective magnetic moment μ_{eff} does not vary with temperature and corresponds to a spin-only value for a single unpaired electron per molecule (~1.74 μ_B).

The differences between μ_{eff} and the spin-only value observed previously in other studies and their temperature dependence (Table 1) have been attributed either to the inaccuracy of the magnetochemical experiments for low amounts of the technetium compounds or to the presence of an admixture of high-spin technetium(IV) complexes.

The EPR spectra[13,47,48] of frozen vitreous specimens of the Tc_2^{5+} complexes are similar in form and give rise to a well-resolved hyperfine structure due to the two equivalent ^{99}Tc nuclei with a nuclear spin of 9/2. It has also been established that the parameters of the EPR spectra of all the technetium clusters investigated (Table 1, compounds 8, 10, 15, 16, 18, 19, and 21) agree to within experimental error and have the following values: $g_\parallel = 1.85 \pm 0.03$; $g_\perp = 2.13 \pm 0.03$; $A_\parallel = -(188 \pm 5) \times 10^{-4}$ cm^{-1}; $A_\perp = -(78 \pm 5) \times 10^{-4}$ cm^{-1}; $P = (5 \pm 1) \times 10^{-4}$ cm^{-1}. The absence of a dependence of the magnetochemical parameters of the solutions and polycrystalline substances on temperature and the nature of the ligands surrounding the Tc_2^{5+} fragment as well as the observation that $g_\parallel < 2$, $g_\perp > 2$, and $g_{av} > 2$ can be accounted for by the fact that the unpaired electron in this dinuclear fragment is in the $b_{1u}(\delta^*_{M-M})$ MO formed in the main from the $4d_{xy}$ atomic orbitals (AO) of the two equivalent technetium atoms (Table 2). In other words, the formal multiplicity of the M–M bond in the d^4–d^5 complexes is 3.5. Thus the experimental results confirm the main conclusions reached earlier from calculations of the electronic structure of $[Tc_2Cl_8]^{3-}$ by the X_α method.[40]

Table 2. The possible ground electronic states and the ratios of the g-factors in the Tc_2^{5+} cluster compounds.[13,47,48]

Ground state	HOMO	Technetium AO forming the HOMO	n	Energy of interacting MO	$g$theor		
					$g_\parallel$	$g_\perp$	g_{av}
B_{1u}	δ^*_{M-M}	$4d_{xy}$	3.5	$E(b_{2u}) > E(b_{1u}) > E(e_u)$	<2	>2	≳2
A_{1g}	σ'_{M-M}	$5s+4d_{z^2}+5p_z$	4.5—4.0	$E(e_g) > E(a_{1g})$	~2	≲2	~2
B_{2g}	δ'_{M-M}	$4d_{xy}$	4.5	$E(e_g) > E(b_{1g}) > E(b_{2g})$	<2	<2	<2
A_{2u}	σ''_{M-M}	$5s+4d_{z^2}+5p_z$	4.5—4.0	$E(a_{2u}) > E(e_u)$	~2	>2	≳2
B_{1g}	δ''_{M-M}	$4d_{x^2-y^2}$	4.5	$E(e_g) > E(b_{1g}) > E(b_{2g})$	>2	<2	~2
E_g	π^*_{M-M}	$4d_{xz}+4d_{yz}$	3.5	$E(b_{1g}) > E(e_g) > E(b_{2g})$	—	—	—

2. Dinuclear Cluster Compounds of Technetium with the d^4–d^4 Electronic Configuration of the Central Atoms

Compounds 4–7 (Table 1) belong to this group. The physicochemical properties of the given dinuclear clusters are close to those of the analogous rhenium and molybdenum compounds with the quadruple M–M bonds and are as a rule isostructural with them.[4,32–34]

(a) Dinuclear Cluster Compounds with a Structure of the "Lantern" Type

$\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$. The first dinuclear d^4–d^4 technetium complex was obtained by Cotton and Gage[17] and an attempt was made to substitute the chloride ions in the coordination sphere of $[Tc_2Cl_8]^{3-}$ by trimethylacetate ions. The substitution reaction was carried out by heating (t = 150 °C) a suspension of $(NH_4)_3[Tc_2Cl_8].2H_2O$ in pivalic acid under argon for 36 h. After the reaction mixture had been

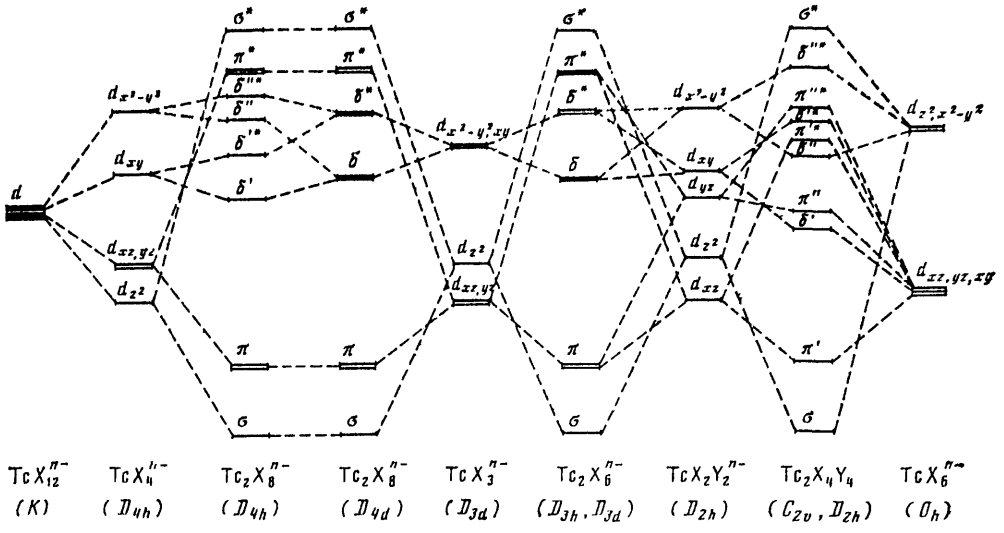


Figure 7. A simplified schematic illustration of the formation of one-electron metallic MO in dinuclear clusters of different symmetry.

cooled, fine red crystals of $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ precipitated; one of them was subjected to X-ray diffraction (Fig.8, Table 1), which demonstrated the similarity of the crystalline and molecular structures with dinuclear technetium and rhenium pivalate complexes.

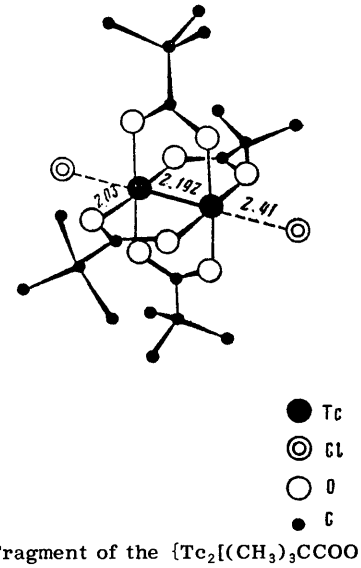


Figure 8. Fragment of the $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ structure.[17]

$[Tc_2(CH_3COO)_4]Cl_2$. The reduction of $[TcO_4]^-$ in a mixture of acetic and hydrochloric acids by molecular hydrogen under pressure yielded red crystals of $[Tc_2(CH_3COO)_4]Cl_2$.[49] The structure of the compound was not investigated by X-ray diffraction, but, in view of the fact that the technetium and rhenium[50] acetate complexes are isostructural, presumably it too has a structure of the "lantern" type with four bridging acetate ions in the equitorial planes and two axial chlorine atoms on either side of the quadruple Tc–Tc bond, i.e. their structure is similar to that of $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ (Fig.8). This structure of the acetate complex has also been confirmed by its diamagnetism and infrared spectroscopic data.

(b) The Octahalogenoditechnetates $M_2[Tc_2X_8]$

$[(C_4H_9)_4N]_2(Tc_2Cl_8)$. In contrast to $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$, the octachloroditechnetate ions have been obtained and characterised by means of chemical,[51] spectroscopic,[22] and X-ray diffraction[27] analytical methods comparatively recently. This is due to the lower stability of the $[Tc_2Cl_8]^{2-}$ ion compared with $[Tc_2Cl_8]^{3-}$ in hydrochloric acid solutions in which dinuclear cluster chlorides are as a rule formed on reduction of technetium(VII)–technetium(IV) by various reductants. However, subsequent investigations showed that the $[Tc_2Cl_8]^{2-}$ ions are much more stable in organic solvents than $[Tc_2Cl_8]^{3-}$.

This property of the octachloroditechnetate ions has been used to develop an optimum method for the synthesis of compounds with the $[Tc_2Cl_8]^{2-}$ anion.[13] For this purpose, the oxo-, oxochloro-, or chloro-complexes of technetium(VII)–technetium(IV) were reduced in concentrated hydrochloric acid (H_3PO_2, metallic zinc, or molecular hydrogen under a pressure of 3–5 MPa in an autoclave at ~140 °C can be used as reductants). An excess of a hydrochloric acid solution of tetrabutylammonium chloride is added to the resulting solution of the mixture of $[Tc_2Cl_8]^{2-}$, $[Tc_2Cl_8]^{3-}$, and $[Tc_2Cl_6]^{2-}$ ions and the solution is then extracted with a mixture of chloroform, carbon tetrachloride, and methylene chloride a characteristic feature of which is a satisfactory separation of the organic and aqueous phases. In order to

increase the solubility of technetium ions in the organic phase, acetone may also be added to the extraction mixture. When the solution is coloured an intense brown or turquoise, which corresponds to the presence of a high content of $[Tc_2Cl_6]^{2-}$ or $[Tc_2Cl_8]^{3-}$ ions respectively in the mixture, it is necessary to pass air through the extraction mixture until it becomes fully coloured bright green, but a yellow colour, indicating the formation of the $[TcCl_6]^{2-}$ ions, is not obtained. After this, the organic phase is separated and allowed to stand in air in order to evaporate the solvent slowly. Crystallisation yields bright green $[(C_4H_9)_4N]_2[Tc_2Cl_8]$ dendrites, which are less soluble than $[(C_4H_9)_4N]_2[TcCl_6]$. After two recrystallisations from acetone or methylene chloride, a pure preparation of tetrabutylammonium octachloroditechnetate is produced. Following the repeated employment of the evaporated mother liquors, formed in all the stages of the experiment, as the starting materials for the reduction of technetium chloride complexes to technetium(III), the overall yield of tetrabuytylammonium octachloroditechnetate can be increased almost to ~100%.

The preparation of crystals of tetrabutylammonium octachloroditechnetate has been described by Cotton et al;[27] they were studied by X-ray diffraction, which showed that the structure of the $[Tc_2Cl_8]^{2-}$ ions is analogous to that of the isoelectronic cluster rhenium and molybdenum chlorides and bromides with a quadruple M–M bond[4,32–36] (Fig.2 and Table 1).

Table 1 shows that the replacement of the chloride ions in $[Tc_2Cl_8]^{2-}$ by trimethylacetate ions $[(CH_3)_3CCOO]^-$ leads to an appreciable increase of the Tc–Tc distance, which is caused by the *trans*-influence of the axial chlorine atoms in $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ on the length of the quadruple M–M bond. The mechanism of the *trans*-influence consists in the fact that the formation of the $Tc-Cl_{ax}$ bond in the carboxylate complexes involves mainly the $4d_{z^2}$, $5s$, and $5p_z$ electrons of the technetium atoms and the $3p_z$ electrons of the chlorine atoms. Since the $4d_{z^2}$, $5s$, and $5p_z$ electrons of technetium also participate in the formation of the σ-component of the Tc–Tc bond (Fig.7), there is a mutual correlation of the $Tc-Cl_{ax}$ and Tc–Tc bond lengths. Analogous effects have been observed for the dinuclear complexes of rhenium, molybdenum, chromium, platinum metals, etc.[4,32–34,52,53]

$[(C_4H_9)_4N]_2[Tc_2Br_8]$. When several drops of hydrobromic acid are added to an acetone solution of $[(C_4H_9)_4N]_2[Tc_2Cl_8]$ and the reaction mixture is then heated briefly to boiling, a carmine-red solution is formed; this colour corresponds to the $[Tc_2Br_8]^{2-}$ ions.[22] When the solution is evaporated, carmine-red $[(C_4H_9)_4N]_2[Tc_2Br_8]$ dendrites are formed, but their exact molecular structure has not so far been established.

(c) The Electronic Structure of Dinuclear d^4–d^4 Clusters

All the dinuclear technetium complexes with the d^4–d^4 electronic configuration of the central atoms known at present are diamagnetic. According to the one-configuration approximation, the eclipsed conformation of these complexes, like that of the isoelectronic Cr, Mo, W, and Re compounds having no bridging ligands, is determined by the δ-component of the M–M bond formed mainly as a result of the overlap of the $4d_{xy}$ AO of the M atoms.[4,32–34,41,42] Fig.7 illustrates a simplified scheme for the formation of the M–M bond in dinuclear clusters with the D_{4h} symmetry, from which it follows that the highest MO in the d^4–d^4 complexes is the $b_{2g}(\delta_{M-M})$ orbital, while the M–M bond has a formal multiplicity of 4.0.

After the determination of the formal multiplicity of the Tc–Tc bonds in $[Tc_2Cl_8]^{n-}$ (n = 2, 3) and its isoelectonic technetium complexes, the question arises of the cause of the lower stability of the dinuclear d^4–d^4 clusters compared with the d^4–d^5 clusters and of the possibility of the formation of analogous dinuclear complexes by other d elements with a multiplicity of the M–M bonds of 3.5. It has been shown[13,41,48,54] that the real electronic structure of the clusters of d transition elements can be described within the framework of the MO method only when account is taken of configuration interactions (CI). Thus allowance for the CI in the d^4–d^4 complexes results in a decrease of the effective multiplicity of the M–M bond approximately to 3.0; on the other hand, allowance for the CI in the d^4–d^5 complexes hardly affects the effective multiplicity of the M–M bond, which is a direct consequence of the Brillouin theorem,[55] according to which singly excited states do not contribute to the ground electronic state of the system when account is taken of the CI by the self-consistent field methods. The quadruple bond in the d^4–d^4 complexes is therefore "diluted" as a result of the doubly excited $\sigma^2\pi^2\delta^0(\delta^*)^2$ state with an M–M double bond, whereas in the d^4–d^5 complexes the low-lying excited $\sigma^2\pi^2\delta^0(\delta^*)^1$ state makes no contribution to the overall M–M bond energy, while all the doubly excited states, occupying high positions, make a very small contribution to the ground state.

The above mechanism of the increase of the stability of the clusters with a single unpaired electron does not extend to all the dinuclear clusters of the d transition elements. It is known that the d^4–d^3 molybdenum clusters, namely $[Mo_2Cl_8]^{3-}$ and $[Mo_2(SO_4)_4]^{3-}$, are much less stable than their analogues with a quadruple M–M bond, i.e. $[Mo_2Cl_8]^{4-}$ and $[Mo_2(SO_4)_4]^{4-}$.[4,32–34] An analogous phenomenon has been observed for the dinuclear rhenium complexes $[Re_2X_8]^{3-}$, which have not so far been isolated in a pure form and whose formation has been observed only in electrochemical processes.[20,56] The complex $\{Re_2Cl_4[P(n\text{-}C_3H_7)_3]_4\}PF_6$[45,46] (where the Re–Re bond length is so far unknown) apparently constitutes an exception to this rule; the increase of its stability may be caused by the σ-donor influence of the phosphine ligands, which increases the energy of the σ-component of the Re–Re bond compared with the $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_6(PR_3)_2]$ complexes.

Allowance for the CI should not therefore always increase the stability of the dinuclear clusters with a single unpaired electron. We believe than an additional cause[13] is the decrease of the effective charge Z_{eff} on the metal atoms following the formation of an M–M bond by the latter. This phenomenon had been recently observed for technetium clusters by X-ray electronic spectroscopy.[57,58] An analogous decrease of Z_{eff} is not observed in the rhenium clusters, while in the molybdenum clusters [judging from the skeletal electron energies $\varepsilon(Re_{4f_{7/2}})$ and $\varepsilon(Mo_{3d_{5/2}})$],[59–64] Z_{eff} is actually increased on the metal atoms following the formation of M–M bonds.

Estimates of the influence of the addition (or removal) of the "superfluous" electron to certain rhenium, technetium, and molybdenum clusters with the d^4–d^4 configuration have been published.[13] They showed that in the case of technetium clusters the addition of the "superfluous" electron does indeed result in the maximum gain in the repulsion energy between M atoms with like charges, the gain being greater than the loss in the δ-overlap energy. Conversely, the removal of a single electron always leads to an increase of the repulsion energy with a simultaneous decrease of the δ-overlap energy. From this it follows that the d^4–d^3 complexes should be always less stable in relation to the dissociation of the M–M bonds than the d^4–d^4 complexes with a

similar structure. We may note that the factor involving the increase of the ionic radius with decrease of the oxidation state of the metal atoms in the cluster acts in the opposite direction. Whether or not the acceptance of a superfluous electron in the d^4–d^4 system has a favourable effect depends on the ratios of all these factors. In the case of technetium the addition of the electron is energetically favourable not only for dinuclear clusters but, as will be shown below, also for the polynuclear clusters.

Cotton et al[21] recently gave another explanation of the strengthening of the M–M bonds in the d^4–d^5 technetium clusters compared with the d^4–d^4 clusters. The explanation is based on the hypothesis that, on passing from $[Tc_2Cl_8]^{2-}$ to $[Tc_2Cl_8]^{3-}$, the decrease of the energy of the δ-component of the M–M bond is accompanied by the simultaneous increase of the energy of the π- and possibly also the σ-component of this bond. If this hypothesis is valid, then, on passing from the d^4–d^4 complexes to the d^4–d^5 complexes, either an increase of the energy difference between the π_{M-M} and π^*_{M-M} MO, on the one hand, and the σ_{M-M} and σ^*_{M-M} MO, on the other, or an increase of the "metallic" character of the π_{M-M} and σ_{M-M} MO should take place.

However, the X-ray electronic spectroscopic data[13,57] have shown that none of these conditions is in reality fulfilled. For example, an increase of the splitting between the lines corresponding to the π- and δ-components of the M–M bond in the valence X-ray electronic spectrum is not observed on passing from the $[Tc_2Cl_8]^{2-}$ ion to $[Tc_2Cl_8]^{3-}$ and $Tc_2(CH_3COO)_4X$ (where X = Cl or Br) (the lines of the σ-components of the Tc–Tc bond are not shown in the spectra). An increase of the "metallic" character of the σ_{M-M} and π_{M-M} MO would have been manifested by a decrease of $\varepsilon(Tc_{3d_{5/2}})$ on passing from the d^4–d^4 complexes to the d^4–d^5 complexes, since this would have entailed an appreciable decrease of Z_{eff} on the technetium atoms. However, the real decrease of $\varepsilon(Tc_{3d_{5/2}})$ is small and corresponds to an average decrease of this quantity with decrease of the formal oxidation states of technetium by 0.5. Furthermore, with increase of the energy of the σ-component of the M–M bond in the d^4–d^4 complexes, the energy of the skeletal electrons of the axial halogen atoms would have decreased appreciably; however, the real values of $\varepsilon(Cl_{2p_{3/2}})$ and $\varepsilon(Br_{3d_{5/2}})$ (Table 1) correspond to typical values of this electron energy in the dinuclear clusters of other *d* elements.[52,53,59,60]

3. Dinuclear Clusters of Technetium Compounds with the d^5–d^5 Electronic Configuration of the Central Atoms

Six complexes with this electronic structure, having the general formula $M_2[Tc_2X_6].nH_2O$, where M = K, NH_4, or $(C_4H_9)_4N$, X = Cl or Br, and *n* = 0 or 2, have been described hitherto[10,12,13] (Table 1, compounds 23–25). These compounds are formed under the conditions of far-reaching reduction of the technetium halide complexes in concentrated solutions of the corresponding hydrogen halides. The $[Tc_2X_8]^{3-}$ ions are the direct precursors of $[Tc_2X_6]^{2-}$. Atomic hydrogen (metallic zinc or aluminium in concentrated HCl) or molecular hydrogen (under a 3–5 MPa pressure in an autoclave at 140–180 °C) can be used as the reductant. The compounds are dark-brown cryptocrystalline powders or conglomerates of acicular crystals forming flat and three-dimensional stars. The complexes are sparingly soluble in organic polar and non-polar solvents, the $[(C_4H_9)_4N]_2[Tc_2X_6]$ salts constituting an exception, since they are easily soluble in polar organic solvents and readily dissolve in hot solutions of the corresponding hydrogen halides with formation of brown solutions, which are rapidly oxidised in air to $[Tc_2X_8]^{3-}$ and further to $[TcX_6]^{2-}$. All compounds of this type are diamagnetic. The X-ray electronic spectra[13,57] (Table 1) indicate the absence of bridging halogen atoms from the molecules of these compounds.

There are at present no X-ray diffraction data for the structures of the $M_2[Tc_2X_6].nH_2O$ complexes, but the set of their chemical and physicochemical properties indicates their dinuclear structure with an M–M bond having a high multiplicity. The D_{3h} or D_{3d} symmetry of the $[Tc_2X_6]^{2-}$ ions is the most likely. Evidently, for this symmetry of the dinuclear complexes, the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium becomes degenerate (Fig. 7) and the Tc–Tc bond in the $[Tc_2X_6]^{2-}$ ions is quintuple—of the $\sigma^2\pi^2\delta^2_{xy}\delta^2_{x^2-y^2}$ type in contrast to the hypothetical dinuclear d^5–d^5 complexes with D_{4h} symmetry in which the multiplicity of the M–M bond would have been three: $\sigma^2 2\pi^2\delta^2_{xy}(\delta^*_{xy})^2$.

We may note that in this case the rotation of one of the (TcX_3) fragments about the Tc–Tc bond by 60° does not result in a gain of the δ-overlap energy; the hindered conformation with D_{3d} symmetry (the ethane-like structure), in which the interligand repulsions are manifested to the smallest extent, should therefore be the most preferred for the $[Tc_2X_6]^{2-}$ ions.[13]

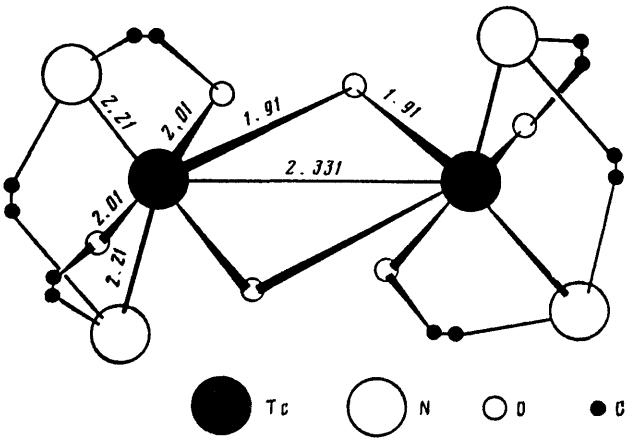


Figure 9. Schematic illustration of the immediate environment of the technetium atoms in the $[Tc_2(H_2EDTA)_2\mu\text{-}O_2].5H_2O$ structure (according to the data of Burgi et al[65]).

4. Dinuclear Clusters of Technetium Compounds with the d^3–d^3 and d^3–d^2 Electronic Configurations of the Central Atoms

$[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$. This compound has been obtained by reducing $[TcO_4]^-$ with an excess of $NaHSO_3$ in the presence of an excess of Na_2H_2EDTA with heating (70–80 °C) of the reaction mixture for several days.[65] After recrystallisation from 0.01 M $HClO_4$, the complex consisted of a diamagnetic cryptocrystalline red-brown powder. In constrast to all the dinuclear technetium clusters examined above, the ethylenediamine tetra-acetate complex with two bridging oxygen atoms, additionally binding the technetium

atoms, has the idealised C_{2v} symmetry. The ethylenediaminetetra-acetate ions behave as tetradentate ligands, coordinating each technetium atom to 2 nitrogen atoms and 2 oxygen atoms in the acetate group (Fig.9); the coordination polyhedra of the technetium atoms formed in this process consist of two distorted octahedra with a common edge made up of bridging oxygen atoms.

TcO_2. Technetium dioxide has a structure close to that of the ethylenediaminetetra-acetate complex described above#. According to the results of X-ray diffraction analysis of the TcO_2 powder,[66] the technetium dioxide cluster has a distorted rutile structure: six oxygen atoms are located at the vertices of a distorted octahedron in the centre of which the technetium atom is present (Fig.10). The TcO_6 octahedra are linked to one another along the edges made up of oxygen atoms forming an infinite three-dimensional network. The technetium atoms in the octahedra have been brought closer together in pairs so that one may expect the formation of Tc–Tc bonds, but their strength is much lower (and their length much greater—see Table 1) than in the ethylenediaminetetra-acetate complex. This is shown indirectly by the paramagnetism of technetium dioxide, indicating the presence of approximately one unpaired electron at each technetium atom.[13]

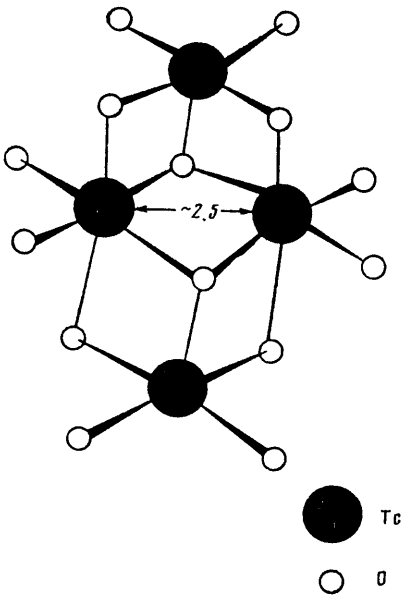


Figure 10. Fragment of the TcO_2 structure (according to the data of Magneli and Andersson[66]).

$K_3[Tc_2Cl_8O_2]$. This compound is hitherto the only representative of dinuclear technetium clusters with the d^3–d^2 electronic configuration of the central atoms. The complex has been obtained by refluxing a solution of $K_3[Tc_2Cl_8].2H_2O$ in ethyl methyl ketone in air.[11,13] This compound is a yellow–green powder sparingly soluble in ethyl methyl ketone and other organic solvents and readily soluble in inorganic acids. The complex is resistant to the action of oxidants and reductants both in the solid phase and in solutions. It can be oxidised to $[TcO_4]^-$ only after prolonged refluxing with strong oxidants such as Ce^{4+} in 0.4 M H_2SO_4. In the presence of complex-forming agents (for example, concentrated hydrochloric acid), the $[Tc_2Cl_8O_2]^{3-}$ ions decompose comparatively rapidly with formation of initially equivalent amounts of $[TcCl_6]^{2-}$ and $[TcOCl_5]^{2-}$.

Infrared spectroscopy of $K_3[Tc_2Cl_8O_2]$ indicates the presence of two types of bonds between the oxygen and technetium atoms in the structure of this complex: $\nu(Tc{=}O) = 1020\ cm^{-1}$ (strong); $\nu(Tc{-}O) = 680\ cm^{-1}$ (medium); $\delta(Tc{-}O{-}Tc) = 475\ cm^{-1}$ (medium). The X-ray electronic spectra of this compound[57] indicate the absence of bridging chlorine atoms from its structure. Thus, although there are no direct data concerning the structure of $K_3[Tc_2Cl_8O_2]$, the physicochemical properties of this complex suggest that it has a dinuclear structure with a weak metal–metal bond.

The electronic structure of the hypothetical complex $[(NH_3)_2(OH)_2Tc(\mu\text{-}O)_2Tc(OH)_2(NH_3)_2]$, with a molecular structure analogous to that of the complex $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2]$, has been calculated[65] by the extended Hückel method. The calculation led to the conclusion that a single Tc–Tc bond with the $\sigma^2\pi^2(\delta^*)^2$ electronic structure is formed in the technetium ethylenediaminetetra-acetate complex and not a triple bond ($\sigma^2\pi^2\delta^2$), which might have been suggested on the basis of the scheme in Fig.7. According to Burgi et al,[65] the reverse sequence in terms of the energy of the δ_{M-M} and δ^*_{M-M} MO responsible for the formation of the δ(Tc–Tc) bond in the given complex arises by virtue to the destabilising effect of the 2*p* orbitals of the bridging oxygen atoms. This explains the greater length of the Tc–Tc bond in the ethylenediaminetetra-acetate complex (~2.33 Å) compared with the expected length of the "truly" triple M–M bond.

However, even if this type of effect, involving the destabilisation of the δ(Tc–Tc) bond under the influence of bridging ligands, does occur, its extent is not as great as has been suggested.[65] Indeed, Table 1 shows that the expected length of the Tc–Tc triple bond should be ~2.22 Å, i.e. shorter by ~0.1 Å than in the ethylenediaminetetra-acetate complex. On the other hand, the length of the single Tc–Tc bond should be ~2.55 Å, which is greater by ~0.23 Å than the analogous length in $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$. From this it follows that the difference between the energies of the δ_{M-M} and δ^*_{M-M} MO should be positive (and not negative as suggested by Burgei et al[65]) and greater in absolute magnitude than the energy of the interelectron repulsion, since otherwise the complex $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$ would have been paramagnetic with two unpaired electrons (as in the case of TcO_2).

Thus it is most likely that the formal multiplicity of the Tc–Tc bond in the ethylenediaminetetra-acetate complex is 3.0 ($\sigma^2\pi^2\delta^2$). However, the δ-component of the bond is weakened, so much that its contribution to the overall energy of the M–M bond is close to zero.

The δ-level is apparently destabilised to an even greater extent in the TcO_2 and $[Tc_2Cl_8O_2]^{3-}$ complexes having a similar structure, which leads to their paramagnetism (Table 1), the value of μ corresponding to the presence of two or three unpaired electrons per molecule.

#The methods of synthesis and properties of TcO_2 have been described in detail in a monograph.[1]

5. The Cluster Carbonyls

Several technetium carbonyl complexes in which metal–metal bonds are observed have been described.

$[Tc_2(CO)_{10}]$. Ditechnetium decacarbonyl was first obtained simultaneously by two groups of investigators[67,68] via the reaction

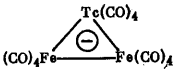
$$Tc_2O_7 + 17CO \rightarrow [Tc_2(CO)_{10}] + 7CO_2 .$$

The carbonylation was carried out in an autoclave at ~200 °C and an initial carbon monoxide pressure of ~20 MPa. It was later reported[69] that the carbonylation of TcO_2 with formation of ditechnetium decacarbonyl also takes place under milder conditions: ~2 MPa and 250 °C.

The compound $[Tc_2(CO)_{10}]$ is a colourless crystalline substance with a melting point of ~160 °C, which readily sublimes *in vacuo* (~10^{-4} Pa) at 50 °C. The compound is diamagnetic and readily dissolves in diethyl ether and other non-polar organic solvents.

In contrast to the molecules of the dinuclear complexes discussed above, the $[Tc_2(CO)_{10}]$ molecule (Fig.11 and Table 1) has the following structural features: (1) idealised D_{4d} symmetry (staggered conformation); (2) a weak M–M bond; (3) a higher strength of the bonds between the technetium atoms and axial ligands than that of the bonds involving equatorial ligands. In broad outline, the structure of the ditechnetium decacarbonyl molecule resembles those of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$.[70] The chemical and physicochemical properties of these compounds are likewise similar. For example, the interaction of $[M_2(CO)_{10}]$ (where M = Mn, Tc, or Re) with elemental halogens in organic solvents results in the formation of compounds of the type $M(CO)_5X$ (where X = Cl, Br, or I), i.e. the oxidative addition of the X_2 molecules to the M–M bond, accompanied by dissociation, takes place.[69] The interaction of $M(CO)_5X$ with dimetal decacarbonyls in the presence of sodium amalgam results in the formation of mixed carbonyls of the type $[MnTc(CO)_{10}]$ and $[ReTc(CO)_{10}]$,[71] whose structure resembles that of ditechnetium decacarbonyl.

Irradiation of a mixture of ditechnetium decacarbonyl and iron pentacarbonyl (in molar proportions of 1 : 4) with ultraviolet light in tetrahydrofuran for 1 h yielded the mixed technetium iron carbonyl cluster $[Fe_2Tc(CO)_{12}]^-$.[72] The anion was also precipitated in the form of the tetrabutylammonium salt. A trinuclear structure of this anion has been postulated:[70]



The formation of an M–M bond is also possible in the dimeric technetium carbonyl halides having the general formula $[Tc(CO)_4X]_2$ (where X = Cl, Br, or I), which are formed when $[Tc_2(CO)_{10}]$ interacts with elemental halogens in carbon tetrachloride or chloroform on heating in a sealed tube.[69]

The interaction of cobalt carbonyl in tetrahydrofuran in the presence of an excess of the Na/K alloy in an atmosphere of CO at room temperature for 1 h yielded the anion $[Co(CO)_4]^-$, which reacted with $[Tc(CO)_5X]$ to form after 5 h a yellow-red compound having the composition $[CoTc(CO)_9]$, which is readily soluble in organic solvents. The diamagnetism of this complex suggests the presence of the heteropolar M–M bond in its structure.[73]

The formation of M–M bonds may also be expected in the structure of the polynuclear technetium tetracarbonyl hydride having the tentative structure $[HTc(CO)_4]_3$.[74]

The compound is formed as the side product in the synthesis of $[HTc(CO)_5]$ [69,75] by the interaction of ditechnetium decacarbonyl with sodium amalgam in tetrahydrofuran with subsequent acidification of the reaction mixture using concentrated orthophosphoric acid.

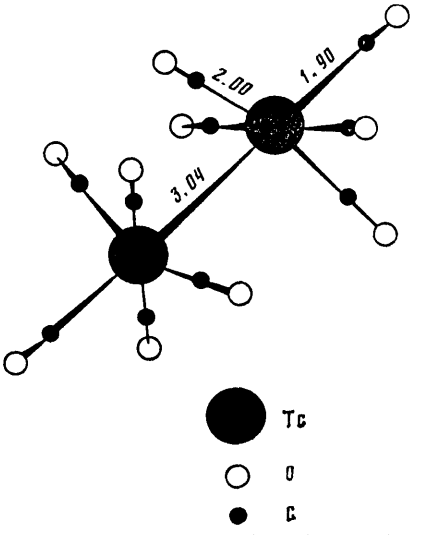


Figure 11. Molecular structure of $Tc_2(CO)_{10}$ (according to the data of Hileman et al[67]).

It is seen from the data for the chemistry of cluster technetium carbonyls presented above that in the case of strong-field ligands technetium exhibits a tendency towards the formation of clusters. In terms of this property, technetium resembles the platinum group elements.

6. Polynuclear Cluster Compounds of Technetium

Until recently, there was no information in the literature about polynuclear ($n > 4$) clusters not only of technetium but also of all the Group VIIB elements. However, such compounds are known[2,3] for Group V, VI, and VIII transition metals and the elements of the vanadium and chromium subgroup clusters with weak-field ligands have been observed, while for the platinum subgroup metals clusters with strong-field ligands have been found. Thus the possibility of the formation of polynuclear clusters by Group VIIB elements and, in particular, of technetium clusters with weak-field ligands is of undoubted interest for general chemistry.

The first communications about the synthesis[10,13] and structure[76–79] of polynuclear technetium halides appeared in 1982–83. These studies demonstrated the enhanced capacity of technetium for the formation of polynuclear clusters with metal–metal bonds. Furthermore, the compounds isolated constituted a type of cluster compounds with conjugated quadruple metal–metal bonds previously unknown for other elements. It was therefore useful to consider in greater detail the results of studies in the chemistry of polynuclear technetium clusters carried out at the present time by the authors of this review.

In the deliberate search for ways to form polynuclear technetium clusters, the authors were guided by the following postulates:[13] (1) the stability and probability of the formation of polynuclear clusters should be greater in the case of a smaller effective charge on the technetium atoms, i.e. for complexes with a lower electronegativity of the ligand; (2) it is most likely that the polynuclear technetium clusters constitute a kind of intermediate link in the reduction of dinuclear clusters with multiple Tc–Tc bonds to the metallic state; (3) other conditions being equal, the probability of the formation of polynuclear clusters should be greater at high concentrations of technetium ions in solutions; (4) in the presence of a large assortment of reductants capable of reducing dinuclear technetium clusters to polynuclear clusters, it is preferable to employ reductants which do not contaminate the final products.

It was found[10,13] that all the requirements enumerated above are satisfied by the autoclave method for the reduction of technetic acid in concentrated hydrogen halide solutions by molecular hydrogen under a pressure of 3–5 MPa at 140–220 °C. A series of experiments showed that the final product of the reduction of $H(TcO_4)$ under these conditions is a mixture of outwardly similar crystalline substances with similar physicochemical properties. The mixture composition can be described by the general overall formula $[TcX_{1.8\pm0.3}\cdot .m(H_2O, OH^-, H_3O^+)]_n$, where X = I or Br and $n > 2$§.

According to X-ray electronic data,[13,57] the technetium atoms in the compounds comprising this mixture are in an average oxidation state of 2.0–1.5 [a single narrow peak with $\varepsilon(Tc_{3d_{5/2}}) = 254.7 \pm 0.3$ eV for X = Br and $\varepsilon(Tc_{3d_{5/2}}) = 254.5 \pm 0.3$ eV for X = I is observed in the spectra], while the halogen atoms in the structures of these compounds belong to at least two types: terminal [$\varepsilon(Br_{3p_{3/2}}) = 181.1 \pm 0.3$ eV; $\varepsilon(I_{4d_{5/2}}) = 48.4 \pm 0.4$ eV] and bridging [$\varepsilon(Br_{3p_{3/2}}) = 182.8 \pm 0.3$ eV; $\varepsilon(I_{4d_{5/2}}) = 49.8 \pm 0.4$ eV]. Magnetic data indicate a weak paramagnetism of the $[TcX_2.0.5H_2O]_n$ complexes, which include ~1 unpaired electron for 4–6 technetium atoms¶.

The results of the studies of the physicochemical properties of $[TcX_2.0.5H_2O]_n$ described above suggested a polynuclear structure of the compound constituting this mixture. Subsequently this hypothesis was confirmed by the X-ray diffraction analysis of single crystals of a series of compounds forming part of a mixture of polynuclear technetium bromides.[13,76–79] Using the differences between the outer appearances and physicochemical properties of the crystals, initially investigated by methods of microcrystal chemical analysis, it was later possible to achieve an initial resolution of the mixture into its constituent parts under the microscope. Such resolution made it possible subsequently to investigate thoroughly the physicochemical properties of each phase in $[TcBr_2.0.5H_2O]_n$ and to develop the optimum methods for the synthesis of these compounds. Methods for the synthesis of hexanuclear tetramethylammonium chloride cluster compounds of technetium were developed analogously.

(a) Polynuclear Cluster Bromides

$[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$. This octanuclear technetium cluster is the first representative of polynuclear clusters of *d* transition elements with a complex system of M–M bonds including four conjugated quadruple Tc–Tc bonds. The compound is formed on reduction of a concentrated solution of $H[TcO_4]$ or $H_2[TcBr_6]$ by molecular hydrogen under pressure (3–5 MPa) in an autoclave at 140–160 °C in concentrated hydrobromic acid. The complex crystallises in the form of black elongated tetrahedral prisms with a metallic cluster (a black powder is obtained on grinding). The crystals are insoluble in organic acids and polar and nonpolar organic solvents.

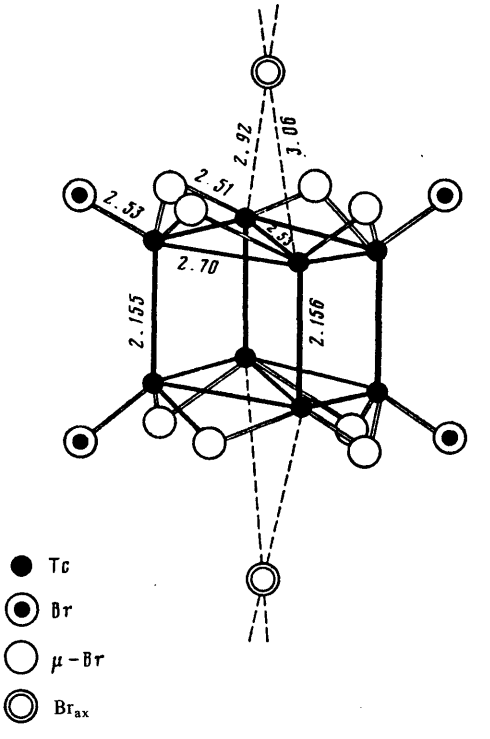


Figure 12. Fragment of the $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ structure.[78]

Fig.12 illustrates a fragment of the $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ structure. The molecule is constructed from four dinuclear Tc_2^{n+} fragments with quadruple M–M bonds located in vertical planes. Each of the eight technetium atoms is additionally bound in two "horizontal" planes by a system of M–M bonds forming two rhombs (upper and lower). Each

§ For brevity and also in view of the difficulty of the determination of the exact composition of this mixture, the above formula was used initially[10,13,57] and will be used in the present review in the form $[TcX_2.0.5H_2O]_n$.

¶ The values of μ_{eff} for $[TcX_2.0.5H_2O]$ have been determined with a low accuracy because the diamagnetic and paramagnetic contributions to the total magnetic susceptibility are comparable and the exact diamagnetic corrections for technetium compounds of this kind are unknown. For this reason, it was initially assumed[10] that the constituent compounds of this mixture are diamagnetic and only subsequent more accurate magnetic susceptibility data confirmed their weak paramagnetism,[13] the nature of which has not so been established.

technetium atom is also linked to two bridging bromine atoms which additionally span the technetium atoms in pairs in the horizontal planes. The technetium atoms located on the long diagonals of the rhombs form bonds also with the terminal bromine atoms; the remaining four technetium atoms are bound in pairs by weak electrostatic interactions in the vertical plane with two bromine atoms, each of which is analogously linked to a neighbouring polynuclear fragment.

The authors of the structural investigation[76–78] assume that the $[H(H_2O)_2]^+$ cations are present in the structure of the octanuclear complex instead of water molecules, although the location of hydrogen atoms was not established objectively. We believe[12,13] that this hypothesis requires additional investigation because the infrared spectra of this compound [namely the presence in the spectra of only the $\nu(O-H)_{H_2O} \cong 3500\ cm^{-1}$ and $\delta(H-OH)_{H_2O} \cong 1600\ cm^{-1}$ absorption bands] and its weak paramagnetism failed to confirm the presence of the $[H(H_2O)_2]^+$ cations.

$[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$. Under analogous conditions but at lower temperatures (130–150 °C) one of the products of the reduction of the $[TcO_4]^-$ or $[TcBr_6]^{2-}$ ions in hydrobromic acid is the complex $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$. It crystallises in the form of black (without metallic lustre) elongated hexahedral prisms. On grinding, the crystals give rise to a black powder with a green tint which is soluble in hydrobromic acid and polar organic solvents with formation of a dark-green solution having a brown tint. The compound does not dissolve in non-polar organic solvents. According to preliminary data, this octanuclear complex is paramagnetic. However, a definite conclusion concerning the number of unpaired electrons is not so far possible owing to the difficulty of separating the phases and the low accuracy of the magnetochemical measurements for systems of this kind.

Preliminary X-ray diffraction data obtained for the $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$ single crystal (the compound was synthesised by the authors of this review at the Institute of Physical Chemistry of the USSR Academy of Sciences and the X-ray diffraction analysis was carried out by P.A.Koz'min and co-workers at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences) have shown that its structure resembles that of $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ (Fig.12). The principal difference consists in the fact that in the case of $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$ the octanuclear fragments made up of technetium atoms are not linked into infinite chains by weak electrostatic interactions with the axial bromine atoms and are separated from one another to give isolated molecules, while the axial bromine atoms are no longer bridging. The principal interatomic distances and angles in the structure of this complex are the same as in $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ (Table 1).

$[Tc_6Br_6\mu_3\text{-}(Br, OH)_6][H_3O(H_2O)_3]_2$. Following an increase of the synthesis temperature in the autoclave to ~180–200 °C and a slight decrease of the concentration of technetium ions in solution, one of the products of the reduction of $H[TcO_4]$ or $H_2[TcBr_6]$ in hydrobromic acid is a hexanuclear complex which has the tentative composition $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6][H_3O(H_2O)_3]_2$ according to X-ray diffraction data for the single crystals.[79] The compound crystallises in the form of dark red-brown crystals (a red-brown powder is obtained after grinding), which are very readily soluble in polar organic solvents but less so in non-polar solvents and concentrated hydrobromic acid. The $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6]^{2-}$ solutions are dark-brown and are stable in air. The hexanuclear complex is weakly paramagnetic (Table 1).[12,13]

The structure of the hexanuclear cluster technetium bromide[79] is similar to the structures of the known octahedral cluster molybdenum and tungsten halides.[2] The difference consists in the fact that in the case of technetium the positions of the bridging halogen atoms are not fully occupied (Fig.13) and some of these atoms have been substituted by bridging oxygen atoms, probably the oxygen atoms in the OH groups.

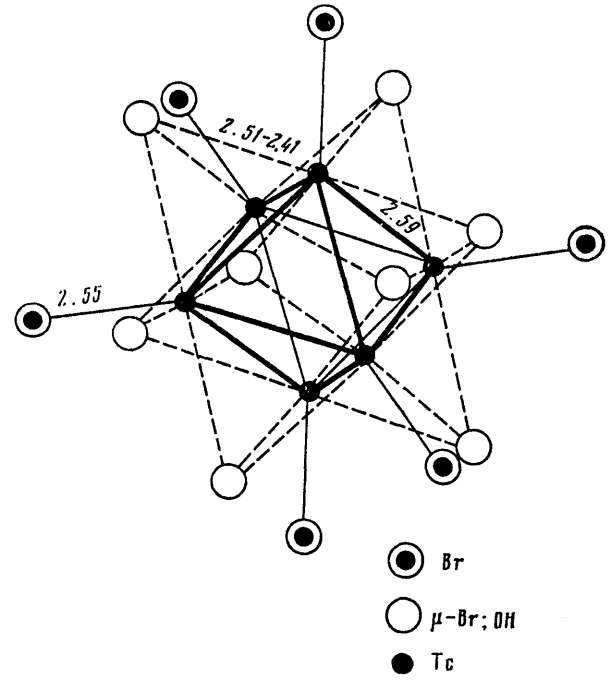


Figure 13. Fragment of the $[H_3O(H_2O)_3]_2(Tc_6Br_6\mu_3\text{-}(Br, OH)_6]$ structure (according to the data of Koz'min et al[79]).

Since X-ray diffraction analysis did not permit in this instance an unambiguous demonstration of the presence of hydrogen atoms in the structure, the above formula of the octahedral hexanuclear technetium complex cannot be regarded as finally established. Nevertheless, even the available data concerning the structure of the octahedral technetium cluster permit the important conclusion that, apart from the outer AO of the type $4d_{z^2}$, $4d_{xy,yz}$, and $4d_{x^2-y^2}$, also AO of the $4d_{xy}$ type are involved in the formation of its 15 bonding "metallic" MO.[13] We may note that a similar phenomenon has not been observed in the octahedral molybdenum and tungsten clusters, whose electronic structure is described by twelve bonding "metallic" MO formed by the AO of the metals of the d_{z^2}, $d_{xy,yz}$, and $d_{x^2-y^2}$ types.[2,80,81] Furthermore, one can state with confidence that in the technetium cluster 1–3 electrons are located in MO which are antibonding either in relation to

M–X† or M–M bonds. By virtue of the presence of these electrons, the cluster becomes paramagnetic and probably loses some of the bridging bromine atoms.

(b) Polynuclear Cluster Chlorides

The reduction of $[(CH_3)_4N]_2[TcCl_6]$ or $[(CH_3)_4N][TcO_4]$ in concentrated hydrochloric acid by molecular hydrogen under pressure (3–8 MPa) in an autoclave at 140–220 °C leads to the formation of a mixture of dark-brown almost black crystals of different geometrical shapes (tetrahedral rods, dendrides, and planar layer polyhedra). Using methods analogous to those described for $(TcBr_2.0.5H_2O)_n$, it was possible to resolve this mixture and to find the optimum conditions for the synthesis of crystals of two compounds: $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ and $[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$#.

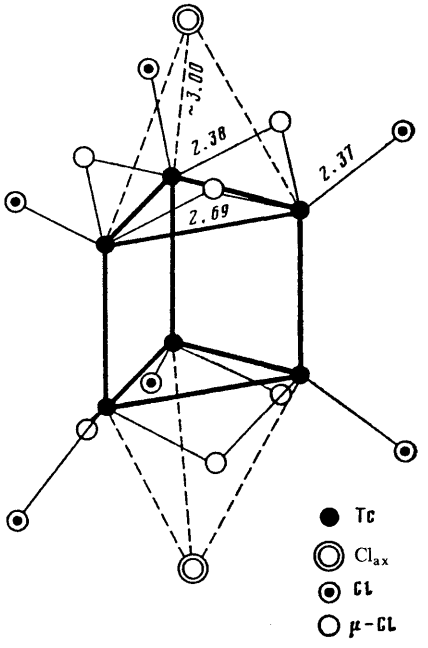


Figure 14. Fragment of the $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ structure (according to the data of Koz'min et al[79]).

$[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ is formed with a maximum yield at 140–150 °C and an initial hydrogen pressure in the autoclave of 3–5 MPa. The compound forms elongated tetragonal rods—frequently conglomerates of such rods in the form of dendrites. After grinding, the crystals give rise to a dark-brown powder soluble in hydrochloric acid, water, alcohol, and other polar solvents, giving rise to brown solutions.[12,13]

The molecular structure of the compound is presented in Fig.14 and Table 1.[79] Evidently, in broad outline, the $\{[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2\}^{3-}$ structure resembles that of the octanuclear cluster technetium bromide, but in the structure of the hexanuclear complex the Tc atoms are located at the vertices of a prism whose base consists of an equilateral triangle and not a rhomb as, for example, in the $[Tc_8Br_4\mu\text{-}Br_8].Br[H(H_2O)_2]$ structure. The vertical edges of this prism are much shorter than the horizontal edges and correspond to the quadruple Tc–Tc bonds, while the horizontal edges correspond to M–M bonds with a lower multiplicity. In addition, the technetium atoms are linked in the horizontal planes by bridging chlorine atoms. Furthermore, in the $[(CH_3)_4N]_3[Tc_6Cl_{12}]Cl_2$ molecule there are six terminal chlorine atoms and two chlorine atoms of the ionic type, which constitute a kind of axial ligands. The compound is paramagnetic (Table 1), μ_{eff} corresponding to the presence of approximately one unpaired electron per molecule.

$[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$ is formed under analogous but more severe conditions (150–180 °C) in an autoclave on reduction of $[(CH_3)_4N]_2[TcCl_6]$ or $[(CH_3)_4N][TcO_4]$ in concentrated hydrochloric acid. The crystals of this compound resemble anthracite under the microscope and have the form of orthorhombic layered plates. After grinding, a dark-brown powder with a violet tint is produced. It is soluble in hydrochloric acid, water, alcohol, and other polar solvents, giving rise to brown solutions. The complex is paramagnetic (Table 1) but it is so far impossible to specify with confidence the number of unpaired electrons in the molecule in view of the low accuracy of the magnetochemical study.

According to preliminary X-ray diffraction data, obtained by P.A.Kos'min and co-workers, the structure of the cluster is close to that of $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ (Fig.14, Table 1). The differences consist in the length of the Tc–Tc bonds. For example, in the case of $[(CH_3)_4N]_2[Tc_6Cl_{12}]$ the three Tc–Tc bonds located in the vertical planes are lengthened at the expense of the shortening of the M–M bonds in two horizontal planes. Furthermore, the terminal chlorine atoms in the neighbouring polynuclear fragments play the role of axial ligands in the structure of this hexanuclear complex.

The similarity of the molecular structures of the hexanuclear technetium chlorides and the octanuclear technetium bromides suggests also the similarity of their electronic structures. For example, the vertical edges of the prism made up of the technetium atoms in the $[Tc_8Br_{12}]$, $[Tc_8Br_{12}]^+$, and $[Tc_6Cl_{12}]^-$ complexes (Figs.12 and 14 and Table 1) correspond to the quadruple M–M bonds {triple in the case of $[Tc_6Cl_{12}]^{2-}$}, formed, as in the dinuclear clusters, by the $4d_{z^2}$, $4d_{xz}$, $4d_{yz}$ AO of technetium. In addition, the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium also participate in the formation of this bond. However, the AO of the last two types are also involved in the formation of many-centre "metallic" MO in the horizontal planes.

Precisely because of the formation of these many-centre MO, the electron densities at the technetium atoms in the polyhedral cluster bromide are equalised, as shown by the equality of the values of $\varepsilon(Tc_{3d_{5/2}})$ for the formally heterovalent technetium atoms in these complexes (Table 1). The nature of these MO is such that they can have simultaneously both bonding (or antibonding) character in relation to

†This follows from the fact that the involvement of 5s AO of technetium in the formation of M–M bonds is unlikely, since they are as a rule[2–4] occupied in the formation of M–X bonds and the filling of the antibonding "metallic" MO by 7–9 electrons would have led to a considerable lengthening of the Tc–Tc bonds.

#K.E.German participated in the development of the method of synthesis of these compounds.

vertical M–M bonds and the bonding (or antibonding) character in relation to the Tc–Tc bonds in the horizontal planes. In other words, the many-centre "metallic" MO, formed mainly by the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium, are highly delocalised, while the remaining components of the M–M bonds remain predominantly localised at the pairs of technetium atoms.[13]

The sequence in the distribution of the many-centre MO in each specific instance can be different and depends, for example, on the ligand environment or the nuclearity of the cluster. The addition of new electrons to these MO therefore either does {as in the case of $[Tc_6Cl_{12}]^-$ and $[Tc_6Cl_{12}]^{2-}$} or does not {as in the case of $[Tc_6Br_{12}]^+$ and $[Tc_6Br_{12}]$} lead to a significant rearrangement of the system of M–M bonds in the cluster. On further addition of electrons to these MO, the role of the $4d_{xz}$, $4d_{yz}$, and even $4d_{z^2}$ AO of technetium in the formation of the many-centre M–M bonds is enhanced to an increasing extent, while their role in the formation of the Tc–Tc bonds located in the vertical planes is diminished. Ultimately, this leads to a radical rearrangement of the polynuclear cluster accompanied by the equalisation of the energies and lengths of all the M–M bonds—for example the octahedral $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6]^{2-}$ cluster is formed.[13]

In conclusion of this Section, we may note that only the first steps have been taken in the chemistry of polynuclear cluster compounds of technetium: in the first place much remains obscure not only in the description of the electronic structure and mechanism of the formation of these compounds but also even in the determination of their exact composition. The unusual structure of these compounds, which have no analogues among the polynuclear clusters of other elements, the similarity of the properties and compositions of various compounds of this class to one another, and also the ease of their interconversions are all factors hindering the identification and isolation of the polynuclear technetium clusters in a pure state and hence also the investigation of their physicochemical properties. However, the data already available in this field indicate, on the one hand, the enhanced capacity of technetium for the formation of polynuclear clusters with weak-field ligands and, on the other hand, the "anomaly" in the properties of the technetium clusters compared with the typical clusters of other *d* elements. The increased capacity of technetium for the formation of paramagnetic clusters as well as clusters with a complex system of non-equivalent M–M bonds may be included among such "anomalous" properties.

III. CHEMICAL PROPERTIES IN SOLUTIONS

1. The Formation of M–M Bonds

A study[7] of the reduction of $[PyH]_2[TcCl_6]$ by molecular hydrogen under pressure in an autoclave in hydrochloric acid with a gradual increase of the working temperature showed that the $(PyH)_2.[Tc_2Cl_8]_3.2H_2O$ cluster is formed at an HCl concentration of 4–5 M. The $[TcCl_6]^{2-}$ ions, which are present prior to the formation of the clusters, are hydrolysed partially under these conditions at ~120 °C:

$$[TcCl_6]^{2-} + 2H_2O \rightarrow [Tc(OH)_2Cl_4]^{2-} + 2HCl. \qquad (1)$$

The hydrolysed technetium(IV) ions are readily reduced by molecular hydrogen, which is accompanied by the formation of M–M bonds:

$$[Tc(OH)_2Cl_4]^{2-} \xrightarrow{H_2} [Tc_2Cl_{8-x}(OH)_x]^{3-} \xrightarrow{HCl} [Tc_2Cl_8]^{3-}. \qquad (2)$$

The hydrolysed $[Tc_2Cl_{8-x}(OH)_x]^{3-}$ ions thus formed are rapidly converted into $[Tc_2Cl_8]^{3-}$ on interaction with concentrated hydrochloric acid. We may note that the substitution of chloride ions by H_2O molecules is also possible in reactions (1) and (2).

The above study[7] showed that the formation of $[Tc_2Cl_8]^{3-}$ ions must be preceded by a stage involving the formation of the hydrolysed clusters. The hydrolysis in an autoclave at an elevated temperature is promoted by a decrease of the concentration of hydrochloric acid as a result of its partial evaporation. We may note that the formation of hydrolysed cluster complexes is observed also in the reduction of technetium(IV) in concentrated hydrochloric acid on refluxing with metallic zinc.[5]

2. The Behaviour of the $[Tc_2X_8]^{3-}$ Ions in Solutions of Hydrogen Halides

In order to elucidate the causes of the increased stability of the hydrolysed cluster ions compared with the unhydrolysed ions, further studies were made of the behaviour of $[Tc_2X_8]^{3-}$ (where X = Cl, Br, or I) in solutions of hydrogen halides.[8,23,24,82] They were performed mainly in relation to the most stable and most readily synthesised $[Tc_2Cl_8]^{3-}$ ion (Fig.2); kinetic methods with optical recording were employed. The identity of the reaction products was in most cases confirmed by their isolation in the solid phase. The studies showed that the stability of the $[Tc_2X_8]^{3-}$ ions (where X = Cl, Br, or I) in aqueous solutions is determined by the sum of competing processes: acid hydrolysis, complex formation with subsequent disproportionation and dissociation of the M–M bonds, and oxidative addition of atmospheric oxygen to the Tc–Tc multiple bond. We shall consider these processes in greater detail.

(a) Acid Hydrolysis (Anation Reactions)

$$[Tc_2X_8]^{3-} + nH_2O \rightleftarrows [Tc_2X_{8-n}(H_2O)_n]^{(3-n)-} + nX^-. \qquad (3)$$

The acid hydrolysis (anation) reactions predominate when the concentration of hydrogen halide in solution is $\lesssim$3 M. They are not accompanied by the dissociation of the M–M bonds and the oxidation of the hydrolysis product by atmospheric oxygen. The final product of reaction (3) is the hydrated cluster technetium oxide $Tc_4O_5.14H_2O$ (Table 1). The tendency towards hydrolysis increases in the sequence of halogens Cl < Br < I.[11,13,23,24,82]

(b) Complex Formation

$$[Tc_2X_8]^{3-} + X^- \rightleftarrows [Tc_2X_9]^{4-}. \qquad (4)$$

The complex formation reactions predominate in concentrated hydrogen halide solutions. When the ligands are replaced in the sequence X = Cl, Br, and I, the equilibrium in reactions (4) shifts increasingly to the right. The $[Tc_2X_9]^{4-}$ ion formed under these conditions apparently no longer has an eclipsed conformation, its Tc–Tc bond is appreciably weakened, and it can readily undergo further reactions leading to the dissociation of the M–M bonds.[8,11,13,24,82]

(c) Disproportionation with Dissociation of the M–M Bond

$$[Tc_2X_9]^{4-}+X^- \rightleftarrows [Tc(II)]+[Tc(III)]. \quad (5)$$

The mononuclear technetium(II) and technetium(III) formed as a result of this reaction are unstable and undergo further rapid reversible reactions involving disproportionation, oxidation by atmospheric oxygen, and dimerisation:[13,24]

$$[Tc(II)]+[Tc(II)] \overset{HX}{\rightleftarrows} [Tc_2X_6]^{2-}; \quad (6)$$

$$[Tc(III)]+[Tc(III)] \overset{HX}{\rightleftarrows} [Tc_2X_8]^{2-}; \quad (7)$$

$$[Tc(III)]+[Tc(III)] \overset{HX}{\rightleftarrows} [TcX_6]^{2-}+[Tc(II)]; \quad (8)$$

$$[Tc(II)] \xrightarrow[HX]{O_2} [TcX_6]^{2-}; \quad (9)$$

$$[Tc(III)] \xrightarrow[HX]{O_2} [TcX_6]^{2-}. \quad (10)$$

In the absence of oxidants, for example atmospheric oxygen, an overall mobile equilibrium is established:[13,24]

$$4[Tc_2X_8]^{3-} \rightleftarrows 2[TcX_6]^{2-}+3[Tc_2X_6]^{2-}+2X^-. \quad (11)$$

Analysis of reactions (1)–(8) and (11) shows that there exists a narrow range of HX and technetium ion concentrations in which there is a possibility of a prolonged existence of $[Tc_2X_8]^{3-}$ and the limits of this range become very markedly narrower in the sequence of halogens Cl > Br > I. For example, at an initial concentration $[Tc_2Cl_8]^{3-} > 10^{-2}$ M and for ~3 M < [HCl] < ~6 M, the solutions of the octachloroditechnetate can exist indefinitely without visible changes in the absence of atmospheric oxygen, while the octaiododitechnetates decompose almost at the instant of their formation in hydriodic acid. The octabromoditechnetates, which can be obtained at a high (~1 M) concentration of technetium ions and a high temperature in the autoclave {when the autoclave is cooled, crystals of $M_3[Tc_2Br_8].nH_2O$ are precipitated and virtually only the $[TcBr_6]^{2-}$ and $[Tc_2Br_6]^{2-}$ ions remain in the mother liquor}, occupy an intermediate position.

Thus partial evaporation of HCl in the synthesis of $[Tc_2Cl_8]^{3-}$ by the method of Eakins et al[5] and by the autoclave method[6–8] creates favourable conditions (from the standpoint of the acidity and the concentration of technetium ions in solution) for the formation of the octachloroditechnetates(+2.5), since, on the one hand, the rate of reduction of the technetium(IV) ions increases owing to their hydrolysis,[7] and, on the other, the stability of the hydrolysed cluster ions formed increases in relation to the reactions involving disproportionation and oxidation by atmospheric oxygen.[13,23,24,82] We may note that, under the conditions of more pronounced hydrolysis, the rate of reduction of technetium(IV) increases so much that the formation of metallic technetium becomes possible.

3. Oxidation-reduction Reactions

In solutions with a high $[Tc_2Cl_8]^{3-}$ concentration the octachloroditechnetate ions can enter into reactions in which oxygen undergoes oxidative addition to the Tc–Tc multiple bond:[11,13,24,82]

$$[Tc_2Cl_8]^{3-}+O_2 \rightarrow [Tc_2Cl_8O_2]^{3-}. \quad (12)$$

The Tc–Tc bond in dinuclear $Tc^{4.5+}$ complexes formed is greatly weakened (Table 1) and the complexes readily decompose in HCl solutions to the mononuclear complexes of quinquevalent and quadrivalent technetium:

$$[Tc_2Cl_8O_2]^{3-} \xrightarrow{HCl} [TcO(OH)Cl_4]^{2-}+[TcCl_6]^{2-}. \quad (13)$$

In the absence of complex-forming agents and in aprotic solvents the $[Tc_2Cl_8O_2]^{3-}$ ions are comparatively stable and can be isolated in the form of the salt $K_3[Tc_2Cl_8O_2]$ (Table 1). We may note that the analogous reactions involving the addition of oxygen to the quadruple M–M bond in the $[Tc_2Cl_8]^{2-}$ complexes lead to the formation of mononuclear oxohalogenotechnetium(V) complexes even in aprotic solvents:[13]

$$[Tc_2Cl_8]^{2-}+O_2 \rightarrow [Tc_2Cl_8O_2]^{2-} \rightarrow 2[TcOCl_4]^-. \quad (14)$$

Oxidative addition reactions have been recently observed also for the dinuclear clusters of other *d* transition elements with multiple M–M bonds.[83] The multiplicity of the M–M bonds must decrease in these reactions. It is known from organic chemistry that similar reactions are extremely characteristic of unsaturated organic compounds. We believe that the capacity for oxidative addition reactions is a common property of homeopolar multiple bonds.

Apart from the reactions involving the oxidative addition of oxygen, the usual oxidation-reduction reactions have also been observed for dinuclear technetium clusters with multiple M–M bonds (in this case they must be accompanied by a change in the multiplicity of the Tc–Tc bonds up to their complete dissociation):[10,13,20,22,24]

$$[Tc_2Cl_8]^{2-} \xrightarrow[HCl]{O_2} [Tc_2Cl_8]^{3-}; \quad (15)$$

$$[Tc_2Cl_8]^{3-} \xrightarrow[-e^-]{O_2} [Tc_2Cl_8]^{2-}. \quad (16)$$

Reaction (15) is very rapid and takes place in hydrochloric acid solution. Reaction (16) is slower and is characteristic of aprotic solvents since the $[Tc_2Cl_8]^{2-}$ ions rapidly decompose in hydrochloric acid solutions via reactions of type (4)–(11). In the presence of an excess of the reductant, reactions (15) and (16) can also proceed in the reverse direction.

4. The Ligand Substitution Reaction

Three types of ligand substitution reactions are now known for technetium clusters.

(a) Reversible substitution of monodentate ligands by other monodentate ligands:[10,11,13,22,24]

$$[Tc_2Cl_8]^{2-}+8X^- \rightleftarrows [Tc_2X_8]^{3-}+8Cl^-; \quad (17)$$

$$[Tc_2Cl_8]^{2-}+8X^- \rightleftarrows [Tc_2X_8]^{2-}+8Cl^-; \quad (18)$$

$$[Tc_2Cl_8]^{2-}+8X \rightleftarrows [Tc_2X_8]^{2}+8Cl^-. \quad (19)$$

The equilibria in these reactions are strongly displaced to the right for X = Br or I. The formation of mixed complexes has not been observed.

(b) Reversible substitution of monodentate ligands by bidentate ligands (Figs.3–6):[9–11,13,18]

$$[Tc_2Cl_8]^{3-}+4CH_3COO^- \rightleftarrows [Tc_2(CH_3COO)_4Cl_2]^-+6Cl^-; \quad (20)$$

$$[Tc_2(CH_3COO)_4Cl_2]^- \overset{CH_3COOH}{\rightleftarrows} [Tc_2(CH_3COO)_4Cl]+Cl^-; \quad (21)$$

$$[Tc_2Cl_8]^{3-}+4o\text{-}C_5H_4(OH)N \rightleftarrows [Tc_2(C_5H_4ON)_4Cl]+7Cl^-+4H^+. \quad (22)$$

These reactions proceed in the forward direction only at high temperatures (~120 °C) and in the presence of an excess of the bidentate complex-forming agent, while the reverse reactions (20)–(22) take place also at room temperature in the presence of an excess of HCl.

(c) Oxidative substitution of monodentate ligands by bidentate ligands (Figs.4, 6, and 8):[10,13,17]

$$[Tc_2Cl_8]^{3-} \xrightarrow[-6Cl^-;\ -e^-]{(CH_3)_3CCOOH} \{Tc_2[(CH_3)_3CCOO]_4Cl_2\}; \qquad (23)$$

$$[Tc_2X_6]^{2-} \xrightarrow[-5X^-,\ -e^-]{CH_3COOH} [Tc_2(CH_3COO)_4X]. \qquad (24)$$

These reactions are irreversible; organic acid ions apparently behave in the reactions as oxidants, being converted into the corresponding alcohols and their esters.[13] Reactions (23) and (24) take place only at high temperatures (>150 °C) and in the presence of a large excess of organic acid.

Disproportionation reactions of type (11) with formation of $[Tc_2X_6]^{2-}$ and $[TcX_6]^{2-}$ take place simultaneously with the ligand substitution reactions (17), (18), and (20) involving the $[Tc_2X_8]^{3-}$ complexes. However, the analogous complexes with bidentate bridging ligands (the d^4–d^5 complexes with the "lantern" structure—see Figs.4–6) do not undergo disproportionation reactions.[9] This fact constitutes additional confirmation that the disproportionation of $[Tc_2X_8]^{3-}$ is accompanied by the dissociation of the Tc–Tc bond, while the bidentate bridging acetate ions stabilise these bonds. We may note that the dinuclear complexes with Tc–Tc bonds behave analogously also in thermal decomposition reactions.

5. Reactions of Polynuclear Cluster Compounds

On further reduction of the $[Tc_2X_6]^{2-}$ ions in an autoclave with molecular hydrogen under pressure in concentrated solutions of hydrogen halides, there is a possibility of cycloaddition reactions:[10,12,13]

$$n[Tc_2X_6]^{2-} \xrightarrow[-kX^-]{me^-} [Tc_{2n}X_{6n-k}]^{(2n+m-k)-}. \qquad (25)$$

Since reactions with an order greater than two are unlikely in solutions, one may postulate that reaction (25) takes place in stages, i.e. tetranuclear, hexanuclear, octanuclear, etc, technetium clusters should be formed in the $[Tc_2X_6]^{2-}$ reduction processes.

Hexanuclear and octanuclear technetium clusters of this type, which have not so far been synthesised for other *d* elements, have now been characterised by means of X-ray diffraction[76,79] (Figs.12 and 14 and Table 1). A characteristic feature of these clusters is the presence in their structure of several quadruple Tc–Tc bonds and of a system of many-centre M–M bonds. Several $[Tc_2X_2\mu\text{-}X_4]$ fragments, which are residues of the $[Tc_2X_6]^{2-}$ ions, can be readily differentiated in both structures. Since the appearance of the quintuple Tc–Tc bond (σ^2, $2\pi^2$, δ^2_{xy}, $\delta^2_{x^2-y^2}$) is most likely in the $[Tc_2X_6]^{2-}$ ions, reaction (25) may be regarded as a kind of cyclic polycondensation reaction involving the binding of the $[Tc_2X_6]^{2-}$ monomers to one another via the formation of many-centre M–M bonds with a simultaneous decrease of the multiplicity of the Tc–Tc bond in the monomers to 4.0. Some of the halogen ions are then split off from the monomers, while others become bridging species linking the monomers to one another.

One must note the similarity of these reactions to the analogous cycloaddition reactions of unsaturated organic compounds (for example, to the trimerisation of acetylene with formation of benzene). However, inorganic cycloaddition reactions are not accompanied by the initial formation of a system of conjugated equivalent M–M bonds of high multiplicity, although in the present instance there are grounds for such hypothesis. From our point of view,[13] the reason for this is the higher potential barrier for this kind of redistribution of electron density in the case of quadruple M–M bonds.

Special mention must be made of the role of unpaired electrons in inorganic cycloaddition reactions of type (25). For example, according to preliminary data,[13] the $[Tc_2X_6]^{2-}$ anions do not enter directly into reaction (25) and only the products of their one-electron reduction, which are probably the $[Tc_2X_6]^{3-}$ ions with unpaired electron, initiate these reactions. Thus monomers of the type of $[Tc_2X_6]^{3-}$ with a single unpaired electron behave, on the one hand, as analogues of organic radicals in polymerisation reactions and, on the other hand, the presence of the unpaired electron leads to the removal of the prohibition of cycloaddition reactions with thermal excitation (this conclusion follows from the theory of the conservation of orbital symmetry in cycloaddition reactions[85,86]).

A further increase of the temperature of the synthesis in the autoclave (in hydrobromic acid) leads to the formation of octahedral technetium clusters with equivalent M–M bonds (Fig.13 and Table 1) of the type of $[H_3O(H_2O)_3]_2[Tc_6Br_6\mu\text{-}(Br, OH)_6]$.[10,13] On the basis of general considerations, one can postulate that the compound is formed either directly in the cycloaddition reactions of the $[Tc_2X_6]^{n-}$ anions (where $n = 2$ or 3) or via a rearrangement of the hexanuclear or octanuclear clusters with quadruple M–M bonds which have already been formed. Thus, an unambiguous solution of the problem of the mechanism of the formation of the given octahedral cluster requires in the first place the elucidation of the form (polynuclear or dinuclear) in which the hexanuclear and octanuclear technetium clusters with quadruple M–M bonds exist in solution. Since the solubility of these compounds becomes appreciable only at a high temperature in the autoclave, the elucidation of the form in which these clusters exist in solutions of hydrogen halides involves considerable experimental difficulties.

Thus, the chemical properties of the technetium clusters are similar to those of the usual mononuclear complexes (hydrolytic reactions, reactions involving the substitution of monodentate ligands by other monodentate ligands, complex formation reactions, and oxidation-reduction processes) as well as typical polynuclear clusters of other *d* transition elements (reactions accompanied by a change in the multiplicity of the M–M bonds up to their complete dissociation and by the substitution of monodentate ligands by bidentate ligands with formation of complexes having a structure of the "lantern" type). However, some of the reactions of the dinuclear and polynuclear technetium clusters are characteristic also of unsaturated organic compounds with multiple homeopolar bonds: reactions involving oxidative addition to multiple bonds and reactions in which multiple bonds undergo cycloaddition with formation of closed cyclic systems.

In a number of cases "anomalies" were observed in the properties of technetium cluster compounds compared with the clusters of other *d* transition elements, for example an increased capacity for the formation of stable paramagnetic clusters or clusters with complex systems of M–M bonds, including several quadruple Tc–Tc bonds. Naturally one cannot exclude the possibility that these "anomalies" are caused solely by the lack of adequate experimental data on the clusters of other *d* transition elements and that in the future similar properties will be observed also for clusters

of other metals. However, it is likewise probable that by virtue of its "crossing" position in Mendeleev's Table, technetium should possess simultaneously the capacity for the formation of both dinuclear clusters with weak-field ligands and M–M bonds having a high multiplicity and polynuclear clusters with strong- and weak-field ligands. It may be that the "anomalous" properties of technetium clusters are due precisely to this factor and also the fact that the theory of clusters is as yet too inadequate to explain unambiguously and to predict all the wide variety of the properties of these compounds.

IV THERMOCHEMICAL BEHAVIOUR

The thermal stability of the dinuclear clusters has been studied in order to elucidate the mechanisms of the thermal decomposition and the composition of the intermediates, to establish the relation between composition and thermal stability, and to elucidate the possibility of obtaining metallic technetium and coatings based on it. Investigations have shown that the thermal decomposition of technetium cluster compounds is a multistage process, which depends on the composition and structural features of the initial compound. In many cases the thermal decomposition is accompanied by disproportionation into technetium(IV) and metallic technetium:[39,87]

$$K_3[Tc_2Cl_8]\cdot 2H_2O \xrightarrow{130-160^\circ} K_3[Tc_2Cl_8] + 2H_2O \xrightarrow{370-450^\circ} \rightarrow 5/4K_2[TcCl_6] + 1/2KCl + 3/4Tc; \quad (26)$$

$$K_2[Tc_2X_6]\cdot 2H_2O \xrightarrow{130-150^\circ} K_2[Tc_2X_6] + 2H_2O \xrightarrow{550-650^\circ} K_2[TcX_6] + Tc, \quad (27)$$

where X = Cl or Br. If the hexahalogenotechnetate(IV) formed initially is thermally stable, as, for example, $K_2[TcCl_6]$, it remains in the system up to 1100 °C; otherwise it undergoes further thermal decomposition:[88]

$$K_2[TcBr_6] \xrightarrow{700-750^\circ} 2KBr + 2Br_2 + Tc. \quad (28)$$

We may note that reactions (26)–(28) are characteristic solely of cluster complexes with inorganic cations. For organic cations, the thermal decomposition of the cluster can proceed by one of the following pathways:[39]

$$(PyH)_3[Tc_2Cl_8]\cdot 2H_2O \xrightarrow{130^\circ} (PyH)_3[Tc_2Cl_8] + 2H_2O \xrightarrow{250-280^\circ} \rightarrow (PyH)Cl + [Tc_2(Py)_2Cl_5] + 2HCl \xrightarrow{415^\circ} 2Tc + 2Py + {}^5/_2Cl_2; \quad (29)$$

$$[(C_2H_5)_4N]_2[Tc_2Cl_6] \xrightarrow{298-305^\circ} 2Tc + 5/2Cl_2 + 2(C_2H_5)_3N + HCl + C_2H_4. \quad (30)$$

The second stage of the thermolysis of $(PyH)_3[Tc_2Cl_8]\cdot 2H_2O$ (at 250–280 °C) proceeds via the mechanism of Andersen's reaction and is accompanied by the migration of pyridine to the inner coordination sphere of the dinuclear complex [the ν(Tc–N) are 234 and 258 cm^{-1}]. The disproportionation of the dinuclear complex is not observed at this stage and its Tc–Tc bond is retained.[39] This is indicated by infrared and ESCA spectroscopic data as well as measurements of the static magnetic susceptibility (Table 1). In the case of the mononuclear pyridinetechnetium(IV) chloride complex the migration of pyridine into the coordination of sphere of technetium consists of two stages:[89,90]

$$(PyH)_2[TcCl_6] \xrightarrow{250^\circ} (PyH)[TcPyCl_5] + HCl \xrightarrow{316^\circ} [TcPy_2Cl_4] + HCl. \quad (31)$$

The thermal decomposition of the tetraethylammonium cluster via reaction (30) takes place in one stage, but the metallic technetium formed in this process is frequently contaminated by the carbide TcC.[39]

The thermal decomposition of $K[Tc_2(CH_3COO)_4]Cl_2$ also takes place in one stage with absorption of much heat:

$$2K[Tc_2(CH_3COO)_4]Cl_2 \xrightarrow{400-460^\circ} 2KCl + 4Tc + 4(CH_3CO)_2O + Cl_2 + 2O_2. \quad (32)$$

In contrast to reactions (29) and (30), reaction (32) is relatively unsuitable for the preparation of pure metallic technetium in the laboratory, as in this case the final products contain large amounts of potassium chloride.

Studies of the thermal stability of dinuclear cluster carboxylates with a structure of the "lantern" type, not containing inorganic cations (Figs.4 and 6), are of considerable interest, since in this instance the decomposition of the complexes is preceded by a sublimation stage and the gaseous product formed decomposes to metallic technetium on the walls of the reaction vessel:[39]

$$2[Tc_2(CH_3COO)_4]Cl \xrightarrow{400-460^\circ} 4Tc + 4(CH_3COO)_2O + Cl_2 + 2O_2; \quad (33)$$

$$2[Tc_2(CH_3COO)_4]Br \xrightarrow{400-460^\circ} 4Tc + 4(CH_3COO)_2O + Br_2 + 2O_2. \quad (34)$$

The metallic technetium deposited on the walls of the reaction vessel is not contaminated by solid extraneous impurities. When the conditions are chosen appropriately, this method can be used to prepare technetium coatings which nowadays can be of great practical importance, in the preparation of sources of β-radiation for radiography[91] and also of anticorrosion materials and materials resisting surface growth.[92]

Thus the data presented in the review permit the conclusion that technetium is one of the most powerful cluster forming agents: in the lowest oxidation states it is characterised by a tendency towards the formation of dinuclear and polynuclear clusters with both strong-field and weak-field ligands and M–M bonds of different multiplicity. The properties of the technetium clusters are closest to those of the analogous rhenium and molybdenum compounds.[1-4,32-34,93-106] However, there are also certain unusual properties. In the first place there is an increased tendency towards the formation of stable paramagnetic dinuclear and polynuclear clusters with a single unpaired electron in one of the antibonding "metallic" MO. The presence of this electron leads to the additional stabilisation of the technetium clusters. This phenomenon has been observed also for the clusters of other *d* elements, but in technetium it is more pronounced owing to the reduction of the effective charge on its atoms on formation of M–M bonds. Such reduction of Z_{eff} is responsible for the appearance in technetium of an increased tendency towards the formation of different types of cluster compounds with weak-field ligands which are readily interconverted. By virtue of this property, polynuclear clusters belonging to a new class with a complex system of M–M bonds, including several quadruple or triple Tc–Tc bonds, have been obtained for the first time for technetium. The polynuclear technetium clusters have an excess of electrons and are of interest for experimenters and theoreticians.

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