



# The Second Japanese–Russian Seminar on Technetium

---

## ABSTRACTS

Shizuoka, Japan

Nov. 29 ~ Dec. 2, 1999

### Scientific Topics

1. *Analytical and environmental chemistry of technetium*
2. *Coordination chemistry of technetium and rhenium*
3. *Radiopharmaceuticals of technetium and rhenium*
4. *Reprocessing of technetium*
5. *Other aspects of physics and chemistry of technetium*

*Hosted by*

**Shizuoka University**

*Co-organized by*

**The Chemical Society of Japan**

**Atomic Energy Society of Japan**

**The Japan Society for Analytical Chemistry**

**The Pharmaceutical Society of Japan**

## Scientific Topics

1. Analytical and environmental chemistry of technetium
2. Coordination chemistry of technetium and rhenium
3. Radiopharmaceuticals of technetium and rhenium
4. Reprocessing of technetium
5. Other aspects of physics and chemistry of technetium

Sponsored by      The Ministry of Education, Science, Sports and Culture  
Atomic Energy Society of Japan  
Japan Atomic Energy Research Institute  
Japan Radioisotope Association  
Inoue Foundation for Science  
Shizuoka Science and Technology Foundation  
Research Foundation for the Electrotechnology of Chubu  
Chubu Atomic Conference  
Chubu Atomic Conference, Shizuoka Branch

---

Aloka Co., Ltd.  
Chiyoda Technol Co.  
Chubu Electric Power Co., Inc.  
Kyushu Environmental Evaluation Association  
Nagase Landauer, Ltd.  
Shizuoka Convention Bureau  
Wakaida Engineering Co., Ltd.

## Organizing Committee

Prof. M. Grigoriev (Moscow)	Prof. H. Katsuta (Tokai)	
Prof. K. Komura (Kanazawa)	Prof. S. V. Krutchkov (Moscow)	Co-chairman
Prof. H. Kudo (Sendai)	Prof. Y. Maeda (Fukuoka)	
Prof. N. Oku (Shizuoka)	Prof. K. Okuno (Shizuoka)	
Prof. T. Omori (Shizuoka)    Chairman	Prof. V. F. Peretroukhin (Moscow)	
Dr. T. Sekine (Sendai)    Co-chairman	Dr. S. Tachimori (Tokai)	
Prof. Y. Takashima (Fukuoka)	Prof. K. Yoshihara (Sendai)	

## Executing Committee

*Shizuoka University*

Prof. H. Sato, President of the Shizuoka University

*Radiochemistry Research Laboratory, Shizuoka University*

Prof. T. Omori, Prof. K. Okuno, Dr. H. Yoshioka, Dr. H. Suganuma, Dr. M. Yanaga,  
and Ms. T. Ishida



# The Second Japanese – Russian Seminar on Technetium

---

## ABSTRACTS

Shizuoka, Japan

Nov. 29 ~ Dec. 2, 1999

### Scientific Topics

1. *Analytical and environmental chemistry of technetium*
2. *Coordination chemistry of technetium and rhenium*
3. *Radiopharmaceuticals of technetium and rhenium*
4. *Reprocessing of technetium*
5. *Other aspects of physics and chemistry of technetium*

*Hosted by*

**Shizuoka University**

*Co-organized by*

**The Chemical Society of Japan**

**Atomic Energy Society of Japan**

**The Japan Society for Analytical Chemistry**

**The Pharmaceutical Society of Japan**

# The Second Japanese-Russian Seminar on Technetium

## ----- PROGRAM -----

**November 29 (Monday)**

**9:00–10:00 Registration** (University Hall, Shizuoka University)

**10:00–10:15 Opening** (Chairperson: K. Okuno)

### ***1. Coordination chemistry of technetium and rhenium***

Chairperson: T. Sekine

**2901 (10:15–10:45)**

Behaviour of Technetium Acidoclusters in Acetonitrile Solutions

S. V. Kryutchkov and M. S. Grigoriev (Institute of Physical Chemistry, RAS)

**2902 (10:45–11:05)**

The Results of Quantum-Chemical Investigations of Technetium Cluster Compounds

Yu. V. Plekhanov and S. V. Kryutchkov (Institute of Physical Chemistry, RAS)

**2903 (11:05–11:25)**

Quantum Chemical Study of the Octanuclear Tetragonal Prismatic Cluster of Technetium with Bromide Ligands

Yu. V. Plekhanov and S. V. Kryutchkov (Institute of Physical Chemistry, RAS)

**11:25–11:40 Coffee break**

Chairperson: K. Hashimoto

**2904 (11:40–12:00)**

Investigation of Technetium Compounds by Methods of Conversion Electron Spectroscopy and X-Ray Electron Spectroscopy Combined

V. N. Gerasimov (Institute of General and Nuclear Physics, Russian Research Centre "Kurchatov Institute")

**2905 (12:00–12:20)**

NMR-<sup>99</sup>Tc Study of Technetium Compounds and Alloys

V. P. Tarasov, K. E. Guerman, and V. F. Peretroukhin (Institute of Physical Chemistry and Institute of General and Inorganic Chemistry, RAS)

**2906 (12:20–12:40)**

The Quantum Chemical Models of Metallic Tc

Yu. V. Plekhanov (Institute of Physical Chemistry, RAS)

**12:40–14:00 Lunch**

Chairperson: V. N. Gerasimov

**2907** (14:00–14:30)

Structural Characteristics of Polynuclear Rhenium Complexes and Their Relevance to Technetium Chemistry

Y. Sasaki (Graduate School of Science, Hokkaido University)

**2908** (14:30–14:50)

Unusual Oxidation States of Rhenium and Their Properties

L. V. Borisova (Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS)

**2909** (14:50–15:10)

Synthesis and Structural Characterization of Technetium and Rhenium Complexes with Peptides Having KYC - sequence

T. Takayama, K. Suzuki, T. Sekine, and H. Kudo (Graduate School of Science, Tohoku University)

**2910** (15:10–15:30)

Experimental and Theoretical Study on the Structure of Technetium(V) Amine Oxime Complexes with Nitrido Ligand

Y. Kani\*, T. Takayama\*\*, T. Sekine\*\*, and H. Kudo\*\* (\*Power & Industrial Systems R&D Laboratory, Hitachi, Ltd., \*\*Graduate School of Science, Tohoku University)

**15:30–15:50 Coffee break**

Chairperson: Y. Sasaki

**2911** (15:50–16:10)

Coordination-Chemical Behavior of  $\text{Tc}(\text{CO})_3^+$  in Aqueous Solutions

N. I. Gorshkov, D. N. Suglobov, A. E. Miroslavov, and A. A. Lumpov (Khlopin Radium Institute)

**2912** (16:10–16:30)

Kinetics of the Reaction of Pertechnetate with Sulphide

M. Simonoff, K. E. Guerman, and G. Simonoff (Institute of Physical Chemistry Russian Academy of Science and Laboratoire de chimie analytique et bioenvironnementale, URA 451, Université Bordeaux 1, CNRS)

**2913** (16:30–16:50)

Base Hydrolysis of Bis(acetylacetonato)nitridotechnetium(V)

T. Omori, S. Tanaka, K. Shinotsuka, and H. Sugauma (Faculty of Science, Shizuoka University)

**17:30–19:00 Getting together** (University Hall, Shizuoka University)

**November 30 (Tuesday)**

**2. Radiopharmaceuticals of technetium and rhenium**

Chairperson: V. M. Petriev

**3001** (9:40–10:10)

Development of the  $^{99m}\text{Tc}$ -Kit Production in Russia

G. Kodina and T. Tulska (DIAMED Ltd.)

**3002** (10:10–10:30)

Labelling of Blood Cells with Technetium-99m

A. Malysheva, G. Kodina, and E. Medvedeva (State Scientific Center, Institute of Biophysics)

**3003** (10:30–10:50)

Actual Aspects of Quality Control of  $^{99m}\text{Tc}$ -Radiopharmaceuticals

G. Kodina, A. Inkin, and T. Doronchenkova (State Scientific Center, Institute of Biophysics)

10:50–11:10 **Coffee break**

Chairperson: G. Kodina

**3004** (11:10–11:30)

Potentiometric Definition  $\text{Sn}^{2+}$  during a Labeling of Microspheres of Albumin by Radionuclides of Rhenium

D.N. Dyomin, V.M. Petriev, L.L. Bozadzhiev and V.G.Skvortsov

Medical Radiological Research Center RAMS, Obninsk

**3005** (11:30–11:50)

Production of  $^{186,188}\text{Re}$  and Recovery of Tungsten from Spent  $^{188}\text{W}/^{188}\text{Re}$  Generator

K. Kobayashi, S. Motoishi, K. Terunuma, and Abdul A. Rauf\* (Department of Research Reactor, Japan Atomic Energy Research Institute and \*National Atomic Energy Agency (Indonesia))

**3006** (11:50–12:10)

Synthesis and HPLC Analysis of Rhenium-188 Aminomethylenephosphonate Complexes

K. Hashimoto (Department of Research Reactor, Japan Atomic Energy Research Institute)

**3007** (12:10–12:30)

Development of the Method of the Preparation of Albumin Microspheres Labeled 188-Re

V. M. Petriev, D. N. Dyomin, V. G. Skvortsov, and T. P. Rizhikova (Medical Radiological Research Center RAMS)

12:30–14:00 **Lunch**

Chairperson: N. Oku

**3008** (14:00–14:30)

Strategies on Functional Biomimetic  $^{99m}\text{Tc}$ -Radiopharmaceuticals (Tc-RPs) Development

K. Horiuchi S, A. Yokoyama, and H. Saji (Kyoto University, Graduate School of Pharmaceutical Sciences)

**3009** (14:30–14:50)

Studies on Uptake and Distribution of Tc and Re Using the Mutitracer Technique

M. Yanaga , T. Ohyama, T. Yoshida, M. Iwama, M. Noguchi, T. Omori, K. Endo\*, R. Hirunuma\*\*, S. Enomoto\*\*, S. Ambe\*\*, and F. Ambe\*\* (Faculty of Science, Shizuoka University, \*Showa College of Pharmaceutical Sciences, \*\*The Institute of Physical and Chemical Research(RIKEN))

**3010** (14:50–15:10)

Synthesis of Aqueous  $\text{Tc}(\text{CO})_3^+$  and Some Data on Its Pharmacokinetics

V. Yu. Sukhov, N. I. Gorshkov\*, A. A. Lumpov\*, A. E. Miroslavov\*, D. N. Suglobov\*, and G. E. Kodina\*\* (Central Research Institute of Roentgenology and Radiology, \*Khlopin Radium Institute, \*\*Institute of Biophysics)

15:10–15:30 **Coffee break**

### **3. Environmental chemistry of technetium**

Chairperson: N. Momoshima

**3011** (15:30–15:50)

Behaviour of Technetium in Eutrophic and Dystrophic Fresh Water Lakes

K. E. Guerman, T. V. Khijnyak, V. F. Peretroukhin, E. S. German, E. V. Firsova, and N. N. Lyalikova (Institute of Physical Chemistry and Institute of Microbiology, RAS)

**3012** (15:50–16:10)

Development of a Separation Method for  $^{99}\text{Tc}$  in Environmental Samples Using a TEVA Resin and Its Concentration Levels in Japan

K. Tagami and S. Uchida (National Institute of Radiological Sciences)

16:10–16:30 **Coffee break**

Chairperson: K. Komura

**3014** (16:30–16:50)

The Concentrations of Technetium-99 in *Sargassum thunbergii* around the Coasts of the Japanese Islands

S. Hirano (National Institute of Radiological Sciences)

**3015** (16:50–17:10)

Measurement of Radionuclide Distribution Coefficients for Leached Mortar

N. Ashikawa\*, N. Matsuoka\*, T. Tajima\*\*, H. Saito\*\*, and A. Fujiwara\*\*\* (\* Kyushu Environmental Evaluation Association, \*\* Obayashi Corporation, \*\*\*Radioactive Waste Management Center)

3016 (17:10–17:30)

Concentration of Technetium-99 in Litter/Humus Layer of the Japanese Forest  
N. Momoshima, M. Sayad, and Y. Maeda (Faculty of Science, Kyushu University)

19:00–21:00 **Banquet** (Hotel Associa Shizuoka Terminal)

## December 1 (Wednesday)

### 4. *Reprocessing of technetium*

Chairperson: S. Tachimori

0101 (9:30–9:50)

Extraction Behavior of Technetium in Nuclear Fuel Reprocessing

G. Uchiyama, T. Asakura, S. Hotoku, H. Mineo, K. Kamei, M. Watanabe, and S. Fujine (Department of Fuel Cycle Safety Research, Japan Atomic Energy Research Institute)

0102 (9:50–10:10)

Technetium Problem during Spent Nuclear Fuel Reprocessing and Possible Methods of Its Solution

V. I. Volk, A. Yu. Vakhrushin, and B. S. Zakharkin (SSC of RF Bochvar All-Russia Research Institute of Inorganic Materials)

0103 (10:10–10:30)

Technetium Extraction from High Radioactive Waste

V. I. Volk, A. Yu. Vakhrushin, and S. N. Veselov (SSC of RF Bochvar All-Russia Research Institute of Inorganic Materials)

Q104 (10:30–10:50)

Diffusion Coefficients of Rhenium(VII) and Technetium(VII) in Nitric Acid and Tri-butyl Phosphate Diluted in Dodecane

M. Miratsu, R. Ludwig, N. T. K. Dung, G. Marx and M. Nabeshima\* (Freie Universitaet Berlin, \*Sumitomo Metal Mining Co. Ltd.)

0105 (10:50–11:10)

Evaporation Behavior of Diluted Nitric Acid Solutions of Nitrosyl Ruthenium and Perrhenate Ions with a Thin Film Evaporator

K. Ito (Institute for Advanced Materials Processing, Tohoku University)

11:10–11:25 **Coffee break**

Chairperson: V. I. Volk

**0106** (11:25–11:45)

Methods of Technetium Recovery in Fuel Reprocessing

S. Tachimori and S. Suzuki (Japan Atomic Energy Research Institute)

**0107** (11:45–12:05)

Solvent Extraction of Technetium(VII) from Alkaline Waste Using Crown Ethers: Fundamental Principles and Process Chemistry

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, T. J. Haverlock, R. A. Leonard\*, C. Conner\*, and G. J.

Lumetta\*\* (Oak Ridge National Laboratory, \*Argonne National Laboratory, \*\*Pacific Northwest National Laboratory)

**0108** (12:05–12:25)

Estimation of Necessary Separation Factor of  $^{99}\text{Tc}$  and Ru after  $^{99}\text{Tc}$  Transmutation for Use of Nuclear Ruthenium in Industry

A. A. Kozar, V. F. Peretroukhine, and B. F. Gulev (Institution of Physical Chemistry, RAS)

**0109** (12:25–12:45)

Properties of Technetium and Technetium-Ruthenium Alloys for Transmutation of Technetium

K. Minato and Y. Shirasu (Japan Atomic Energy Research Institute, Department of Materials Science)

12:45–14:00    **Lunch**

##### **5. *Other aspects of physics and chemistry of technetium***

Chairperson: H. Suganuma

**0110** (14:00–14:20)

Technetium Ion Catalysis of Some  $\text{HNO}_3$  Oxidation Reactions

V. S. Koltunov (A. A. Bochvar All-Russia Research Institute of Inorganic Materials (VNIINM))

**0111** (14:20–14:40)

Laser Photoacoustic Spectroscopy Applied to a Study on Coagulation Processes of Tc(IV) Colloids

T. Sekine, S. Kino, Y. Kino, and H. Kudo (Graduate School of Science, Tohoku University)

**0112** (14:40–15:00)

The Acceleration of U(VI) Reduction of Hydrazine in Alkaline Media in Presence of Technetium or Some Transition Elements Ions

V. I. Silin (Institute of Physical Chemistry, Russian Academy of Sciences)

**0113** (15:00–15:20)

Physico-Chemical and Catalytic Properties of a Bimetallic System Me-Tc/Support

G. N. Pirogova, N. N. Popova, and Yu. V. Voronin (Institute of Physical Chemistry, RAS)

**0114** (15:20–15:40)

The Effect of Support on Catalytic Properties of Tc in the Reactions of Different Types

G. N. Pirogova, N. M. Panich, Yu. V. Voronin (Institute of Physical Chemistry, RAS)

15:40–16:00      **Coffee break**

Chairperson: K. Okuno

**0115** (16:00–16:20)

Effect of Chemical Matrix on  $^{99m}\text{Tc}$  Decay Constant

V. V. Koltsov, D. N. Suglobov, L. G. Mashirov, A. E. Miroslavov, and N. I. Gorshkov (V. G. Khlopin Radium Institute)

**0116** (16:20–16:40)

Half-lives of Technetium 97,98

T. Kobayashi, K. Sueki\*, M. Ebihara\*, and H. Nakahara\* (College of Humanities & Sciences, Nihon University, \*Tokyo Metropolitan University )

**0117** (16:40–17:20)

Reevaluation of Ogawa's 'Nipponium' as the Element 75 (Rhenium) instead of 43 (Technetium)

K. Yoshihara (Japan Isotope Data Institute)

17:20–17:40      **Closing**      (Chairperson: K. Okuno)

## **December 2 (Thursday)**

Scientific tour to the Nuclear Training Center, the Hamaoka Nuclear Power Station of Chubu Electric Power Co., Inc.

**November 29 (Monday)**

*Coordination chemistry of technetium and rhenium*

## BEHAVIOUR OF TECHNETIUM ACIDOCLUSTERS IN ACETONITRILE SOLUTIONS

S.V.Kryutchkov, M.S.Grigoriev

Institute of Physical Chemistry, Russian Academy of Sciences

31 Leninsky prosp., Moscow, 117915, Russia

Cluster compounds are among the most interesting objects of the contemporary chemistry. The data available today for technetium cluster compounds prove that technetium is not only one of the most strong clusterforming agents, but also possesses a number of anomalous cluster-forming properties. Previous studies have shown than technetium forms several cluster structural types, unknown for other elements. One can mention, as an example, a novel type of polynuclear clusters with delocalized Tc-Tc bonds of high multiplicity [1, 2]. However, earlier studies in the field of the chemistry of technetium cluster compounds were carried out, for the most part, in aqueous solutions, and the ligands, coordinated around the cluster core, were anions of mineral acids (acidoligands) and the cluster fragments themselves - complex anions with metal-metal bonds of various formal multiplicity. Recently [3-5], a possibility of formation of binuclear cationic cluster with quadruple Tc-Tc bond has been shown using aprotonic solvents.

In the present work we have begun a study of the possibility of the conservation of Tc-Tc bonds in other structural types of technetium clusters (in particular, in hexanuclear clusters with delocalized Tc-Tc bonds of high multiplicity) for reaction in acetonitrile solutions. The reactions of the formation and destruction of the binuclear cationic technetium clusters in acetonitrile solutions were studied for the first time in [3]. A binuclear  $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}]^{4+}$  complex with formally triple Tc-Tc bond has been separated and structurally characterized. It has been shown that this complex is stable against oxidation but not against reduction in acetonitrile solutions. The formation of this complex takes place in the process of the ligand substitution in other binuclear complexes as well as in the process of the reduction of mononuclear Tc(IV-III) complexes.

In the present work we have in general proved these conclusions and undertaken attempts to study the behaviour of technetium polynuclear clusters  $[\text{Tc}_6\text{X}_{14}]^{n-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with Tc-Tc bonds of high multiplicity in acetonitrile solutions.

It has been shown that the stability of these clusters in acetonitrile solutions against destruction of Tc-Tc bonds and reduction is essentially lower then that of binuclear ones. Mononuclear complexes of the  $[\text{TcX}_2(\text{CH}_3\text{CN})_4]^+$  type were found to be one of the products of the destruction of polynuclear ones.

Earlier [1, 2] it had been shown that the stability of the  $[\text{Tc}_6\text{X}_{14}]^{n-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) clusters in aqueous solutions of hydrohalogenic acids is significantly higher, especially in reducing conditions. In oxidizing conditions the most stable product of the destruction of polynuclear clusters in aqueous solutions of hydrohalogenic acids is  $[\text{Tc}_2\text{X}_8]^{3-}$  ion with formal multiplicity of Tc-Tc bond of 3.5.  $[\text{Tc}_2\text{X}_6]^{2-}$  ion is the intermediate form of the existence of these clusters under the conditions described.

The X-ray structural study of  $[\text{TcBr}_2(\text{CH}_3\text{CN})_4][\text{BF}_4]$  single crystal (CAD4 autodiffractometer,  $\lambda\text{MoK}\alpha$ , graphite monochromator) has shown that this compound is isostructural with analogous chloride complex, separated earlier [4]. This compound was synthesized according to the method described in [4] for  $[\text{TcCl}_2(\text{CH}_3\text{CN})_4][\text{BF}_4]$ , but using  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Tc}_6(\mu\text{-Br})_6\text{Br}_6]$  as initial material.

Crystal data: orthorhombic, space group *Ibam*,  $a = 6.272(2)$ ,  $b = 12.459(5)$ ,  $c = 20.864(8)$  Å,  $Z = 4$ ;  $R = 0.033$ ,  $R_w = 0.033$  for 440 independent reflections with  $I > 3\sigma(I)$  and 59 variables. Nonhydrogen atoms refined anisotropically, H atoms localized from difference Fourier synthesis and refined isotropically.

The structure is formed by pseudooctahedral  $[\text{TcBr}_2(\text{CH}_3\text{CN})_4]^+$  cations with *trans*-positions of bromide ligands and tetrahedral  $[\text{BF}_4]^-$  anions. Atomic coordinates are presented in Table 1. The main bond lengths are: Tc-N 2.078(6) Å, Tc-Br 2.447(1) Å, N-C 1.11(1) Å, C-C 1.44(1) Å. The differences between the structures of bromide and chloride complexes are connected with the change in the size of halide ligands.

Table. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{Å}^2$ ,  $\times 10^3$ )

Atom	x	y	z	U
Tc	5000	5000	0	27 (1) *
Br	2656 (2)	6570 (1)	0	47 (1) *
B	0	0	2500	60 (3) *
F	1195 (12)	617 (8)	2118 (4)	124 (2) *
N	3082 (9)	4300 (4)	-696 (3)	31 (1) *
C (1)	2056 (11)	3901 (5)	1057 (4)	35 (2) *
C (2)	725 (15)	3404 (7)	1536 (5)	60 (2) *
H (2a)	123 (5)	357 (4)	-193 (3)	80
H (2b)	-58 (5)	369 (4)	163 (3)	80
H (2c)	68 (5)	292 (4)	-155 (4)	80

\* Equivalent isotropic U defined as one third of the trace of the orthogonalised  $U(i, j)$  tensor

## References

1. Kryutchkov S.V. In: Topics in Current Chemistry. V.176. P. 189. Springer-Verlag, Berlin, Heideberg, 1996.
2. Kryutchkov S.V. Russian Chem. Rev. V.67 (1998), p. 883.
3. Burns C.J., Burell A.K., Cotton F.A. et al. Inorg. Chem. V.33 (1994), p. 2257.
4. Bryan J.C., Cotton F.A., Daniels L.M. et al. Inorg. Chem. V.34 (1995), p. 1875.
5. Cotton F.A., Haefner S.C., Sattelberg A.P. Inorg. Chem. V.35 (1996), p. 1831.

THE RESULTS OF QUANTUM-CHEMICAL INVESTIGATIONS  
OF TECHNETIUM CLUSTER COMPOUNDS

Plekhanov Yu.V., Kryutchkov S.V.

Institute of Physical Chemistry RAS, 31, Leninskii prosp., Moscow, 117915 Russia

All calculations were carried out in approximation of the ab initio self-consistent field  $X_\alpha$ -scattered waves method with the improved computing algorithm [1]. For low-symmetry complexes the ordinary algorithm for solving the system of nonlinear equations sometimes requires a number of reductions of the subintervals in solution area and accordingly, an increase in calculation time. So we used a linear approximation for matrix of the problem  $S = A_i - EB_i$  in each rather wide energy interval  $[E_i, E_{i+1}]$  and following solution by standard methods of linear algebra for equation  $\det\{S\}=0$ . Width of these intervals is equal 0.5- 2eV in comparison with a usual one which could be less than 0.001eV. For the speedup of self-consistency the electronic density in each area of cluster is approximated on results of preceding iterations as a linear function from electronic densities in all cluster areas by the least squares method and is then corrected in the necessary direction.

In the diatomic models  $[\text{Tc}_2]^{n+}$  [2] we determined the influence of bond length  $r(\text{Tc-Tc})$  and cluster charge  $n$  on the position of electronic levels. With reduction of a charge is found rapprochement of group occupied molecular orbitals (MO-s) ( $4d\text{-Tc}$ ) and free MO  $2\sigma_{ga}$  ( $5s\text{-Tc}$ ). This is connected with the diffuse nature of  $2\sigma_{ga}$ . Unlike occupied " $4d$ " MO-s, its energy and composition weakly depend on the distance  $r$  and the charge  $n$ . It turned out that for the real Tc cluster compounds, when efficient charge  $n < 2$ , there always exists a distance  $r_0$ , under which the energies of empty free bonding level  $2\sigma_{ga}$  and occupied anti-bonding level  $1\delta_{u\beta}$  ( $4d\text{-Tc}$ ) are equal. Profit in bond strength for configuration  $2\sigma_{ga}(1)1\delta_{u\beta}(0)$  makes up 18% in contrast with  $2\sigma_{ga}(0)1\delta_{u\beta}(1)$ . For neighbors of technetium Mo and Ru such a change of electronic levels scheme is not found. Thereby, participation of the Tc 5s-orbital in M-M bond forming could possibly explain peculiarities of Tc cluster compounds discovered experimentally: forming a quintuple Tc-Tc bond in  $[\text{Tc}_2\text{Cl}_6]^{2-}$ , forming the infinite chains with the direct electronic exchange and so on.

The structure of binuclear cluster  $[\text{Tc}_2\text{Cl}_8]^{n-}$  [3] (and their Mo-analogues) is the result of M-M bonds forming between two pyramid fragments  $[\text{TcCl}_4]$ . Eclipsed conformation  $D_{4h}$  (fig.1-1) is found experimentally, excluding the ion  $[\text{Tc}_2\text{Cl}_8]^{4-}$ . The latter formally enter into the polymeric compound in staggered geometry  $D_{4d}$  (fig.1-2) with torsion turning of pyramid bases on  $45^\circ$ . We determined the influences of symmetry, length of Tc-Tc bond and cluster charge  $n$  on features of electronic structure, in particular, for structure forming frontier MO-s. In  $D_{4h}$  clusters  $[\text{Tc}_2\text{Cl}_8]^{2-}$  and  $[\text{Mo}_2\text{Cl}_8]^{4-}$  the highest occupied (HO)MO is bonding  $\delta$ -orbital  $2b_{2g}$ . When Tc oxidation state decreases the occupation of anti-bonding  $\delta^*$ -MO  $2b_{1u}$  takes place. In the staggered cluster  $[\text{Tc}_2\text{Cl}_8]^{4-}$  MO-s  $2b_{2g}$  and  $2b_{1u}$  are degenerated into non-bonding  $5e_2$  ( $\delta$ ), and an M-M bond was formed because of underlying bonding MO. Calculation of orbital forces, model potential curves [3] and orbital population indexes [5] for Tc-Tc bond has shown: 1)strength of Tc-Tc bond for all oxidation states is greater than for Mo-Mo bond 2)for the Tc complexes  $D_{4h}$  symmetry is preferred, and for  $n=4$  only  $D_{4d}$  becomes advantageous 3)when changing a state of Tc oxidation weakening of bond strength does not exceed 20%,-whereas for the Mo complex it runs up to 50% (probably going over a threshold of stability), so the state with  $n=5$  is not excluded for Tc-cluster 4)existing conception about M-M bond strength based both on cluster geometry and on formal multiple index have no



























































































































































