



6th International Symposium on Technetium and Rhenium

-SCIENCE and UTILIZATION-

**7 - 10 October 2008
Port Elizabeth, South Africa**

IST-2008

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Welcome Message

Dear Colleagues

On behalf of the Organizing Committee it is my privilege to welcome you to the *Sixth International Symposium on Technetium and Rhenium-Science and Utilization (IST-2008)*, which is meant to be an informal, instructive and festive occasion, where we can meet, learn, deliberate and celebrate.

The IST-2008 is an important milestone in this series of Symposia, since it is the first to be held outside the Japanese/Russian sphere. The first Symposium was held in Sendai in 1993, and it was followed every three years in Moscow (1996), Shizuoka (1999), Dubna (2002) and Oarai (2005).

The previous Symposia have been an excellent showcase for the innovative abilities of scientists working on the elements technetium and rhenium, and we trust that IST-2008 will be no different. It is a platform to meet old and make new friends and colleagues, to present the most recent results and to exchange and discuss the newest ideas.

We believe that the scientific program is superb, with the five plenary speakers undoubtedly world-renowned experts in their fields.

A special word of welcome is extended to our distinguished delegates from outside South Africa. The local chemical community is honoured by your participation, and we hope that your visit to Port Elizabeth and the country will be stimulating and enriching.

The Organizing Committee has worked with endless enthusiasm and dedication to make IST-2008 the international chemistry event of the year in South Africa.

Finally, we wish you a pleasant stay in Port Elizabeth, the Friendly City of South Africa.

Thomas Gerber
Chairman: Organizing Committee

Symposium Committees

International Advisory Committee

- R. Alberto (Switzerland)
- J. Dilworth (England)
- Y. Fujii (Japan)
- T.I.A. Gerber (South Africa) Chairman
- K. Guerman (Russia)
- G. Kodina (Russia)
- H. Kudo (Japan)
- B.F. Myasoedov (Russia)
- T. Nagata (Japan)
- J.A. Rard (USA)
- V.F. Peretroukhine (Russia)
- P.R.V. Rao (India)

Local Scientific Committee

- T.I.A. Gerber (Chairman, NMMU)
- O. Knoesen (Necsa)
- W. Purcell (Univ. of the Free State)
- Z.R. Tshentu (Rhodes University)

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- Medical emergencies: Tel. 10177
- Police: Tel. 10111

Prof. Kenji Yoshihara

The delegates to the *Sixth International Symposium on Technetium and Rhenium-Science and Utilization (IST)* honour Prof. Kenji Yoshihara for his scientific achievements as a whole, and in particular, for his pioneering role in the chemistry of technetium.

Prof Yoshihara was the driving force behind this series of Symposia. The first *IST* was held in his home town of Sendai, and we enjoy the fruits of his vision today with the Sixth Symposium.

Kenji Yoshihara was born on the 16th of September 1929 in Niigata City. He graduated from Tohoku University in 1953, and he was awarded a D.Sc. in 1961. He started his professional career in 1954 as a researcher in the Japanese Government Electrotechnical Laboratory in Tokyo. In 1957 he joined the Japan Atomic Energy Research Institute in Tokyo (and later Tokai). His academic career started in 1968 as an associate professor in the radiochemistry laboratory at Tohoku University, where he was promoted to professor in 1982. He retired from academia in 1993, and is currently Emeritus Professor at Tokoku.

During his career Prof Yoshihara made major contributions to the field of radiochemistry. His doctoral study focused on the nuclear excitation of Rh and In by ^{60}C . In the period 1957-1993 he worked extensively on hot atom chemistry and its application to radioisotopes, on tritium chemistry, implantation reactions and technetium chemistry. Since his retirement he re-evaluated the discovery of the element nipponium (in 1908) by Mastaka Ogawa, who assigned it as element 43. For this work Prof Yoshihara was awarded the Prize of the Japanese Society of the History of Chemistry.

Prof Yoshihara published more than 250 research papers, mainly in nuclear and radiochemistry. Since 1982 he served as an associate editor of *Radiochemical and Radioanalytical Letters*, and he is a member of the Advisory Board of *Radiochimica Acta* since 1983. He published 3 books, which were also translated into English.

Young academics considered Prof Yoshihara as a father figure. His warm personality endeared him to his colleagues and peers, and he is admired by everyone who knows him for his great humility, respect for others and humanity.

Prof Yoshihara enriched the lives of everyone who worked with him and who had the honour of meeting him.



Symposium Programme

Tuesday 7 October

	Page
17:00 Registration (At the foyer of the NMMU Conference Centre)	
[Chairman: Prof. Gerber]	
18:00 Welcome (NMMU Conference Centre)	
<i>Yoshihara Prestige Lecture</i>	
Prof. J. Dilworth <i>Applications of Complexes of Rhenium and Technetium with Metal-Nitrogen Bonds as Radiopharmaceuticals</i>	19
19:15 Ice Breaker	

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Wednesday 8 October

		Page
	[Chairman: Prof. German]	
9:00	Plenary Session: Prof. M. Chinol <i>The Role of Technetium and Rhenium in Anticipation of Therapy Trials</i>	17
10:00	Prof. K. Czerwinski <i>Separation Uranium/Technetium for the UREX Process. Synthesis of Tc-Zr Waste Form</i>	27
10:40	Tea	
	[Chairman: Prof. Kremer]	
11:00	Prof. K. German <i>Stabilisation of Tc(V) Ions in Nitric Acid and Hydrazinium Nitrate Media in Presence of Th(IV)</i>	29
11:40	Prof. T.S. Sekine <i>Oxidative Dissolution of Tc(IV) Oxide Colloids Induced by Ultrasound</i>	38
12:20	Prof. A.M. Maes <i>A New Method for Technetium Speciation and Quantification in Humic Rich Natural Groundwater: Determination of the Tc Colloid/HS-Colloid Conditional Interaction Constant</i>	31
13:00	Lunch	
	[Chairman: Prof. Purcell]	
14:00	Dr. Z.R. Tshentu <i>Rhenium Complexes of Pyridylimidazole Derivatives</i>	41
14:30	Mr. I.N. Booyesen <i>Imido, Amido and Amino Complexes of Re(V) with Multidentate Aromatic Amines</i>	25
15:00	Mr. A. Abrahams <i>Rhenium(V)-Mediated Syntheses and Structures of Oxypyridinium-Ammonium Zwitterions</i>	24
15:30	Tea	
	[Chairman: Dr. Visser]	
16:00	Dr. E.B. Breynaert <i>Technetium Interaction with Natural Organic Matter: Complexation Versus Colloid/Colloid Association</i>	26
16:30	Dr. T.N. Mtshali <i>Rhenium(V)-Nitrido Complexes with Bidentate N,O- and N,N-Donor Atoms: $[ReN(\kappa^2-LL)(CN)_3]^{2-}$</i>	32

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Thursday 9 October

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	[Chairman: Prof. Dilworth]	
9:00	Plenary Session: Prof. Y. Fujii <i>Comprehensive Separation System for Spent-Fuel Reprocessing by Ion Exchange</i>	20
10:00	Prof. A.P.S. Sattelberger <i>Synthesis and Characterization of Multiply Metal-Metal Bonded Technetium Dimers</i>	37
10:40	Tea	
	[Chairman: Prof. Sekine]	
11:00	Prof. C. Kremer <i>Synthesis and Magneto-Structural Studies of Re(IV) Mononuclear Complexes</i>	30
11:40	Dr. T.Y. Yoshimura <i>Synthesis and Redox Properties of Octahedral Hexatechnetium(III) Complexes with Terminal Halide</i>	43
12:20	Dr. H.G. Visser <i>Rhenium(I) Compounds in Nuclear Medicine. Crystallographic and Kinetic Investigation of Different $[Re(CO)_3(L_1)(L_2)]^{n-}$ Complexes</i>	42
13:00	Lunch	
	[Chairman: Prof. Sattelberger]	
14:00	Plenary Session: Dr. J.R. Zeevaart <i>Technetium in the Third World Setting; R&D in South Africa</i>	22
15:00	Poster Session	
-	Each poster author will be requested to present a 5 minute session regarding their work.	
17:00		
19:30	Symposium Dinner	
-	The Kelway Hotel: Tanner Conference Venue	
24:00	(see page 11 for more information)	

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Friday 10 October

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	[Chairman: Prof. Fujii]	
9:00	Plenary Session: Prof. K. German <i>Recent Advances in Technetium Environmentally Focused Studies</i>	21
10:00	Dr. F. Poineau <i>Electro-Dissolution of Metallic Technetium in Acidic Media</i>	34
10:40	Tea	
	[Chairman: Dr. Tshentu]	
11:00	Dr. E.E.R. Rodriguez <i>Technetium Oxides: New Materials, New Insights</i>	36
11:40	Dr. M. Ozawa <i>Separation and Utilization of Technetium and Nuclear Rare Metals</i>	33
12:20	Prof. M. Fattahi <i>Speciation of Tc, effect of Eh-pH</i>	28
13:00	Lunch	
	[Chairman: Dr. Ozawa]	
14:00	Dr. T. Suzuki <i>Adsorption Behavior of Technetium on Tertiary Pyridine Resin in Hydrochloric Acid Solution</i>	39
14:40	Prof. W. Purcell <i>A Structural and Kinetic Comparison Between $[ReO(H_2O)(CN)_4]^-$ and $[ReN(H_2O)(CN)_4]^{2-}$</i>	35
15:20	Prof. I.D. Troshkina <i>Metallurgy of Rhenium</i>	40
16:00	Closing	

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Information

Symposium Venue

The Symposium will be held at the Conference Centre on the North Campus of the Nelson Mandela Metropolitan University in the suburb Summerstrand, Port Elizabeth. The venue is equipped with a complete range of conference and recreational facilities, and there is ample, comfortable accommodation nearby. See page 14 for a map showing the location of the Conference Centre. Venue coordinates: 34°00'04" S, 25°40'25" E (WGS 1984).



Registration Desk and Hours

The Registration Desk, where delegates can collect their Symposium material, will operate in the foyer of the Conference Centre from 17:00 on Tuesday the 7th of October before the symposium opening, and from 8:30 to 17:00 on each symposium day.

Language

The official language of the symposium is English.

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Lunch & Refreshments

Coffee/tea during the coffee breaks and lunch on the 8th, 9th and 10th of October will be available free of charge for registered participants.

Symposium Dinner

The Symposium Dinner will be held on Thursday the 9th of October at **The Kelway Hotel** in the *Tanner Conference Venue* at 19:30. The dinner is free of charge to all delegates and accompanying persons. After the dinner there will be transport available to take delegates back to their accommodation.



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Instructions for Presentations

Oral presentations

Plenary sessions will be 1 hour, and normal oral presentations 30 or 40 minutes including time for questions. Please consult the Symposium Programme (page 6) to determine duration of your presentation.

The following audio-visual equipment will be available:

- Notebook PC
- Data projector
- Overhead projector

Software installed on the notebook will include:

- Microsoft Windows XP
- Microsoft Office 2007 (including PowerPoint 2007)
- Windows Media Player (latest version)
- Adobe Reader (latest version)
- QuickTime (latest version)

All speakers should ensure that their presentations are viewable on the above hardware and software. PowerPoint presentations that use special fonts should have the font embedded in the file. If you need to use other software, please bring it with you.

Authors of oral presentations are kindly requested to ensure that the secretariat have a copy of the presentation before the presentation. Please bring your presentation along to Registration on at the start of the Symposium. The following media types are recommended:

- CD-R
- USB memory stick or flash drive
- CD-RW and DVD are **not** recommended.

It will also be possible for speakers to connect their own computer directly to the projector. The computer should have a standard 15 pin VGA port. If the computer's display port is different, then an appropriate converter must be brought along.

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Poster presentations

The posters should be A0 in size (width 0.84 m and height 1.2 m) and in portrait alignment. The poster layout is left to the author's discretion, but should be clearly readable from a distance of 1.5 m.

The posters will be hung on boards in the NMMU Conference Venue foyer. Materials to affix the poster to the boards will be supplied. Authors are requested to hang their posters up at the start of the symposium and to leave them up for the duration of the symposium.

At the poster session authors will be requested to do a 5 minute presentation on their work.

Symposium Tours

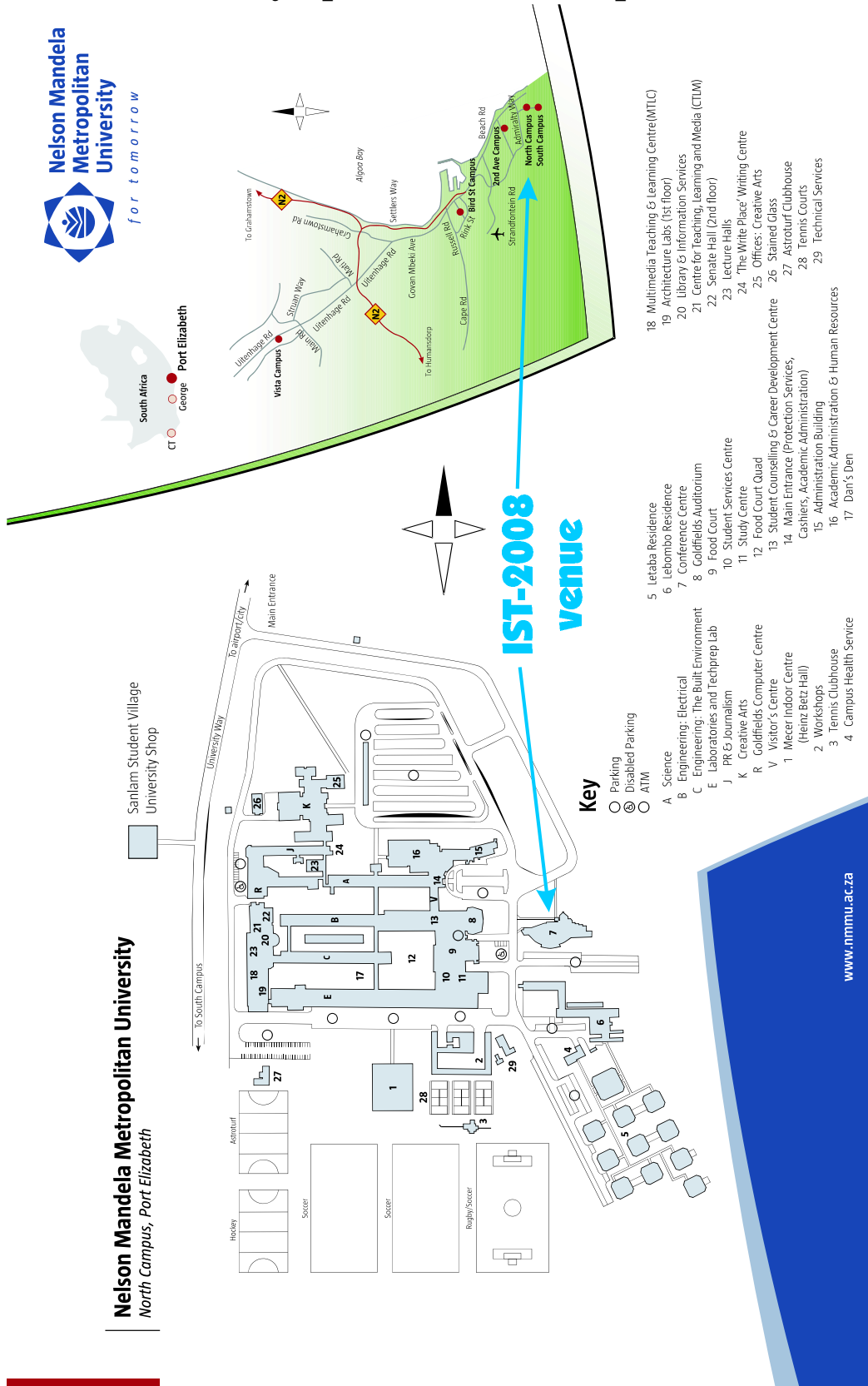
City Tour

The Port Elizabeth City Tour for accompanying persons will take place on Wednesday the 8th of October. The tour will start at 08h30 from the Conference Venue.

Addo Tour

The Addo Elephant National Park Tour will take place on Saturday the 11th of October. The cost for this tour is R800 and includes transport, entrance fee, open vehicle game drive through the park and lunch. The bus will leave at 08h00 from the Marine Drive entrance of the Boardwalk Casino and Entertainment World. The bus will return to Port Elizabeth in the late afternoon.

Maps Symposium Venue Map



Port Elizabeth



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THE ROLE OF TECHNETIUM AND RHENIUM IN ANTICIPATION OF THERAPY TRIALS

Marco Chinol: Division of Nuclear Medicine
European Institute of Oncology
Milano, Italy

The major objective of cancer radioimmunotherapy (RIT) is to enhance the effectiveness of the radionuclide by concentrating it at the tumor site with fewer side toxic effects to normal organs. However RIT is limited by a poor tumor to non tumor ratio. Thus, tumor targeting with long-circulating radiolabeled monoclonal antibodies (mAbs) has achieved success in the treatment of leukemias and lymphomas, in which the tumors are radiosensitive and the cancer cells are relatively accessible.

In the attempt to improve the therapeutic efficacy of radiolabeled mAbs various studies have examined the concept of tumor pretargeting. The so called three-step pretargeting technique employing the avidin–biotin system, was applied in several phase I-II clinical trials showing low toxicity and therapeutic efficacy.

Based on our previous clinical experience in locoregional treatments and recurrent high-grade glioma using the avidin-biotin pre-targeting technique, we have foreseen a potential application of ^{90}Y -biotin radionuclide therapy in breast cancer. We have developed IART[®] the *Intra-operative Avidination for Radionuclide Therapy* that relies on the avidin-biotin binding system. In fact, the “avidination” of the anatomical area of the tumor with native avidin, directly injected by the surgeon into and around the tumor bed, provides a target for the radiolabeled biotin intravenously (iv) injected one day later.

Ten patients with early breast cancer were enrolled in a phase I trial specifically designed to study dosimetry and biodistribution of ^{90}Y -DOTA-biotin in target and non-target organs through simulation studies based on ^{111}In -DOTA-biotin. Biokinetic studies were based on measured radioactivity in timed blood samples, 48-h urine collection and through scintigraphic images. The ^{111}In -DOTA-biotin simulation studies to predict dosimetry with ^{90}Y -DOTA-biotin showed that the mean absorbed dose in non-target organs was below 0.15 Gy/GBq, with the exception of kidneys and urinary bladder, where the doses \pm standard deviation (SD) were 1.20 ± 0.42 and 1.39 ± 0.10 Gy/GBq, respectively.

Interestingly, such absorbed dose reached 5.5 Gy/GBq – 50% ISOROI and 4.8 Gy/GBq - 30% ISOROI in the target area. Images showed early and long-lasting radioactive biotin uptake in the operated breast. Rapid blood clearance and urine excretion were observed.

The preliminary results from this study suggested that IART[®] is a simple and feasible procedure that may be combined to a reduced whole-breast external beam radiation therapy (EBRT) in a patient-tailored accelerated irradiation after breast conservative surgery.

However, it is crucial the determination of the dose distribution in the breast gland in order to predict the complementary dose by EBRT.

Rhenium-188 which decays by emission of high-energy beta particles ($E_{\text{max}} = 2.11$ MeV) similar to those of ^{90}Y , accompanied also by imageable 155 keV gamma

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photons (15.88% abundance) seems to possess the ideal characteristics to perform therapy and dosimetry at the same time.

The biotin molecule has been derivatised by adding a chain of amino acids containing two adjacent cysteines. The approach, developed by the University of Ferrara (Italy), consisting of the initial formation of a nitrido complex by reduction of perrhenate in presence of N^{3-} followed by the addition of a phosphine and the cys-cys biotin derivative has been proposed.

The initial experiments have been carried out using ^{99m}Tc instead of ^{188}Re .

Labeling yields higher than 95% at a specific activity of approximately 400MBq/ μ mol have been achieved. Avidin binding studies showed that more than 98% of the new ^{99m}Tc -biotin derivative was bound to avidin at a 1:4 molar ratio. Labeling studies using generator produced ^{188}Re are in progress to evaluate the potential use of ^{188}Re -biotin in the IART[®] application.

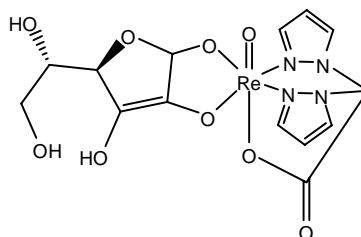
APPLICATIONS OF COMPLEXES OF RHENIUM AND TECHNETIUM WITH METAL-NITROGEN BONDS AS RADIOPHARMACEUTICALS

Jonathan Dilworth, Paul Donnelly, Maria Salichou and Xin Sun

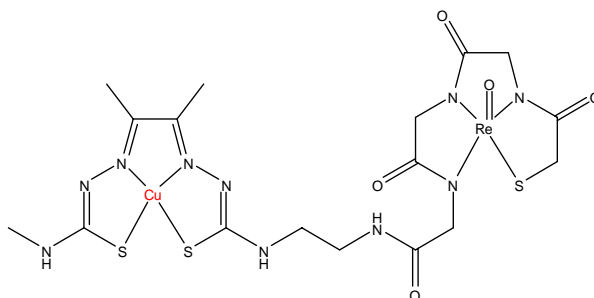
Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR. E-mail: jon.dilworth@chem.ox.ac.uk.

The ability of technetium and rhenium to form metal-nitrogen multiple bonds is unique among the elements with radioactive isotopes of use in diagnostic imaging and therapy. Multiply bonded nitrogen ligands provide an alternative approach to the provision of sites of attachment for biologically active molecules to direct the complexes to specific sites in vivo. Moreover such complexes can readily be synthesised from perrhenate and pertechnetate (the only available precursor for ^{99m}Tc and ^{188}Re complexes) by controlled reactions with hydrazines. This area of chemistry will be surveyed briefly and some recent developments presented.

Although PET and SPECT provide much valuable diagnostic information in vivo, their resolution is not sufficient to determine the intracellular fate of radiopharmaceuticals. We have therefore investigated several routes to the synthesis of Re and Tc complexes with intrinsically fluorescent ligands to enable the use of confocal or epifluorescence microscopy to determine their behaviour inside cells. The synthesis of some new polypyrazole complexes of Tc and Re directly from tetroxometallates is described (example shown above) together with their emission spectra. The use of these ligands with other metals such as gallium and indium with isotopes suitable for imaging or therapy will also be outlined.



There is much current interest in the development of PET and SPECT agents for the selective imaging of the hypoxic content of tumours. Copper(II) bis(thiosemicarbazone) complexes are known to be selective for hypoxic tissue, and the synthesis of conjugates of complexes of this type to Tc and Re complexes will be described (see figure above). These conjugates retain the hypoxic selectivity of the copper complex and the results of in vitro and in vivo biological studies will be presented together with their implication for the hitherto poorly understood mechanism of action of the copper complexes.



COMPREHENSIVE SEPARATION SYSTEM FOR SPENT-FUEL REPROCESSING BY ION EXCHANGE

Yasuhiko Fujii

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A concept of HCl ion exchange system is proposed as a comprehensive separation system for spent fuel reprocessing. In this process the nuclear spent fuels are dissolved in HCl solution with the aid of oxidation reagents. The major dissolved component of uranium in U(VI) form is easily adsorbed in anion exchange resin at the HCl concentration above 6M. Plutonium is also adsorbed in the resin at that concentration of HCl, while major fission products of Cs, Sr, Ba, lanthanides, are not adsorbed in the resin. Therefore uranium and plutonium can be easily separated from strongly radioactive nuclides. Another merit of this process is the weak adsorption of tri-valent minor actinides of Am and Cm. These ions are separated from lanthanides at highly concentrated HCl solutions.

The comprehensive separation is attained by several steps:

1. separation of Pd and Tc from other components by anion exchange resin,
2. separation of U, Pu from other fission products and minor actinides,
3. separation of minor actinides and lanthanides with highly concentrated HCl,
4. separation of some transition elements.

From the engineering view point, there are several interesting features in the present system. The small-particle ion exchange resin is used in the packed column like the liquid chromatography. The surface area of the packed resin is quite large and exchange rates are very fast. Due to this nature, the HETP, or a separation plate height, of ion exchange column becomes much smaller than that of solvent extraction. Therefore, the system is expected to be very compact. Different elements with small difference in the distribution coefficients can be successively separated by one column involving the large number of separation stages.

In addition chlorine has the nature of neutron absorption. Criticality consideration is much easier than in the case of solvent extraction using the nitric acid. Probably the most important aspect of the HCl solution system is chemical safety. HCl is not oxidizing reagent like HNO₃. There is no possibility of ion-exchange firing by using HCl solution.

However, serious concern is directed to the material safety or corrosion, when HCl is used in the industrial plants. Recently metals and alloys have been developed as the strong materials against HCl solutions. Since these special materials are available in highly industrialized countries and the fabrication of these materials are quite difficult, the international safeguards system is easily applicable to the present process. This fact would meet the policy of non-proliferation.

RECENT ADVANCES IN TECHNETIUM ENVIRONMENTALLY FOCUSED STUDIES

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An exceptional issue of “Technetium in the environment” in 1986 although made of independent parts was a complete presentation of all the pre-Chernobyl ideas and results [1]. 13 years later an excellent review of NEA-TDB summed up the chemical thermodynamics of Tc [2]. Time passed being characterized with the controversy of nuclear industry present and future status, drastic for Tc-99 originating mostly as the uranium fission product. The definite stop in nuclear development would fix the further accumulation but now is clearly not the case and we appreciate the authors were continuing efforts in Tc environmentally focused sciences. Several main directions could be drawn out: firstly those dealing with already accumulated Tc [3-5], then, focused on the construction of the migration barriers at the depositories [6-9] and finally examining the Tc in vitrification. The understanding of Tc interaction with microbial extremophiles was importantly advanced [10-11]. The review is devoted to these and numerous other results of environmental importance.

1. “Technetium in the Environment” (Proc. CEC-RPP – SERE CEA Seminar - Cadarache, 1984), Eds.: G. Desmet and C. Myttenaere, Elsevier Publishers, L&N-Y. (1986).
2. Rard J.A., Rand M.H., Anderegg G., Wanner H., Chemical thermodynamic of technetium. Eds. Sandino Amalia M., Osthols E. NEA (1999) Elsevier Publ. Amsterdam.
3. K. Guerman, C. Delegard, A. Ananiev et al. Abstracts of 12-th Symp. on separations sciences and technology for energy applications. Gatlinburg, October 15-18, (2001).
4. Guerman K.E., Kosareva I.M., Peretroukhin V.F. et al. In: ICEM'95. V.1. Cross-cutting Issues and management of high-level waste and spent fuel. (Eds.: S.Slate, Feizollahi, C.Creer), NY, 1995, p. 713 - 722.
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6. V.F. Peretrukhin, Ph. Moisy, A.G. Maslennikov, C. Sergeant, K.E. Guerman et al. *Journ. chim. russe (J. de la Soc. de Chim. D.I.Mendeleiev)*, **51**, No 6, p. 11 (2007).
7. V.F. Peretroukhine, C. Sergeant, G. Deveset et al. *Radiochim.Acta.* **94**, p. 665(2006).
8. El-Waer S., German K., Peretrukhin V. J. *Radioanal. Nucl. Chem. Articles.*, **157**, p.3 (1992)
9. K.E. German, V.F. Peretrukhin, et al. In: "Technetium and Rhenium Chemistry and Nuclear Medicine 4, (Nicolini M., Bandoli G., Mazzi U.- Eds.) SGEEditoriali, (1994) p. 93.
10. N. A. Chernyh, S. N. Gavrilov, et al. *Appl. Microbiol. Biotechnol.* **76**, p. 467(2007).
11. Khijniak TV, Medvedeva-Lyalikova NN, Simonoff M. Reduction of pertechnetate by haloalkaliphilic strains of Halomonas. *FEMS Microbiol. Ecol.* **44**:109–115(2003)

Technetium in the third world setting; R&D in South Africa

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⁴ Intervet Pty. Ltd and Onderstepoort Faculty of Veterinary Sciences, University of Pretoria, South Africa

⁵ School of Chemistry, University of KwaZulu -Natal, Pietermaritzburg, South Africa

⁶ Nuclear Medicine, Stellenbosch University and Tygerberg Hospital, South Africa

R&D on diagnostic radiopharmaceuticals in the developed world mainly focuses on PET (predominantly F-18 and C-11) while SPECT remains a routine procedure. The first ¹⁸F-FDG scan in South Africa only took place in January 2006 mainly due to the cost of infrastructure associated with PET. Although there are 9 PET-CT and 3 PET cameras currently in the country, Tc-99m remains the radionuclide of choice for diagnostic procedures as it is widely available (through the Mo-99/Tc-99m generator) and has a variety of procedural options via kits. In the third world it is anticipated that Tc-99m will maintain its market share predominantly due to the cost of PET scans as well as the distances between major sentra.

As a major producer of Mo-99, Necsa/NTP has a small but active research programme aimed at bringing Tc-99m radiopharmaceuticals for the third world to light. The current projects at Necsa/NTP with regards to Tc and Re will be discussed.

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Rhenium(V)-mediated Syntheses and Structures of Oxypyridinium-Ammonium Zwitterions

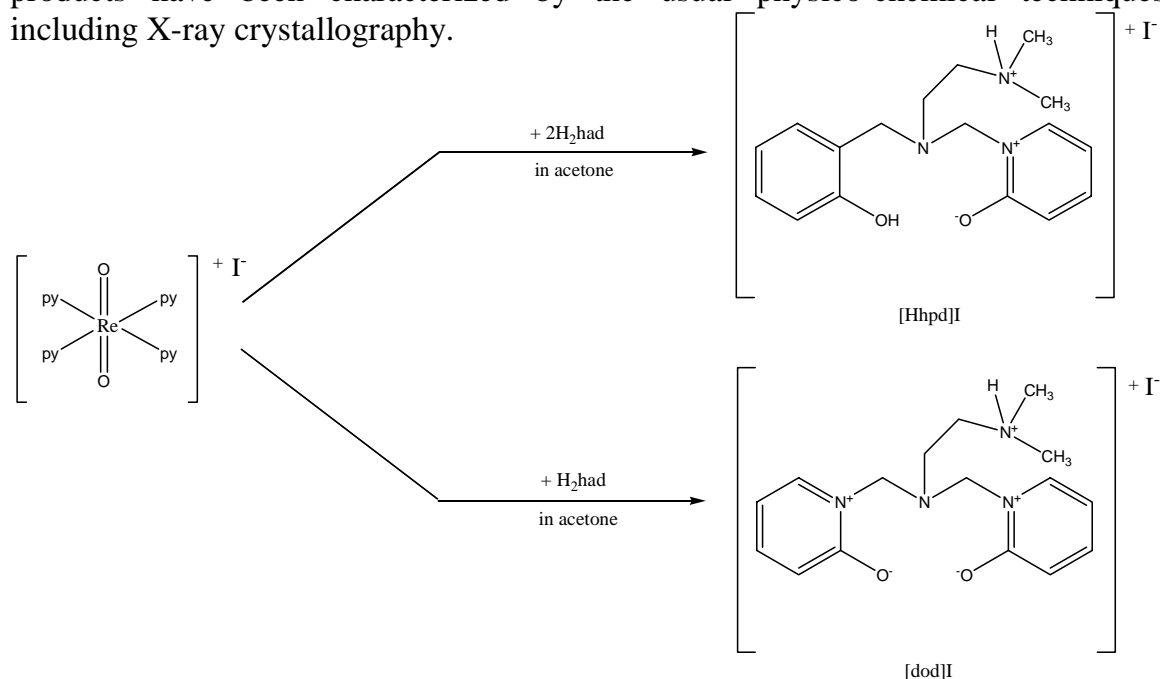
Abubak'r Abrahams^a, Thomas I.A. Gerber^a, Peter Mayer^b and Nonzaliseko C. Yumata^a

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Zwitterions are ions that are electrically neutral overall but contain nonadjacent regions of positive and negative charges. The best-known examples of zwitterions are the free amino acids found in cells. These ions have wide use in industry with applications ranging from detergents, to implants, and to the oil industry¹. Medicinally it is utilized in antihistamines (eg Fexofenadine) and ophthalmology².

The reaction of *trans*-[ReO₂(py)₄]I with *N,N*-bis(2-hydroxybenzyl)-2-(2-aminoethyl)dimethylamine (H₂had) has been studied. Variation in the reaction conditions resulted in the discovery of two new types of oxypyridinium-ammonium zwitterions having the structures depicted in Scheme 1. These reactions are unusual as the metal remains uncoordinated and only acts as a source of pyridines. The products have been characterized by the usual physico-chemical techniques including X-ray crystallography.



Scheme 1: Structures of the Zwitter ions [Hhpd]⁺ and [dod]⁺

1. Brunel *et al*, US Patent #4704229
2. Grace Y. N. Chan, Tim C. Hughes, Keith M. McLean, Gail A. McFarland, Xuan Nguyen, John S. Wilkie, Graham Johnson, *Biomaterials* **27**, 1287 (2006)

IMIDO, AMIDO AND AMINO COMPLEXES OF Re(V) WITH MULTIDENTATE AROMATIC AMINES

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Due to the potential applications in radiotherapy, there is currently considerable interest in the coordination chemistry of rhenium (V), which is dominated by neutral monooxo complexes. This has resulted in the restriction of the variety of rhenium therapeutic agents for cancer treatment. Thus, the further development of new potential therapeutic agents will largely depend on the discovery of new stable rhenium (V) moieties.

Here we report the synthesis of the oxofree rhenium(V) complexes, *trans*-[Re(dab)Cl₃(PPh₃)₂] (H₂dab=1,2-diaminobenzene) and [Re(L₃)₂](ReO₄) (H₂L₃=N-(2-aminobenzylidene) benzene-1,2-diamide).^{1,2} The reaction of equimolar quantities of *cis*-[ReO₂I(PPh₃)₂] with 5,6-diamino-1,3-dimethyluracil (H₂ddd) in acetonitrile led to the formation of [Re(ddd)(Hddd)I(PPh₃)₂](ReO₄) where ddd is coordinated monodentately through the doubly deprotonated amino nitrogen, and the chelate Hddd is coordinated bidentately via the neutral amino nitrogen and the deprotonated amino nitrogen.³ The complex salt *trans*-[Re(mps)Cl(PPh₃)₂](ReO₄)(H₃mps=N-(2-amino-3-methylphenyl)salicylideneimine) was prepared by the reaction of *trans*-[ReOCl₃(PPh₃)₂] with a twofold molar excess of H₃mps.⁴ The six-coordinated complex *cis*-[Re(mps)Cl₂(PPh₃)₂] was prepared by the reaction of *trans*-[ReOCl₃(PPh₃)₂] with a twofold molar excess of H₃mps in benzene.⁵ In both cases mps is the first example of a tridentate ligand with an imido donor atom.

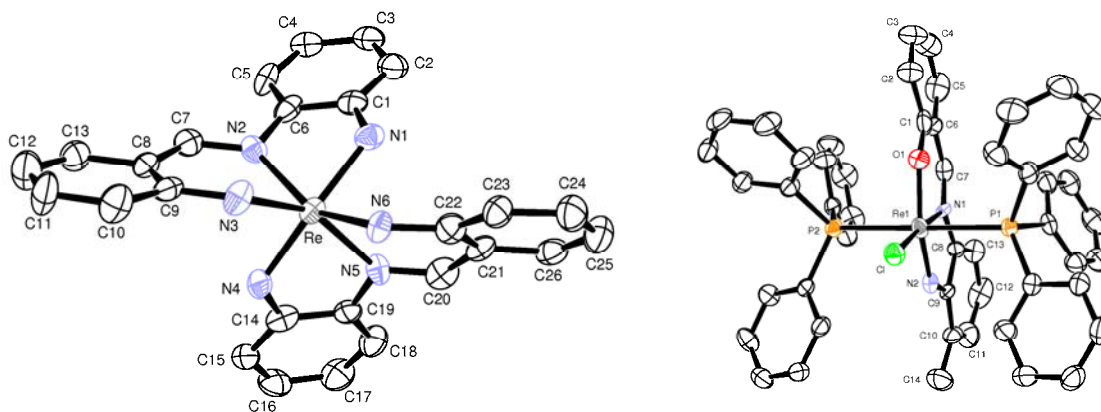


Figure 1: ORTEP plots of [Re(L₃)₂](ReO₄) and *trans*-[Re(mps)Cl(PPh₃)₂](ReO₄).

1. Booysen, T. Gerber, E. Hosten, P. Mayer, *Journal of Coordination Chemistry* **60**, 1749 (2007)
2. Booysen, T. Gerber, E. Hosten, P. Mayer, *Inorganic Chemistry Communications* **11**, 33 (2008)
3. Booysen, T. Gerber, E. Hosten, P. Mayer, H. Schalekamp, *J. Coord. Chem.* **60**, 1755 (2007)
4. Booysen, T. Gerber, E. Hosten, D. Luzipo, P. Mayer, *J. Coord. Chem.* **60**, 635 (2007)
5. Booysen, T. Gerber, E. Hosten, P. Mayer, Z. Tshentu, *J. Coord. Chem.* **60**, 1771 (2007)

Technetium interaction with natural organic matter: complexation versus colloid/colloid association

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The redox-sensitive fission product technetium-99 (Tc) is of great interest in nuclear waste disposal studies because of its potential for contaminating the geosphere due to its very long half-life (2.13×10^5 year) and high mobility under oxidising conditions, where technetium forms pertechnetate (TcO_4^-). Under suitable reducing conditions, e.g. in the presence of an iron(II) containing solid phase which can act as an electron donor, the solubility can be limited by the reduction of pertechnetate followed by the formation of a surface precipitate.¹ However, by association with mobile humic substances (HS) or other associating/complexing species, the solubility of reduced Tc species may be drastically enhanced.²

Detailed multiple scattering analysis of EXAFS data of Tc(IV)/pyrogallol solutions based on DFT modeled reference structures has demonstrated the existence of a stable Tc-pyrogallol complex which is readily formed at pH 11 and remains stable towards technetium colloid or precipitate formation both as function of pH and time in the pH range between 11 and 4.³ The occurrence of stable, readily formed Tc-complexes with pyrogallol, a humic substance model compound, is a strong indication for the existence of similar complexes in natural systems containing dissolved organic matter. The formation of such complexes indicates an extra potential for migration of Tc(IV) in systems containing natural organic matter, in addition to the previously discovered Tc(IV) eigencolloids stabilized by dissolved HS through colloid-colloid interactions.²

The formation of stable Tc(IV)-NOM complexes was investigated as function of pH using dissolved Boom Clay organic matter. Pertechnetate was pre-reduced in supernatant solutions containing natural BC organic matter at different pH. After the pre-reduction and re-setting of the supernatant pH to pH 8.2, the predominant pH in the Boom Clay system, the supernatant solutions were contacted with the Boom Clay solid phases. Comparison of these systems with reference Boom Clay batch systems allows to evaluate the competition between the sorption of technetium on the BC solid phase and the formation of stable Tc(IV)-BC organic matter complexes and Tc(IV)-BC organic matter colloid/colloid associations.

¹Cui, D. Q. and T. E. Eriksen (1996). "Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material." *ES&T* 30(7): 2263-2269.

²Maes, A., K. Geraedts, C. Bruggeman, J. Vancluysen, A. Roßberg and H. Hennig (2004). "Evidence for the Formation of Technetium Colloids in Humic Substances by X-Ray Absorption Spectroscopy." *ES&T* 38(7): 2044-2051.

³Breynaert, E., Maes, A. (2007). Structure elucidation of Tc(IV) Pyrogallol Complexes. Migration Conference, Munich, Oral Presentation

Separation Uranium/Technetium for the UREX Process. Synthesis of Tc-Zr Waste Form

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The US Global Nuclear Energy Partnership Separations Program has proposed a suite of aqueous-based solvent extraction processes (UREX+) to separate used light water reactor fuel into actinide materials for recycle and fission product components for preparation of efficient disposal forms. Uranium and technetium are extracted from the dissolved fuel during the first step (UREX segment); then, technetium is removed from the U/Tc product by an ion exchange process. The main goal of the work described here is to recover the ⁹⁹Tc and convert it into a final disposable waste form. An alloy of Tc with a portion of the metallic zirconium from the cladding hulls is a potential waste form for immobilizing the Tc. Alloying metallic Tc with zirconium has potential advantages in terms of adding no additional materials to make the waste form and the potential to include a high loading of Tc in the waste form. However, little thermodynamic and structural data in the binary metal system technetium–zirconium exist, and data on the synthesis of Tc-Zr alloys and on their potential performance under temporary or geological storage conditions is sparse. The research presented here deals with:

- Separation of uranium from technetium using an anionic exchange resin,
- Development of a process to recover technetium metal and uranium as U₃O₈, and
- Synthesis and characterization of Tc-Zr alloys.

Speciation of Tc, effect of Eh-pH

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Coprecipitation Of radionuclides with secondary phase is currently neglected in safety assessments for radioactive waste repository, although this process is thought to be important in limiting radionuclide solution concentration. The aim of this work is to study the coprecipitation of technetium-99 with siderite as host phase. The coprecipitation has been studied as function of Tc/Fe initial concentration ratio.

A method of coprecipitation has been developed under reducing and anoxic conditions. The study of pure phases shows the formation of crystalline siderite phase whose crystallites size decrease with the precipitation rate. Concerning the pure carbonate of technetium (IV), the soluble complexes stoichiometry is $\text{TcCO}_3(\text{OH})_3^-$.

Solution analyses (liquid scintillation counting) combined with solid phase characterization (XRD, TEM, IR spectroscopy and Mossbauer spectroscopy) show the existence of two phases in the case of a low technetium concentration into solid (from 1 to 2 %). The first one is carbonate green rust and the second is composed of technetium incorporated with siderite structure. In the case of high technetium concentration into the solid, it coprecipitates with a phase assimilated to green rust.

STABILISATION OF Tc(V) IONS IN NITRIC ACID AND HYDRAZINIUM NITRATE MEDIA IN PRESENCE OF Th(IV)

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Two technetium valence states (VII and IV) are commonly considered to be rather stable under the conditions of spent nuclear fuel reprocessing the first one being responsible for Tc co-extraction with actinides while the second is formed under reducing conditions of U/Pu separation. Many of the intermediate species responsible for catalytic cycles rest invisible and are just postulated. Here we present a new approach for the stabilization and the studies of Tc(V) ions in nitric acid and hydrazinium nitrate media in presence of Th(IV) as $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

The experimental procedures of this work involved conventional spectrophotometric methods for the kinetic measurements of Tc in the solution. $C_0(\text{Tc})$ varied as $(0.4 - 1.52) \cdot 10^{-3}$ mol/l and $C(\text{Th})$ as $(0 - 6.32) \cdot 10^{-3}$ mol/l. The initial concentration of 0.255 M $\text{N}_2\text{H}_5\text{NO}_3$ was used in all the experiments. The temperature was 55 °C and 60°C in two different sets. Tc(V) was controlled according to the development of the peak at 470 nm, Tc(IV) was measured by the shoulder at the 400 nm. The reactions were carried out in thermostatic quartz cells. A typical sequence of spectral changes in one experiment is given in Fig.1 a-c. On addition of hydrazine to Tc(VII)+Th(IV) solution in nitric acid the reaction first proceeds as a Tc(VII) reduction to Tc(IV) thus developing the shoulder at 400 nm and following the zero order kinetics (Fig.1a), initiating the hydrazine decomposition with gas evolution. Then, the decomposition of Tc(IV) takes place in similar zero order kinetics (Fig.1b) with formation of unidentified TcX species, then finally forming Tc(V)-Th(IV) complex characterized with a peak at 470 - 473 nm in first order kinetics (Fig.1c), the later being stable for several days at 55 °C.

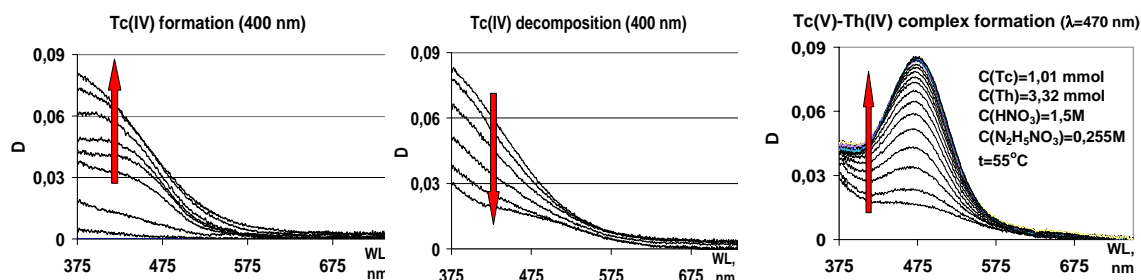


Fig.1. Reduction of Tc with hydrazine in presence of Th in 1.5 M nitric acid
Time : a) 0-26 min, b) 29-47 min, c) 48-105 min

A complete reversibility of the reaction sequence $\text{Tc(V)-Th(IV) complex} \rightarrow \text{TcX} \rightarrow \text{Tc(IV)}$ was observed after adding the hydrazinium nitrate to the Tc(V) solution at 105 min. The efforts in the determination of the Tc(V)Th(IV) complex composition are still in progress.

SYNTHESIS AND MAGNETO-STRUCTURAL STUDIES OF Re(IV) MONONUCLEAR COMPLEXES

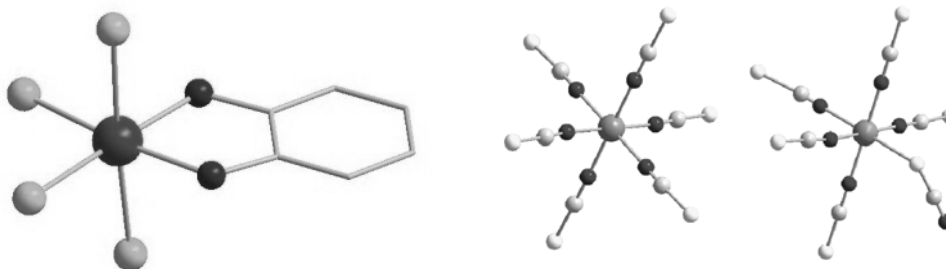
Carlos Kremer, Alicia Cuevas, Ricardo González, Raúl Chiozzone, Juan Faus

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Re(IV) complexes are relatively scarce in comparison to those containing other oxidation states. The lack of a general preparation procedure and the easy oxidation and hydrolysis of Re(IV) complexes are the main drawbacks when designing novel compounds. However, the preparation and structural characterization of stable Re(IV) mononuclear complexes have been increased in the last years. This is due to the use of these compounds as ligands towards coordinative unsaturated preformed complexes including first-row transition metal ions. The isolation of polynuclear compounds allowed the study of the magnetic interactions between *3d* and *5d* spin carriers.

In this communication, the ligand substitution reaction on the easily available anions $[\text{ReX}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) either in *n*-propanol or in DMF is revised. This synthetic route is used to prepare and characterize by X-ray diffraction the complexes $[\text{ReCl}_4(\text{cat})]^{2-}$ (cat = catechol), $[\text{Re}(\text{NCS})_6]^{2-}$ and $[\text{Re}(\text{NCS})_5(\text{SCN})]^{2-}$.



We also report the magnetic properties of the novel compounds. The influence of the zero field splitting and the magnetic interactions through the space on the magnetic behaviour are discussed and compared to other mononuclear Re(IV) compounds prepared by our group: $[\text{ReCl}_4(\text{ox})]$ and $[\text{ReCl}_4(\text{mal})]$.

This work was partially supported by DICYT (Uruguay), project PDT 63/337.

A new method for Technetium speciation and quantification in humic rich natural groundwater: determination of the Tc-colloid/HS-colloid conditional interaction constant

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A new and quick method for direct speciation of Tc in humic rich solutions, based on the induced aggregation of humic substances in the presence of the trivalent cation La^{3+} , is presented. This method (the “ La^{3+} -precipitation method”) allows flocculating all the humic substances and also the Tc associated with humic substances.

The method is tested on solutions containing Tc and Gorleben humic substances. The influence of different parameters (humic substance concentration, Tc concentration, reaction time and pH) is investigated on the observed free Tc concentration after precipitation of all humic substances. None of these parameters had a (significant) influence on the observed Tc concentration in solution after addition of La^{3+} to Tc-HS containing solutions. It is therefore proposed that the method can be used to separate the Tc bound to humic substances from the free inorganic Tc species in solution.

The interaction between colloidal Tc(IV) species and colloidal Gorleben humic substances was quantified after application of the La-precipitation method on supernatant solutions formed under various experimental conditions but at constant ionic strength of the Gorleben groundwater (0.04 mol L^{-1}). The determined interaction constant K^{HS} (2.3 ± 0.3) remained unchanged over a large range of Tc(IV) and HS concentrations and was independent of the pH of the original supernatant solution (pH range 6 – 10), Tc(IV)-HS loading ($10^{-3} - 10^{-6} \text{ mol Tc g}^{-1} \text{ HS}$) and the nature of the reducing surface (Magnetite, Pyrite and Gorleben sand) used for the pertechnetate reduction.

The results were compared with results obtained from a previous study¹ where the interaction between colloidal Tc(IV) species and Gorleben humic substances was quantified using a modified Schubert approach.

¹K. Geraedts, Maes, A. (2008). "Determination of the conditional interaction constant between colloidal technetium(IV) and Gorleben humic substances. Applied Geochemistry 23: 1127-1139.

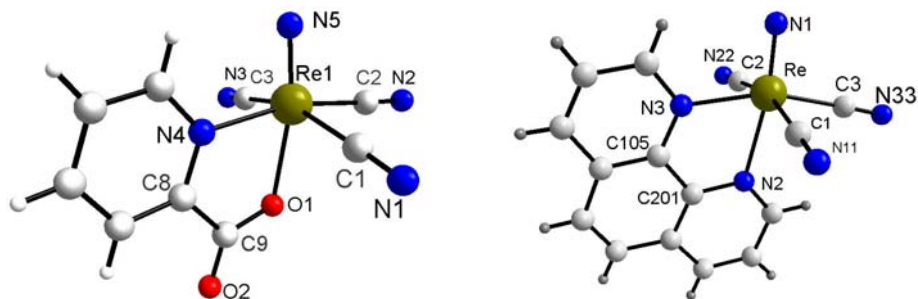
RHENIUM(V)-NITRIDO COMPLEXES WITH BIDENTATE N,O- AND N,N-DONOR ATOMS: $[\text{ReN}(\kappa^2\text{-LL})(\text{CN})_3]^{2-}$

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In-depth studies have shown that the iso-electronic $[\text{MX}(\text{H}_2\text{O})(\text{CN})_4]^{n-}$ complexes ($\text{M} = \text{Re}(\text{V}), \text{Tc}(\text{V}), \text{Mo}(\text{IV}), \text{W}(\text{IV}); \text{X} = \text{O}^{2-} \text{ or } \text{N}^{3-}$) are all labile towards monodentate ligand substitution. The rate of substitution depends on the pH of the solution, the type of terminal ligand and to lesser extent the type of incoming group. A major difference between the chemistry of $[\text{MX}(\text{H}_2\text{O})(\text{CN})_4]^{n-}$ ($\text{M} = \text{Mo}(\text{IV})$ and $\text{W}(\text{IV})$) and that of $[\text{ReO}(\text{H}_2\text{O})(\text{CN})_4]^{n-}$ is the ability of the former to react with bidentate ligands, substituting an aqua and a cyanide ligand to form the corresponding $[\text{MX}(\kappa^2\text{-LL})(\text{CN})_3]^{n-}$ ($\text{LL} =$ bidentate ligands).

The kinetic and structural determination has shown that by changing the "terminal" ligand from an oxo to a nitrido group in these iso-electronic $\text{Re}(\text{V})$ tetracyano complexes has an enormous influence on a number of their physical and chemical properties: the Re-OH_2 bond length as well as the pK_a -values increases from $2.142(7)\text{\AA}$ ($\text{pK}_a = 1.4$) for $[\text{ReO}(\text{H}_2\text{O})(\text{CN})_4]^-$ to $2.496(7)\text{\AA}$ ($\text{pK}_a = 11.7$) for $[\text{ReN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$. This substantial increase in pK_a -values prompted the research for the isolation and the kinetic study of the possible reactions between $\text{Re}(\text{V})$ -nitrido complex with different bidentate ligands. Here we will report the crystal structures and kinetic of the formation of the $[\text{ReN}(\kappa^2\text{-LL})(\text{CN})_3]^{2-}$ ions. Our research shows that incoming bidentate ligands coordinate to the metal center with the substitution of aqua and cyanide ligand from the coordinated sphere $[\text{ReN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ to form the corresponding $[\text{ReN}(\kappa^2\text{-LL})(\text{CN})_3]^{2-}$ complexes, and that the formation of these complexes undergo a two-stepwise reaction process with the aqua ligand substituted in the first fast reaction followed by a second slow chelate ring-closure step with the substitution of the cyanide ligand [1].



[1]. T. N. Mtshali, W. Purcell, H.G. Visser and S.S. Basson, *Polyhedron*, 25, 2415 (2006) and references therein.

SEPARATION AND UTILIZATION OF TECHNETIUM AND NUCLEAR RARE METALS

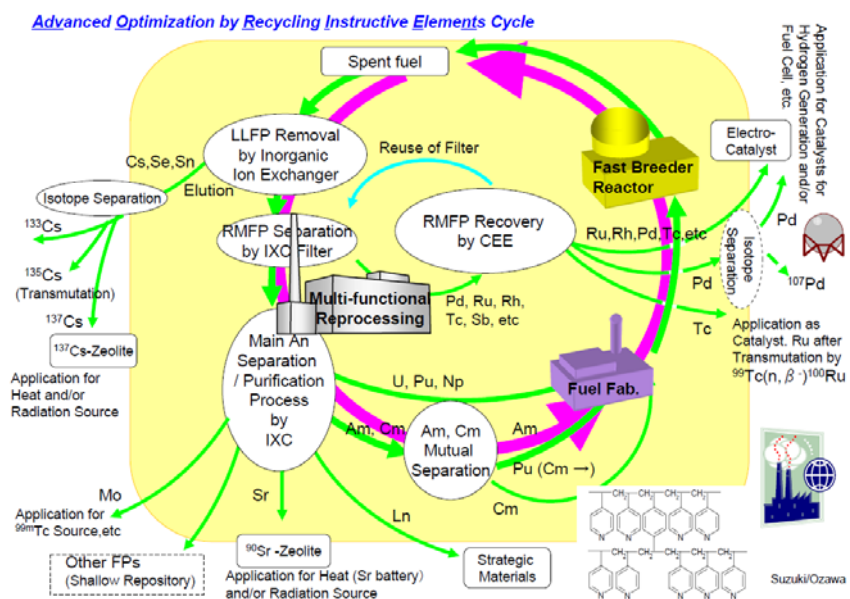
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A Trinitarian R&D strategy on separation, transmutation and utilization of nuclides in the nuclear spent fuel has been actualized as *Adv.-ORIENT Cycle* project, where separation and utilization of nuclear rare metal is the key strategy, based on the main, direct and deep separation of all of actinides till to pure Am and Cm products by tertiary pyridine resin chromatography. FP Pd is very low radio toxic reflecting high BSS value 10^5 Bq/g of ^{107}Pd , despite of its long-lived β^- radioactive. Very short-lived FP Ru and Rh will be used as an ordinary resource after each 40 and 80 years stockpiled. According to hypothetical estimation, nuclear fuel cycle in 2070 can satisfy almost 100%, 40% and 10% of Ru, Rh and Pd, respectively of Japan's domestic demands in 2006.

By catalytic electrolytic extraction (CEE) method, sufficiently high separation ratios as $>99\%$ for Pd, Ru, Rh, Tc and $>90\%$ for Re were achieved in a 0.5M HCl solution, where $\text{Pd}^{2+}/\text{Pd}_{\text{adatom}}$ acted for acceleration of the deposition of Ru. $\text{Rh}^{3+}/\text{Rh}_{\text{adatom}}$ also accelerated the deposition of Ru, Tc and Re. In the application to electrolytic hydrogen production, a mixture, especially quaternary (Ru-Rh-Pd-Re) deposit electrode, having the highest number of proton absorption site, showed the highest catalytic reactivity in either 1M NaOH or artificial sea water. Ru will be a dominant element for the reactivity, while Pd will role-play just crystal nucleus and combinative function during the mixture deposition. In both Pd-Rh and Re-Rh deposit electrodes, increases of Rh atom ratios at the electrode surface will increase the reactivity, but not in the case of Ru-Rh system.

In their combination with Rh, Tc was easily deposited than Re in hydrochloric media, and showed superior catalytic reactivity to smooth Pt as well as Re in an alkali solution.



Electro-Dissolution of Metallic Technetium in Acidic Media

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The isotope ^{99}Tc is a problematic fission product due to its high fission yield, long half-life, and complex solution chemistry. In the proposed UREX process, ^{99}Tc is separated from other elements, converted to the metal, and included in a waste form. Waste forms containing Tc metal are convenient for disposal or eventual transmutation into stable ^{100}Ru . However, little data on the behavior of Tc metal in aqueous media exist. In order to better understand its corrosion mechanisms, a Tc metal electrode was constructed. The electro-dissolution of Tc metal was studied in nitric and hydrochloride acid (0.1 M, 1 M, 2M and 6M) for potential between 500 mV and 1300 mV/ Ag/AgCl. Corrosion rates and dissolution potential were determined, the corrosion products were characterized by UV-Visible spectroscopy in solution and SEM and TEM on the electrode surface. Using the results previously obtained, the stability of Tc metal in acidic media is discussed and compared with other transition metals (Mo, Ru and Re), and also a corrosion mechanism is proposed.

A STRUCTURAL AND KINETIC COMPARISON BETWEEN [ReO(H₂O)(CN)₄]⁻ and [ReN(H₂O)(CN)₄]²⁻

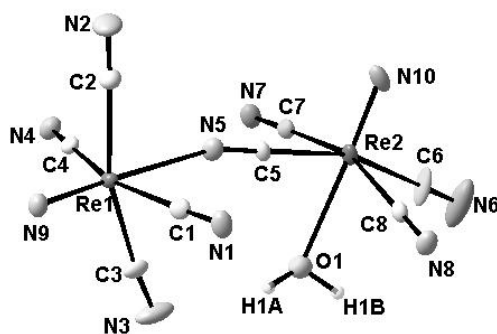
Walter Purcell, Thato.N Mtshali and Hendrik G. Visser

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The subtle change of the "terminal" ligand from an oxo to a nitrido group in these iso-electronic Re(V) tetracyano complexes has an enormous influence on a number of their physical and chemical properties.

Structural studies indicated an increase in the Re-OH₂ bond length from 2.142(7) Å for [ReO(H₂O)(CN)₄]⁻ to 2.496(7) Å for [ReN(H₂O)(CN)₄]²⁻. This change in bond strength not only leads to different kinetic behaviour but also to different bonding behaviour of the aqua complexes. The monodentate kinetic results obtained from these two systems indicate a 10⁶ fold increase in aqua substitution for the nitrido complex compared to the oxo complex, while no bidentate ligand substitution reactions was observed for the oxo complex, possibly due to the low pK_{a1} value of 1.4. The increase in pK_{a1}-value for the nitrido complex (11.7) also results in more complicated substitution mechanisms.

Structural studies indicated successive deprotonation reactions for the oxo complex while absent for the nitrido complex. On the other hand, a number of different nitrido aqua complexes were structurally characterized, while only one for the oxo complex was isolated. One of these nitrido aqua complexes includes the novel cyano-bridged [ReN(H₂O)(CN)₃-(μ₂-CN)-ReN(CN)₄]⁴⁻ [1].



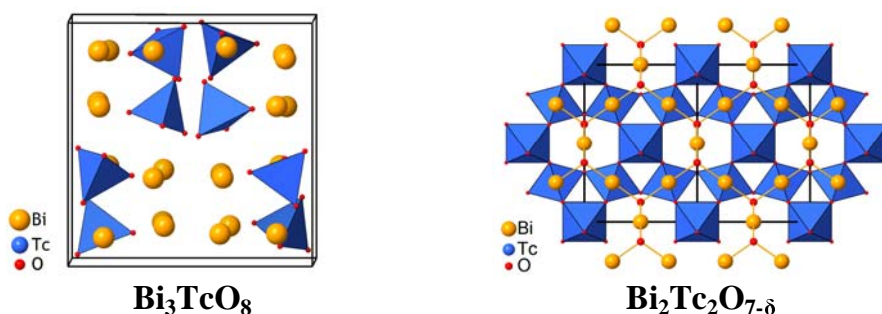
[1]. T. N. Mtshali, W. Purcell, H.G. Visser and S.S. Basson, *Transition Met. Chem.*, Accepted April, (2008)

Technetium Oxides: New Materials, New Insights

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Although its radioactivity limits its applications, Tc-99 could form inorganic materials with interesting chemical and physical properties. In addition, studies of ternary Tc oxides have not been undertaken in over 35 years. This area of the periodic table should not go ignored since phenomena such as superconductivity and strongly competing electronic states have been observed in structurally related ruthenium (4d metal) and rhenium (5d metal) oxides. We recently reported the crystal structure and electronic properties of TcO_2 ,¹ and now we present new phases in the never before studied Bi-Tc-O system² as well as recently prepared compounds from the Sr-Tc-O, Pb-Tc-O, and Cd-Tc-O ternary systems. The new oxides have been characterized by neutron and X-ray powder diffraction and X-ray absorption near-edge structure (XANES) spectroscopy. First-principles calculations have also been performed to gain insight into their electronic structures. In addition, magnetic susceptibility measurements have been performed to characterize their magnetic and transport behavior. Overall, our aim is to have a deeper understanding of the solid state chemistry of this fascinating metal and to make further contributions to the growing field of 4d transition metal oxides.



1.) E. E. Rodriguez, F. Poineau, A. Llobet, A. P. Sattelberger, J. Bhattacharjee, U. V. Waghmare, T. Hartmann, and A. K. Cheetham, *J. Am. Chem. Soc.*, **129** 10244—10248 (2007).

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Synthesis and Characterization of Multiply Metal-Metal Bonded Technetium Dimers

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The technetium(III) dimers $(n\text{-Bu}_4\text{N})_2\text{Tc}_2\text{X}_8$ and $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) were synthesized and studied by X-ray Absorption Fine Structure spectroscopy (XAFS). XAFS analysis gave for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$: $d \text{Tc-Tc} = 2.18(1) \text{ \AA}$, $d \text{Tc-Cl} = 2.43(1) \text{ \AA}$ and for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_2$: $d \text{Tc-Tc} = 2.19(1) \text{ \AA}$, $d \text{Tc-Br} = 2.63(1) \text{ \AA}$. The Tc-Tc separations are in agreement with previous Raman studies, while the Tc-X distances are somewhat longer. Reactions of $(n\text{-Bu}_4\text{N})_2\text{Tc}_2\text{X}_8$ with trimethylphosphine (PMe_3) were performed in dichloromethane; the new compounds $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X} = \text{Cl}, \text{Br}$) were isolated, and characterized by single crystal X-ray diffraction and UV-Visible spectroscopy. The metal-metal distances ($\text{Tc-Tc} = 2.1317(1) \text{ \AA}$ for $\text{X} = \text{Cl}$ and $\text{Tc-Tc} = 2.1315(2) \text{ \AA}$ for $\text{X} = \text{Br}$) are in general agreement with previous studies on Tc(II) dimers. The UV-Visible spectra, recorded in benzene, exhibit a series of absorption bands between 460 nm and 760 nm for $\text{X} = \text{Br}$ and between 440 nm and 740 nm for $\text{X} = \text{Cl}$. By analogy with Re compounds, the low energy bands at 760 nm and 740 nm are assigned to $\delta^* \rightarrow \sigma^*$ transitions.

OXIDATIVE DISSOLUTION OF Tc(IV) OXIDE COLLOIDS INDUCED BY ULTRASOUND

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Redox reactions of Tc by sonolysis were studied to control oxidation states of Tc. Aqueous pertechnetate (Tc(VII)O_4^-) solutions and $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$ colloids solutions ($[\text{Tc}] = 0.1 \text{ mM}$) were sonicated (200 kHz, 200 W) in a glass cell with flat bottom under Ar or He atmosphere at 20°C. No reduction of TcO_4^- was observed in this study. However, we found that $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids dispersed in an aqueous solution were completely dissolved by ultrasonic treatment within 30 min under Ar atmosphere, and TcO_4^- was eventually produced. The formation of TcO_4^- was considerably suppressed in the presence of *t*-butyl alcohol (an effective scavenger of OH radicals), indicating that Tc(IV) was oxidized by OH radicals (produced by dissociation of water molecules) in hot cavitation bubbles created by ultrasound. The formation rate of TcO_4^- under He atmosphere was slower than that under Ar atmosphere. This can be attributed to a difference of the effective maximum temperature in the collapsing bubbles. Because thermal conductivity of He is much higher than Ar, thermal transport effectively occurs from the bubbles to the surrounding liquid. Thus, temperature of cavitation bubbles filled with He should be lower than those filled with Ar, resulting in the slower OH formation rate.

Table 1. Effect of noble gases on the formation rate of Tc(VII)O_4^- in $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$ colloids solutions and that of OH radicals in pure water by sonolysis.

Saturating gas	$\text{Tc}^{\text{VII}}\text{O}_4^-$ formation rate $\mu\text{M min}^{-1}$	OH formation rate $\mu\text{M min}^{-1}$
He	3.30	11.6
Ar	10.1	28.1

ADSORPTION BEHAVIOR OF TECHNETIUM ON TERTIARY PYRIDINE RESIN IN HYDROCHLORIC ACID SOLUTION

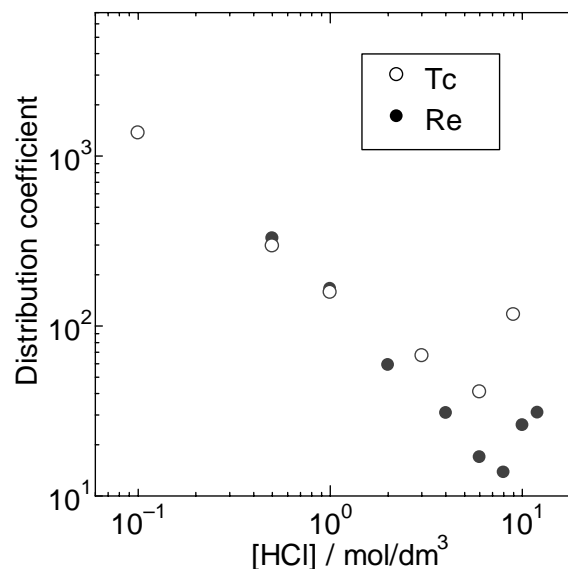
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Advanced nuclear fuel recycling system with nuclide separation has been proposed¹, which system was named “Adv.-ORIENT” (Advanced Optimization by Recycling Instructive Elements) cycle. This cycle is mainly based on the chromatographic technique used by tertiary pyridine resin in hydrochloric acid solution. The adsorption behaviors of several elements on tertiary pyridine resin and the separation phenomena were already investigated². Tc is generated by nuclear fission in nuclear reactors, and Tc-99 is long-lived radioisotope; life time is 2.11×10^5 y. We investigated the adsorption behavior of Tc on tertiary pyridine resin in hydrochloric acid solution. Distribution coefficients of technetium were determined by batch experiments. Adsorption behaviors of Tc and Re were compared. Distribution coefficients of Tc and Re are shown in figure. Technetium has a little larger distribution coefficient in higher concentration hydrochloric acid region than rhenium. However, the tendency of adsorption behavior of technetium and rhenium is similar. We concluded that the rhenium can be used as the substitute for technetium. Adsorption behaviors of platinum group elements were also investigated. The separation of technetium from platinum group elements was discussed.



Distribution coefficient of Tc(VII) and Re(VII) on tertiary pyridine resin in hydrochloric acid solution.

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METALLURGY OF RHENIUM

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Modern methods of rhenium extraction from ores and secondary raw materials as well as methods of metallic rhenium and its industrial goods producing are described in the monograph [1].

The book includes the next main section: introduction, chemical properties of rhenium and its application, rhenium sources, distribution of rhenium by processing of molybdenum and copper sulfide concentrates, methods of rhenium extraction from solution, technological fundamentals of rhenium production, producing of metallic rhenium and its alloys, fundamentals of analytical chemistry of rhenium, conclusion, references.

It gives a current picture of modern problems and developments in rhenium extractive metallurgy.

Great attention is given to the processes of extraction, which are predominated over other methods in rhenium hydrometallurgy. Rhenium solvent extraction and sorption processes in order of historical importance in the metallurgical industry are reviewed.

The concrete examples of technological sheets for rhenium extraction from different types of raw materials are demonstrated as well as its apparatus design.

Some parts of the monograph are devoted to rhenium nontraditional mineral sources and perspective fields of its application.

The book is intended for wide range of scientific and industrial workers, who are occupied with the questions of chemistry and metallurgy of rare metals, post-graduates and students of corresponding specialties.

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RHENIUM COMPLEXES OF PYRIDYLIMIDAZOLE DERIVATIVES

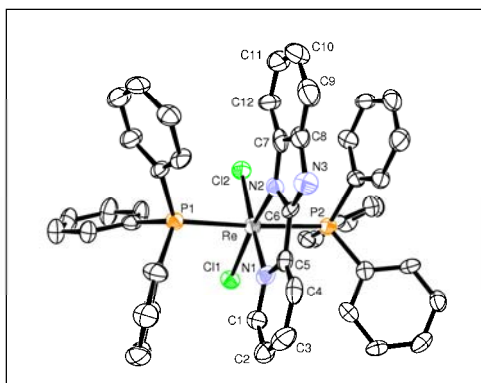
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The reactivity patterns of the bidentate ligands 2,2'-bipyridine (bpy) [1], 2,2'-biimidazole (biimH₂) [2, 3] and pyridylimidazoles with *trans*-[ReOCl₃(PPh₃)₂] differ quite drastically. With 2,2'-bipyridine, a neutral product [ReOCl₃(bpy)] was found, whereas for 2,2'-biimidazole that product was only isolated with the phosphine-free starting material [ReOCl₃(OPPh₃)(Me₂S)]. With *trans*-[ReOCl₃(PPh₃)₂] and excess PPh₃, the cationic Re(III) monomers of the type [ReX₂(PPh₃)₂(biimH₂)]X (X=Cl, Br and I) were isolated [3]. However, the reaction of the pyridylimidazoles with *trans*-[ReOCl₃(PPh₃)₂] did not lead to the expected neutral [ReOCl₃(NN)], as was found with 2,2'-bipyridine, but proceeded directly to the Re(III) monomers without any addition of a reducing phosphine [4,5]. The structure of one of the complexes with 2-(2'-pyridyl)benzimidazole as ligand is given below. The ligand was deprotonated and is bidentately coordinated as a pyridylbenzimidazolate in a neutral Re(III) complex.



Moreover, mononuclear Re(V) complexes of the type *mer*-[ReOCl₃(NN)] in which there is a possibility of some type of structural isomerization observed were only isolated using perrhenate as a starting material and one-equivalent of a reducing phosphine; and the dinuclear Re(V) complexes of the type [(μ -O){ReO(NN)Cl₂}₂] were also isolated using [ReOCl₃(NN)] or (*n*-Bu₄N)[ReOCl₄] as starting material.

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Rhenium(I) compounds in Nuclear Medicine. Crystallographic and kinetic investigation of different $[\text{Re}(\text{CO})_3(\text{L}_1)(\text{L}_2)]^{n-}$ complexes.

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Keywords: rhenium, bidentate ligands, X-ray crystallography

Technetium-99m ($^{99\text{m}}\text{Tc}$) is the radionuclide of choice in diagnostic nuclear medicine, partly because of its availability, favorable decay characteristics and cost. Limited ligands are known that are sufficient in stabilizing the $^{99\text{m}}\text{Tc}$ core in physiological conditions. Analogous Re and Tc complexes have very similar physical characteristics. The Rhenium analogues are harder to reduce, which is a great advantage since it provides an ultimate elimination route when oxidation occurs *in vivo* forming ReO_4^- .

The mixed ligand approach is a well known method to smooth-tune the ligand properties. The [3 + 1] mixed ligand approach [1] was introduced by Pietzsch and co-workers where a tridentate ligand links to the biomolecule and the monodentate coligand is varied or vice versa. [2] This approach have some problems which limits their application.[3]

Research have been done on other mixed ligand systems but are less convenient, like the hynic approach [4] and complexes with umbrella-like tetradentate NSSS ligands and monodentate isocyanides [5].

Alteration of the coligand shows different accumulation patterns in target cells. This emphasize the need to tune the chelators to achieve the optimal *in vivo* behavior.

A [2 + 1] mixed ligand concept was introduced recently, which allows the labeling of bioactive molecules containing a monodentate or a bidentate donor site [6].

With $[\text{Re}(\text{OH}_2)_3(\text{CO})_3]^+$ accepting many types of ligands, the possibility arises to design complexes with properties that's adapted to those of the biomolecule.

Rhenium(I) tricarbonyl complexes of the form $[\text{Re}(\text{L}_1)(\text{L}_2)(\text{CO})_3]^{n-}$ ($\text{L}_1 = \text{Br}, \text{H}_2\text{O}$; $\text{L}_2 =$ various N-O, and O-O ligands) have been prepared from $(\text{Et}_4\text{N})_2[\text{Re}(\text{CO})_3\text{Br}_3]$ as starting material.

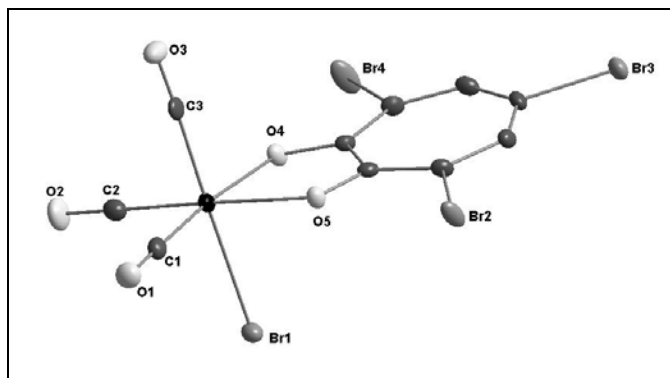


Fig 1: $\text{Re}(\text{CO})_3\text{BrTropBr}_3$

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SYNTHESIS AND REDOX PROPERTIES OF OCTAHEDRAL HEXATECHNETIUM(III) COMPLEXES WITH TERMINAL HALIDE

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The octahedral hexametal complex having $M_6(\mu_3-E)_8$ core (M = transition metal ion, E = chalcogenide, halide) has been studied extensively. The first chalcogenide bridged hexatechnetium complexes, Tc_6E_x (E = S, X = 12-14; E = Se, X = 12, 13) were synthesized by Bronger and colleagues.^{1,2} Here we report synthesis and characterization, and redox properties of sulfide or selenide capping hexatechnetium(III) complexes with terminal halide and hexatechnetium(III) telluride.

Molecular complexes $[Tc_6(\mu_3-S)_8X_6]^+$ (X = Br (**1**), X = I (**2**)) were prepared by the high temperature reaction of technetium metal, sulfur, and halogen with cesium halide. The polymeric complexes $Cs_2[Tc_6Se_8Br_4]$ (**3**) and $[Tc_6Se_8I_2]$ (**4**) were prepared by the similar reaction using selenium instead of sulfur. The hexatechnetium telluride $[Tc_6(\mu_3-Te)_8Te_7]$ (**5**) was afforded from the reaction of technetium metal and tellurium. The Tc–Tc distances, which are in the range of Tc–Tc single bond, increase with the ionic radius (S < Se < Te) of the face capping chalcogenide, while the Tc–Tc–Tc angles of all complexes are nearly 60 or 90°.

The redox potentials of **1** and **2** were measured in $Bu_4NPF_6-CH_3CN$ solution. The redox potential for the first one-electron oxidation process is more positive than that of the hexarhenium analog $[Re_6(\mu_3-S)_8X_6]^+$ (X = Br, I), while that of the second oxidation process shifts to negative. Thus, $Tc_6(III,III,III,III,III,IV)$ mixed valence state is thermodynamically less stable than $Re_6(III,III,III,III,III,IV)$.

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COORDINATION OF PERRHENATE AND PERTECHNETATE BY MACROCYCLIC RECEPTORS

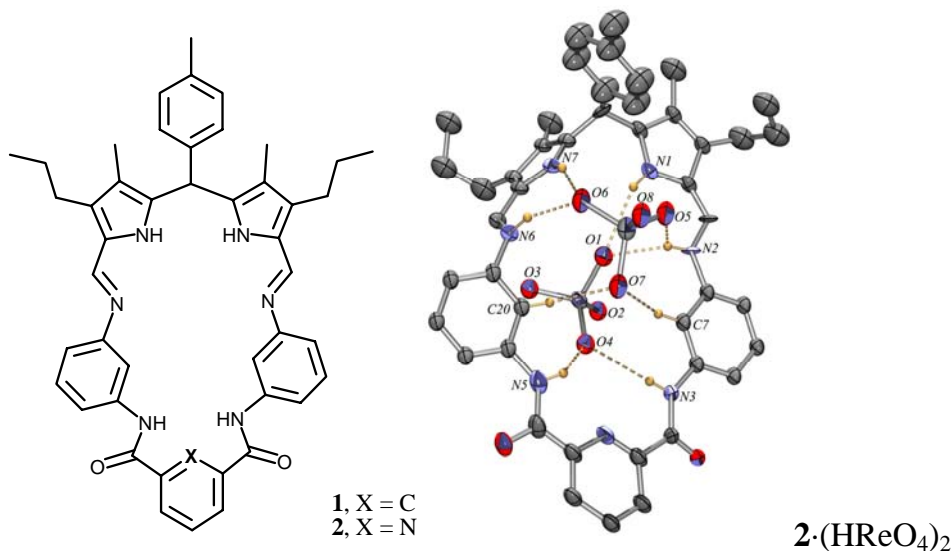
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The design of artificial receptors for anions is a continuing challenge to the supramolecular chemistry community. The development of ReO_4^- and TcO_4^- selective receptors is of particular interest due to their potential application as analytical sensors, selective extractants and technetium cores for nuclear medicine. Preliminary theoretical modeling of the perrhenate-ion first solvation sphere by water molecules has allowed us to propose binding motifs and their spatial orientation for the efficient complexation of TcO_4^- and ReO_4^- . The corresponding dialdehydes and diamines, containing proposed motifs were synthesized. The macrocyclic receptors **1-2** were prepared by the anion-templated Schiff base condensation. For the first time rhenic acid was shown to be an efficient template agent in the macrocyclization *via* imine bond formation.

The anion-binding properties of new receptors were measured using UV-Vis titration method in DMSO. Both receptors **1** and **2** showed very high affinity for TcO_4^- and ReO_4^- binding, stability constants are one of the largest known ($K_{\text{MO}_4} \approx 10^3\text{-}10^5 \text{ M}^{-1}$, $\text{M}=\text{Tc, Re}$). Receptors **1** and **2** have been shown to be selective towards TcO_4^- and ReO_4^- relative to other tetrahedral oxoanions.



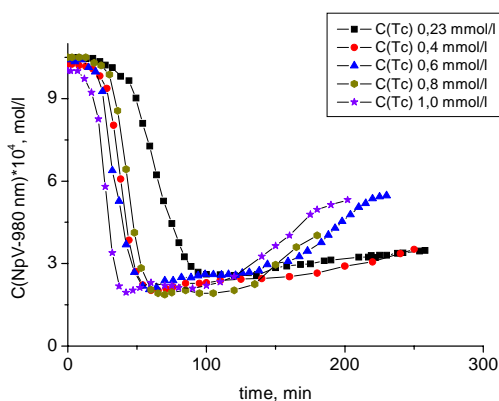
The work was supported by RAS program "Chemistry and Physico-Chemistry of Supramolecular Systems and Atomic Clusters".

CATALYTIC EFFECTS OF Tc IONS ON THE Np - HYDRAZINIUM - NITRIC ACID SYSTEM

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The early 1970-1980 years were characterized by rather simple approach to the description of Tc behavior in PUREX [1,2] – in the 1980-2000-th years it changed to more complicated understanding as the catalytic Tc reactions were found to play the dramatic role causing the destruction of hydrazine with nitric acid and effecting the redox properties of major actinides [3]. Anyhow the effect of Tc onto the neptunium was not studied yet. The experimental procedures of this work involved conventional spectrophotometric methods for the kinetic measurements of Tc and Np. For the observation of Np(V) concentrations the peak at 980 nm was used. The constant initial concentrations of Np(V) and N₂H₅NO₃ were used in all the experiments, while C₀(TcVII) varied as (0.24 – 1.2)*10⁻³ mol/l. The temperature was varied from 35 to 55°C. Tc(V) was controlled according to the development of the shoulder at 470-500 nm (after the corrections for the Np spectra), Tc(IV) was measured at the 400 nm with similar corrections for Np and Tc(V). The reactions were carried out in thermostatic quartz cells.



Tc is effectively accelerating the Np reduction but cause the destruction of hydrazine and partial back oxidation of Np then Np forms some complexes, their composition should be the subject of further study. When Tc(VII) introduced initially, the system Tc-Np-hydrazine in nitric acid takes a short induction period and then follows the 1-st order with $k_3=2 \cdot 10^{-2} \text{ min}^{-1}$ for Np(V) to Np(IV) reduction rate.

Tc itself, when introduced to the Np-hydrazine solution in nitric acid, exhibits more complicated behavior : during the induction period the accumulation of 10-15 % of reduced Tc(IV) occurs, then the reduction of Np takes place. When it is over further reduction to Tc(IV) proceeds initiating hydrazine decomposition and partial Tc(V) accumulation. The final ratio Tc(IV)/Tc(V) depends on the present reducing agents and actinides, temperature and acidity.

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STABILIZATION AND SPECTRAL CHARACTERISTICS OF TECHNETIUM AND RHENIUM PEROXIDES.

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Complex peroxides of transition metals, the close Tc neighbors in Mendeleev Periodic System, have been known for a long time [1]. Tc was considered to form no complex peroxides. At the same time hydrogen peroxide is present in the radioactive wastes as a product of the H₂O radiolysis. In this case an intensive study of this reaction has got an important practical significance. The aim was to find out the stabilization conditions for the reaction between Tc(IV) and H₂O₂. The spectrophotometric analysis was used for a quantitative measuring-in of the Tc – oxidative forms. The high-concentrated sulphuric acid was applied for organic phase modeling. In this work we present the first observation that proved the existence of the intermediate Tc – forms in the system “Tc– H₂O₂” (Fig.1).

The study Tc (IV) time behaviour (the mother solution) in anaerobic conditions indicated the Tc (IV) persistence to oxidation. The stabilization of unstable Tc peroxides was found out when sulphuric acid concentration was 12-18M H₂SO₄. The other requirement was hydrogen peroxide concentration; exactly the C (H₂O₂) increasing has brought the time-life growth of unstable Tc peroxides. Tc peroxides did present in the system as two different Tc-ionic forms.

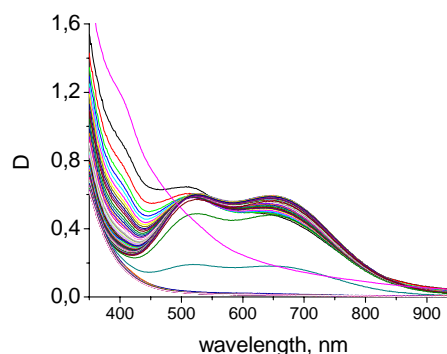


Fig.1 The generation and the decomposing of Tc-intermediate forms.

Peroxides of Tc-intermediate forms made a catalytic impact onto the reaction of the H₂O₂ decomposing. The observed two different Tc-ionic forms were characterized with the peaks at $\lambda = 500$ nm and 650 nm by model spectra deconvolution and the molar extinction coefficients for them and Tc (IV) were calculated: $\epsilon_{400}=2352\pm59$ l/mol·cm; $\epsilon_{650}=5090\pm51$ l/mol·cm; $\epsilon_{500}=2938\pm588$ l/mol·cm. The examination of Tc (V and VI) peroxides formation and decomposing reactions showed that they were ones of 1–st order by C(Tc)_{tot} and 0 – order by C(H₂O₂) and apparent reaction constants for them were calculated. Similar observations were made for rhenium(III and IV) solutions when reacted with H₂O₂.

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⁹⁹Tc-NMR STUDY OF Tc, Tc-Mo AND Tc-Ru SURFACE STATES AND ALLOYS FORMATION AT DIFFERENT OXYDE SURFACES

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Formation of the metallic alloy (so called ϵ -phase) at the surface of uranium dioxide in nuclear reactor is the cause of drawbacks in dissolution of spent nuclear fuel of high burn-ups. Formation of Tc-Ru alloy in course of technetium transmutation gives another type of similar material important from nuclear chemistry point of view. Formation of metallic active states at inert oxide support surface is believed to be the cause of catalytic properties of the materials formed. It is also believed that in case of multicomponent catalysts, the increase in catalytic activity (synergism) is due to intermetallic compound formation. For these reasons NMR is being developed with respect to study the speciation of technetium-99 in ϵ -phase and supported metal-ceramics. NMR spectrum of Tc metal powder obtained by FT of free induction decay accumulated after excitation of the spin system was recorded and used as a reference for analyses of technetium states supported onto the surfaces and formed in Tc-Ru alloys/intermetallics. Knight shift of technetium metal is a linear function of temperature, $K(ppm) = 7305 - 1.52 \times T$. $\nu_Q(^{99}\text{Tc}) = 230 \text{ kHz}$ at 293 K, $C_Q(^{99}\text{Tc}) = 5.52 \text{ MHz}$. ⁹⁹Tc NMR study of bimetallic Ru-Tc samples supported on the different supports i.e.: $\gamma\text{-Al}_2\text{O}_3$ (Fig.1), SiO_2 , MgO , TiO_2 has shown that for all the supports (except for TiO_2), there is an intense signal at $-30 - 40 \text{ ppm}$ arising from the pertechnetate-ion.

For Tc-Mo alloys and surface states the effect of carbon impurities was observed. For the main part of the supports “capsulation” effect (i.e. inclusion of the initial components NH_4TcO_4 , H_2O into the pores non-accessible to reducing agent) takes place. The most intensive signal with asymmetric line-shape were registered at $E = 9250 \pm 100 \text{ ppm}$, which is quite different from knight shift characteristic for powdered technetium metal. Further experiments are in progress to clarify whether this is indicative of an intermetallid Ru_xTc_y , or of a solid solution formation.

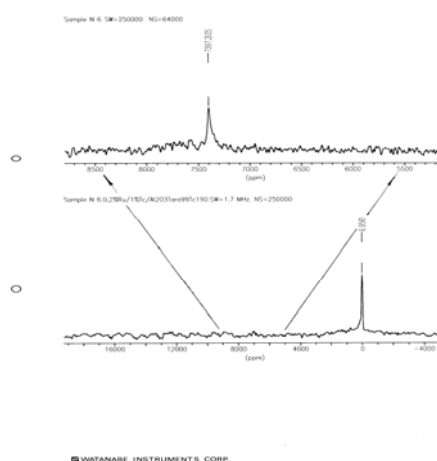


Fig. 1. NMR of 1%Tc + 0.2% Ru supported on $\gamma\text{-Al}_2\text{O}_3$

DIFFERENT REDUCING REAGENTS FOR THE VARIATION OF TECHNETIUM EXTRACTION BEHAVIOR

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Techneium is one of the important components of the spent nuclear fuel that is extractable in frames of PUREX reprocessing and thus could effect the stage of reducing U/Pu separation. Up to 80-90% of Tc are extracted to organic phase in a head extraction stage and goes for the U/Pu reducing separation stage [1-2]. Anyhow the final fate of technetium in the reprocessing is not clear now -the choice in between of long-term storage, transmutation and vitrification being still under consideration [3]. Therefore the aim of this work was to compare the application of different chemical reagents to the technetium reduction in the frames of spent nuclear fuel reprocessing with the possibility of improved technology variability with Tc-99 directed to variable desired flowsheet.

The utilization of hydrazine for improving the reducing agent stability leads imperatively to Tc reduction to Tc(IV), thus provoking its back extraction to the aqueous phase together with Pu. Tc catalytic ability of reducing agents oxidation causes the considerable overdraft of the reagents and the formation of by-side products.

Other "soft" reducing reagents that are able of Pu reduction leaving the Tc in non-reduced state change drastically the extraction behavior of Tc directing it to U flowsheet. The salt-free reagents like acetohydroxamic acid, its decomposition product – hydroxylamine and Fe(II) in presence of some stabilizers could be considered in this frames.

A number of reagents characterized with slow Tc reducing kinetics could act dually: at the initial stage they could be considered as soft reagents, while in several hours they could reduce Tc to lowest oxidation states – thus developing 'hard' behavior. Ascorbic acid and organic derivatives of hydrazine (oxyethylhydrazine, etc.) could be the examples of this behavior.

The application of different approaches to the technetium reduction in the frames of spent nuclear fuel reprocessing provides a wide variety of technologies with Tc-99 directed to a desirable flowsheet.

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REDOX PROPERTIES OF HEXATECHNETIUM AND HEXARHENIUM COMPLEXES WITH MIXED CAPPING LIGAND

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Octahedral hexanuclear cluster complexes have interesting optical and redox properties. In this study, redox properties of two new hexatechnetium complexes with mixed sulfide and bromide as capping ligand $[\text{Tc}_6(\mu_3\text{-S}_7\text{Br})\text{Br}_6]^{3-}$ (**1**) and $[\text{Tc}_6(\mu_3\text{-S}_6\text{Br}_2)\text{Br}_6]^{2-}$ (**2**) are reported.

The complexes **1** and **2** were prepared by the high temperature reaction of technetium, sulfur, bromine and potassium bromide. These complexes were separated by column chromatography. The structures were determined by single crystal X-ray analysis. The Tc_6 octahedral cores are surrounded by two ligands, sulfide and bromide (Fig. 1). Both of the complexes **1** and **2** have six bromides as terminal ligand.

The redox potentials of the complexes **1** and **2** were measured by cyclic voltammetry in $(\text{Bu}_4\text{N})\text{PF}_6\text{-CH}_3\text{CN}$. Respective **1** and **2** are easier to reduce compared with the hexarhenium analogs $[\text{Re}_6(\mu_3\text{-S}_7\text{Br})\text{Br}_6]^{3-}$ (**3**) and $[\text{Re}_6(\mu_3\text{-S}_6\text{Br}_2)\text{Br}_6]^{2-}$ (**4**). Furthermore, the hexatechnetium complexes become easier to reduce with increasing the number of capping bromide. It seems that the difference of electronegativity for bromine and sulfur affects to the redox potentials of the hexanuclear core.

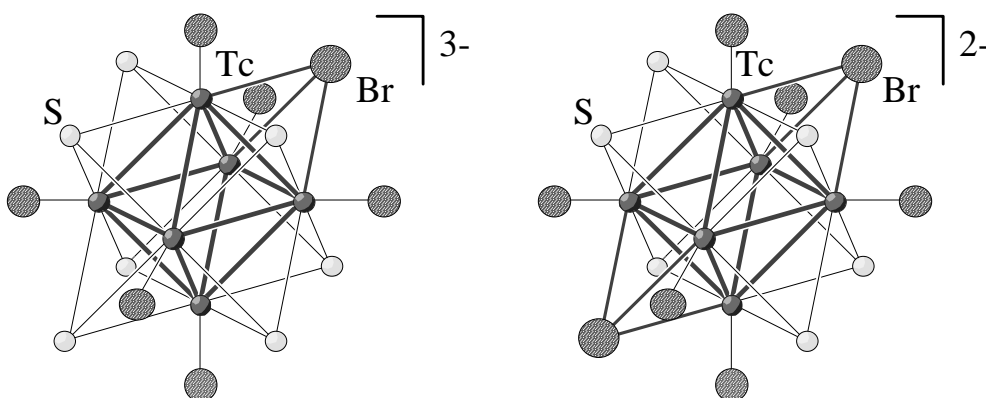


Fig. 1. $[\text{Tc}_6(\mu_3\text{-S}_7\text{Br})\text{Br}_6]^{3-}$ (**1**) and $[\text{Tc}_6(\mu_3\text{-S}_6\text{Br}_2)\text{Br}_6]^{2-}$ (**2**).

SIMPLE ANALYSIS METHOD FOR TECHNETIUM-99 IN SEAWATER USING AN ANION EXCHANGE RESIN

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We developed a simplified analysis method for ⁹⁹Tc in a seawater sample using combination of pre-concentration with a TEVA disc, purification with an anion exchange resin and measurement with an inductively coupled plasma mass spectrometry (ICP-MS). After a water sample was spiked with ⁹⁹Tc-free ^{95m}Tc tracer, which was produced by irradiating Nb metal with alpha-particles from a cyclotron¹, Tc in the sample was pre-concentrated by using a TEVA disc (Eichrom Industries, US). Tc was further purified by an anion exchange resin column (AG 1 x8, Dow Chemical, US), and then was measured with an ICP-MS (PQ-Excel-s, VG Elemental, UK).

The international standard material, IAEA-381, was analyzed in order to confirm accuracy and reproducibility of the method. The standard material was a seawater sample from Irish Sea, and its ⁹⁹Tc concentration had been previously reported². Four aliquot samples of the IAEA-381 were analyzed by the present method. The mean and a standard deviation of ⁹⁹Tc concentration in the IAEA-381 standard were found as 205±6 mBq kg⁻¹, which were in good agreement with the reported value of 217±11 mBq kg⁻¹.² Mean chemical recovery of Tc was 80±5%, and the detection limit of ⁹⁹Tc was 40 μBq kg⁻¹ in 10 kg seawater sample.

Acknowledgement

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Tchnetium Chemistry at the University of Nevada Las Vegas

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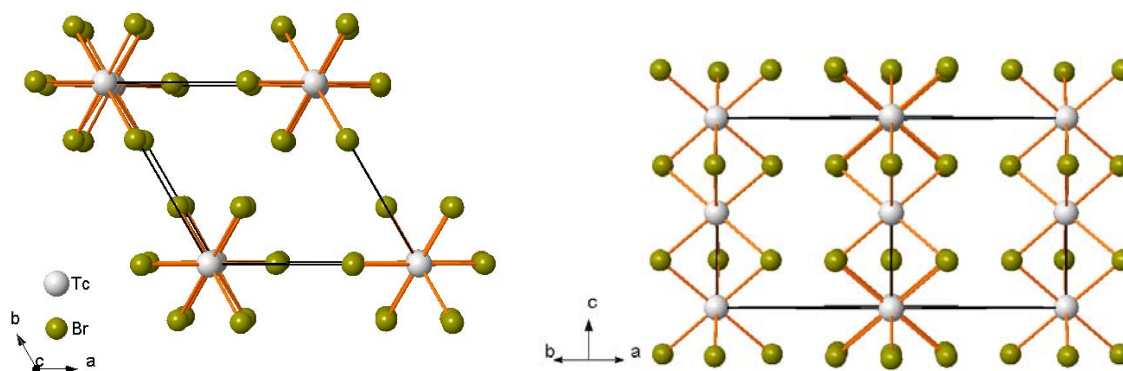
The chemistry of technetium is being explored at the Harry Reid Center for Environmental Studies of UNLV. Our goal is to investigate both the applied and fundamental aspects of technetium chemistry, with a special emphasis on synthesis, separations, and materials science. The synthetic chemistry focuses on metal-metal multiple bonding, oxides, and binary halides. In the last year, two new metal-metal bonded dimers, four new ternary oxides and technetium tri-bromide were prepared and characterized. Separation and materials chemistry is related to UREX process, especially separation uranium/technetium from acid solution, and synthesis of Tc waste forms. The facilities at the Harry Reid Center include modern radiochemistry laboratories where investigators can work with multi-milligram quantities of ⁹⁹Tc, and analytical instrumentation dedicated for radioelement characterization and analysis. Collaborations with other scientific laboratories provide access to additional analytical capabilities (e.g., XAFS, neutron diffraction, solid-state NMR) and structural data on ternary oxides and molecular compounds. In this presentation, an overview of capabilities, collaborations and research on Tc chemistry at UNLV will be presented.

Synthesis and Structure of the New Binary Halide TcBr_3

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Nearly 50 years ago, TcCl_4 was the last simple binary halide of technetium to be discovered.¹ More surprisingly, no simple bromide or iodide of Tc has ever been reported. Although TcBr_4 has been presented in the literature, unambiguous evidence of its existence remains scant.² Through the reaction of bromine vapor on finely powdered Tc metal, a new binary halide of Tc has been prepared. The new compound TcBr_3 is isostructural to MoBr_3 and RuBr_3 , which are composed of infinite chains of face-sharing MBr_6 ($\text{M}=\text{Mo}, \text{Ru}$) octahedra. The black needle-like crystals are hexagonal having space group $P6_3/mcm$ with lattice constants $a = 6.4319(5) \text{ \AA}$ and $c = 6.0205(10) \text{ \AA}$; the compound also appears to be air stable. The crystal structure and solubility of the TcBr_3 in various solvents will be presented.



View of the TcBr_3 crystal structure down the c axis (left) and lattice edge (right).

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Rhenium(I) compounds in Nuclear Medicine. Crystallographic and kinetic investigation of different $[\text{Re}(\text{CO})_3(\text{L}_1)(\text{L}_2)]^{n-}$ complexes.

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Keywords: rhenium, bidentate ligands, X-ray crystallography

Technetium-99m ($^{99\text{m}}\text{Tc}$) is the radionuclide of choice in diagnostic nuclear medicine, partly because of its availability, favorable decay characteristics and cost. Limited ligands are known that are sufficient in stabilizing the $^{99\text{m}}\text{Tc}$ core in physiological conditions. Analogous Re and Tc complexes have very similar physical characteristics. The Rhenium analogues are harder to reduce, which is a great advantage since it provides an ultimate elimination route when oxidation occurs *in vivo* forming ReO_4^- .

The mixed ligand approach is a well known method to smooth-tune the ligand properties. The [3 + 1] mixed ligand approach [1] was introduced by Pietzsch and co-workers where a tridentate ligand links to the biomolecule and the monodentate coligand is varied or vice versa. [2] This approach have some problems which limits their application.[3]

Research have been done on other mixed ligand systems but are less convenient, like the hynic approach [4] and complexes with umbrella-like tetradentate NSSS ligands and monodentate isocyanides [5].

Alteration of the coligand shows different accumulation patterns in target cells. This emphasize the need to tune the chelators to achieve the optimal *in vivo* behavior.

A [2 + 1] mixed ligand concept was introduced recently, which allows the labeling of bioactive molecules containing a monodentate or a bidentate donor site [6].

With $[\text{Re}(\text{OH}_2)_3(\text{CO})_3]^+$ accepting many types of ligands, the possibility arises to design complexes with properties that's adapted to those of the biomolecule.

Rhenium(I) tricarbonyl complexes of the form $[\text{Re}(\text{L}_1)(\text{L}_2)(\text{CO})_3]^{n-}$ ($\text{L}_1 = \text{Br}, \text{H}_2\text{O}$; $\text{L}_2 =$ various N-O, and O-O ligands) have been prepared from $(\text{Et}_4\text{N})_2[\text{Re}(\text{CO})_3\text{Br}_3]$ as starting material.

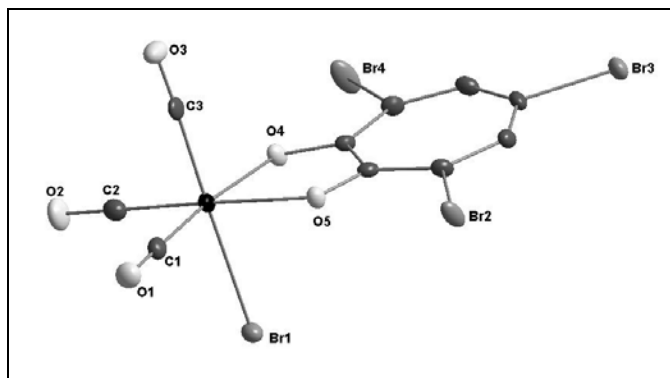


Fig 1: $\text{Re}(\text{CO})_3\text{BrTropBr}_3$

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PHOTOSUBSTITUTION OF TERMINAL IODIDE WITH PYRIDINE IN OCTAHEDRAL HEXARHENIUM COMPLEXES

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The octahedral hexarhenium complexes having six rhenium ions, eight capping ligands, and six terminal ligands are interesting photoemission and redox properties. In this study, we report about photosubstitution of the terminal ligands in the hexarhenium complexes.

The photoreactions of the terminal iodide in $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_6]^{3-}$ or $4-$ with pyridine were performed in acetonitrile at room temperature using a mercury high-pressure lamp. Each reaction was monitored by ^1H NMR. The coordinate pyridine signals shifted lower magnetic field than free pyridine signals. The reaction for $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_6]^{4-}$ proceeded faster than that for $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_6]^{3-}$. The terminal chloride, bromide and cyanide ligands were not substituted with pyridine in this condition. The products from $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_6]^{3-}$ or $4-$ were separated by silica gel columns chromatography. The main product obtained is *cis*- $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_4(\text{py})_2]^{2-}$ (Fig. 1) both for $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_6]^{3-}$, $4-$. The another products, *trans* isomer, *mer*- $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_3(\text{py})_3]^-$, and unreacted hexarhenium complexes have been identified by ^1H NMR spectra. The reaction of $[\text{Re}_6(\mu_3\text{-Se})_8\text{I}_6]^{3-}$ with pyridine gave a complicated mixture. This suggests that the substitution for the selenide complex is much faster than that for sulfide complex.

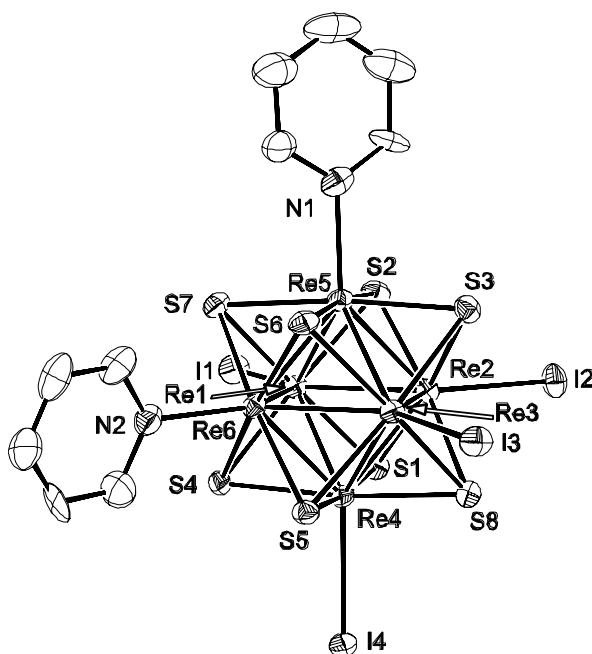


Fig. 1.
Crystal structure of
cis- $[\text{Re}_6(\mu_3\text{-S})_8\text{I}_4(\text{py})_2]^{2-}$.

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