

RECENT DEVELOPMENTS IN TECHNETIUM COORDINATION CHEMISTRY
AND ITS MEDICAL APPLICATION

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Literature Seminar

November 10, 1981

Technetium occupies a unique place in chemistry as the first non-naturally occurring element prepared by nuclear synthesis. Its absence from nature results from the instability of odd atomic numbered elements [1]. Technetium has a number of isotopes of which ^{99}Tc is the most important. This isotope has a ground state with a half-life of 2.15×10^5 y and a metastable state, $^{99\text{m}}\text{Tc}$, with a half-life of 6 h. $^{99\text{m}}\text{Tc}$ is widely used as a radiopharmaceutical for diagnostic organ imaging [2]. Technetium is obtained on a fairly large scale as a by-product of nuclear fission or by neutron bombardment of ^{98}Mo and can be safely used in chemical research using appropriate precautions [3,4].

Technetium chemically resembles the other group VIIb elements, manganese and particularly rhenium. Technetium exhibits a wide range of oxidation states from (-I) to (VII) with (IV) and (VII) the most common. It forms a number of simple oxides, e.g., TcO_2 , Tc_2O_7 ; sulfides, halides, e.g., TcCl_4 , TeF_6^{-2} and oxo halides such as TcOBr_3 and TcO_3F [3-5]. Tc_2O_7 dissolves in water to give pertechnic acid, HTcO_4 . The pertechnetate ion is very stable and is the starting point for most technetium coordination compounds. Low oxidation state complexes can be prepared using phosphine, arsine and phosphonite ligands, including an interesting seven-coordinate species $[\text{TcCl}_3\text{CO}(\text{PMe}_2\text{Ph})_3] \cdot \text{EtOH}$ having capped octahedral symmetry [6]. Another seven coordinate complex has been synthesized by Sn(II) reduction of TcO_4^- in dimethylglyoxime [7]. This complex is of interest since similar procedures are used to prepare technetium radiopharmaceuticals, whose chemical nature are often not well understood. Other high coordination number complexes have been synthesized with cyanide and thiocyanate ligands [8]. An eight coordinate complex has been prepared by oxidative addition of Cl_2 to $[\text{Tc}(\text{diars})_2\text{-Cl}_2]^+$ [9]. This type of oxidative addition is unusual and demonstrates the wide possibilities in technetium coordination chemistry. A Tc(V) compound containing the ligand hydrotris(1-pyrazolyl)borate has been synthesized from aqueous solution [10]. This is of potential importance in preparing lipophilic Tc-labeled radiopharmaceuticals from technetate solutions. A large series of Tc(V) compounds of general form $[\text{TcOY}_4]$ where $Y_4 = X_4$, S_4 , S_2O_2 and S_2N_2 containing ligands have been synthesized and well characterized by spectroscopic methods [11-13]. One point of interest is that in the attempted synthesis of a technetium thioglycolate complex, a mercaptothioacetate complex was obtained instead [11]. This demonstrates that technetium radiopharmaceuticals prepared by reduction of TcO_4^- in the presence of a ligand may not give the expected complex. Technetium phosphate complexes have been prepared and one characterized by x-ray crystallography [14]. The complex consists of infinite polymeric chains of phosphate bridged technetium atoms. Complexes such as this are thought to bind to Ca^{+2} sites in bone via uncoordinated phosphates [15].

Diagnostic organ imaging, for which technetium complexes are used, consists of the intravenous administration of a radiopharmaceutical which becomes distributed throughout the body tissues in a pattern

characteristic of the complex [2]. The distribution is monitored by a scintillation camera which gives a two-dimensional picture showing diseased areas. A large number of isotopes are used; however, ^{99m}Tc has nearly ideal chemical and physical properties as well as ready availability. Many technetium complexes are used for imaging a wide variety of body tissues and new ones are constantly being developed [16,17]. Concomittant with this revolution in medical technology, great advances have been made in recent years in technetium coordination chemistry. However, much further investigation into technetium chemistry is needed in order to better understand the action of existing Tc-labeled radiopharmaceuticals and to design new ones.

References

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