I-67

MÖSSBAUER ^{237}Np AND CRYSTALLOGRAPHIC STUDIES OF $M^{II}NpF_6 \cdot 3H_2O$ (M^{II} = Mn, Fe, Co) COMPOUNDS

H. Abazli, A. Cousson, M. Gasperin, J. Fove and M. Pages

Institut Curie, 75231 Paris, Cedex 05 (France)

The compounds $M^{II}NpF_6 \cdot 3H_2O$ with M^{II} = Mn, Fe, Co were prepared as single crystals by hydrothermal synthesis (T = 400°C, P = 2000 bars). $CoNpF_6 \cdot 3H_2O$ crystallises in a monoclinic system with C2 space group. Cell parameters are a = 12.143(9)Å; b = 6.922(5)Å; c = 7.942(5)Å; β = 92.84°.

The Mössbauer measurements were performed in a conventional He Cryostat. The Mössbauer source used in the experiments was a 500 mCi ^{241}Am metal with a conventional sine mode drive system.

A microbalance magnetometer attached to a varying temperature Cryostat was used for the susceptibility measurements. The maximum applied magnetic field was 14KG.

The Mossbauer spectroscopy of ^{237}Np shows a magnetically split hyperfine spectrum at 4.2K for all those compounds.

The spectra can be fitted with a magnetic hyperfine field associated to a quadrupole splitting using the linear correlation between B_{eff} and e^2qQ. From isomer shift measurements, we confirm the IV charge state of Np in these 3 compounds.

The magnetic susceptibility shows antiferromagnetic type transition. $1/\chi = f(T)$ follows a Curie-Weiss law above T_N.

I-68

THE PREPARATION OF TECHNETIUM OXYFLUORIDES AND THEIR CHARACTERIZATION BY ^{99}Tc, ^{17}O AND ^{19}F NMR SPECTROSCOPY

Kenneth J. Franklin, Colin J. L. Lock, B. G. Sayer and Gary J. Schrobilgen*

Department of Chemistry, McMaster University, Hamilton, Ont., L8S 4M1 (Canada)

Relatively little is known about the chemistry of technetium, especially in its highest oxidation state. At the same time, ^{99}Tc (I=9/2, Q=-0.19 x $10^{-24}cm^2$) is one of the more sensitive NMR nuclei (sensitivity relative to the proton is 0.275 at 100% abundance). Pertechnetate, TcO_4^-, the standard for ^{99}Tc NMR spectroscopy, also displays primary isotopic shifts for $^{17}O^-$ and ^{18}O-enriched samples. Technetium-99 NMR has proven an invaluable structural probe in the study of Tc(VII) oxyfluorides.

Noble gas fluorides (KrF_2 and XeF_6) have been used to synthesize novel Tc(VII) species from solutions of TcO_3F in anhydrous HF, i.e. $Tc_2O_5F_4$ and TcO_2F_3. Pertechnetyl fluoride has also been prepared and its fluoride ion donor properties studied in HF solution. Solid $TcO_3^+AsF_6^-$ has been isolated from these solutions and characterized. In addition to ^{99}Tc NMR, compounds have also been studied by ^{19}F and ^{17}O (enriched) NMR spectroscopy.