Anal. Calcd for $[Ir(C_{10}H_8N_2)_2Cl_2]PF_6$: C, 33.34; H, 2.24; N, 7.78; Cl, 9.84. Found: C, 33.76; H, 2.49; N, 7.81; Cl, 10.16.

Spectra.—Spectra were run and decoupled on a Varian HA-100 spectrometer system.

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Mössbauer Spectra of Some Neptunium(VII) Compounds[1]

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Neptunium has been known for many years to possess stable 3+, 4+, 5+, and 6+ valence states. The discovery of a stable 7+ valence state of neptunium has been reported by Russian workers,[2-4] and the stability of this unexpected oxidation state has been discussed by Jørgensen.[5] Further study of heptavalent neptunium is of interest because the species may be stabilized by the closed-shell $5f^0$ configuration.

Mössbauer spectroscopy has been used to identify neptunium valence states.[6-8] Each valence state from 3+ to 6+ has a characteristic isomer-shift range that is correlated with the number of 5f electrons present. In this note, we report Mössbauer spectra of the hexaamminecobalt(III) complex of neptunium(VII), $Co(NH_3)_6NpO_5 \cdot xH_2O$, and of Np(VII) in two other solid environments. The results extend and are consistent with isomer-shift systematics previously reported for neptunium valence states.

Experimental Section

Materials.—Solutions of Np(VII) in 0.5–2.0 *M* NaOH were prepared by bubbling ozone through a suspension of $Na_2Np_2O_7 \cdot xH_2O$ for 1–2 days and filtering the undissolved solids from the solution. The presence of Np(VII) in these solutions was verified by absorption spectra and by electrolytic reduction with a conducting glass electrode. Samples for Mössbauer studies were prepared by three methods.

(a) $Co(NH_3)_6NpO_5 \cdot xH_2O$ was precipitated by simultaneous addition of equimolar quantities of Np(VII) in 1–2 *M* NaOH and $Co(NH_3)_6Cl_3$ in H_2O. The neptunium content of the solid was 42%, which agreed fairly well with 44.5% reported by Krot, *et al.*[3] The oxidation number of the solid was measured by titrating both Np(VI) and Np(VII) with KI solution and comparing the results with the total amount of neptunium present; from this measurement 96% of the neptunium in the solid was Np(VII). X-Ray diffraction patterns of powdered samples of this compound also verified its reproducibility.

(b) Np(VII) in NaOH solution was evaporated to dryness by an air stream at room temperature.

(c) A suspension of $BaNp_2O_7 \cdot xH_2O$ in NaOH solution was ozonized. In this case Np(VII) that went into solution was not used, but, rather, the solid residue was studied. Neptunium in the solids filtered from the solution contained about 30% Np(VII) and 70% Np(VI).

Mössbauer Spectra.—Velocity spectra were obtained with a loudspeaker-type constant-acceleration Mössbauer spectrometer. All measurements were made with source and absorber at 4.2°K. The source was an alloy of ^{241}Am (3%) in thorium metal, which emits a sharp single line with a very weak secondary line at −2.0 cm/sec from the strong line. The Mössbauer spectrometer,[9] cryogenics system,[10] and Am–Th source[6] have been described previously. Absorber thicknesses were about 200 mg/cm² of neptunium, except for the evaporated Np(VII) material which was estimated to contain 30 mg/cm² of neptunium in a massive amount of solid NaOH.

Results

Isomer shifts, hyperfine parameters, and intensity data derived from Mössbauer spectra of heptavalent neptunium in three solid environments are presented in Table I. The spectrum of the compound $Co(NH_3)_6NpO_5 \cdot xH_2O$, shown in Figure 1, is the best defined of the three. In the environments studied, the isomer-shift range −6.3 to −6.0 cm/sec is indicative of Np(VII).

TABLE I

MÖSSBAUER PARAMETERS OF MATERIALS CONTAINING HEPTAVALENT AND HEXAVALENT NEPTUNIUM

Sample	Site	IS,[a] cm/sec	$eqQ/4$,[b] cm/sec	η[c]	Dip,[d] %
$Co(NH_3)_6NpO_5 \cdot xH_2O$	A	−6.28 ± 0.08	3.1 ± 0.1	0.83 ± 0.03	5.8[e]
	B	−6.28 ± 0.08	2.1 ± 0.1	0.69 ± 0.04	
Np(VII) in NaOH		−6.0 ± 0.1	...	...	0.1
Ozonized $BaNp_2O_7 \cdot xH_2O$	A	−6.2 ± 0.1	2.5 ± 0.2	0.6 ± 0.1	1.0
	B	−4.2 ± 0.1	2.8 ± 0.2	0.6 ± 0.1	1.8
$BaNp_2O_7 \cdot xH_2O$[f]		−4.0 ± 0.1	3.6 ± 0.2	0.8 ± 0.2	0.8

[a] Isomer shift, with respect to NpO_2. [b] Quadrupole coupling constant for neptunium ground state; signs were not determined. [c] Asymmetry parameter. [d] Depth of the strong central peak for quadrupole-split spectra, uncorrected for background. [e] Depth of central peak, common to both A and B sites. [f] Before ozonization.

The principal features of the spectra were different for each of the materials studied. For $Co(NH_3)_6NpO_5 \cdot xH_2O$ (Figure 1) the strong central resonance has satellite peaks typical of quadrupole splitting. Their presence is attributed to two nonequivalent Np(VII) sites (or species) in the sample; both sites are highly asymmetric. The resonance of Np(VII) in solid NaOH was very weak, and splitting was not observed. Experiments with barium neptunate demonstrated

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

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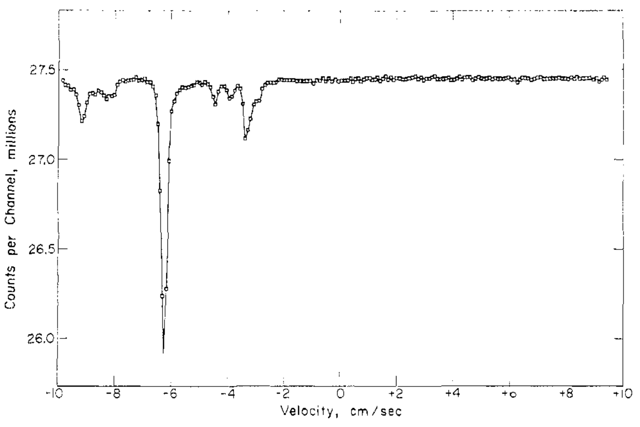

Figure 1.—Mössbauer spectrum of $Co(NH_3)_6NpO_5 \cdot xH_2O$ at 4.2°K.

that Np(VI) could be partially oxidized to Np(VII) in the solid. The Mössbauer spectrum after ozonization indicated the presence of a mixture of Np(VI) and Np(VII) and the occurrence of slight changes in the environment of the unoxidized Np(VI).

Discussion

The experimental isomer-shift range for Np(VII) may be compared with the shifts of neptunium species in other oxidation states and with theoretical calculations. This information is summarized in Table II. The experimental data[6,8] quoted are for the oxygen-bonded neptunium compounds only. Calculated values of relative s-electron density at the nucleus, obtained with nonrelativistic Hartree–Fock–Slater wave functions,[11] are given for the pure configurations $5f^n$ corresponding to the free ions Np^{7+} through Np^{3+}.

TABLE II

EXPERIMENTAL ISOMER SHIFTS FOR OXYGEN-BONDED NEPTUNIUM COMPARED WITH CALCULATED SHIFTS FOR FREE IONS

	Exptl IS,[a] cm/sec		$\Delta\psi_0^2$,[b] cm^{-3}	Calcd IS, cm/sec
NpO_5^{3-}	−6.3 to −6.0	Np^{7+} ($5f^0$)	0	−9.2
NpO_2^{2+}	−3.9 to −3.2	Np^{6+} ($5f^1$)	-1.42×10^{26}	−5.8
NpO_2^{+}	−1.8 to −0.6	Np^{5+} ($5f^2$)	-2.67×10^{26}	−2.8
NpO_2	0.0	Np^{4+} ($5f^3$)	-3.90×10^{26}	+0.2
Np^{3+} [c]	+4.1	Np^{3+} ($5f^4$)	-5.12×10^{26}	+3.1

[a] From ref 6, except NpO_5^{3-} which is from the present work. [b] $||\psi_0(5f^n)|^2 - |\psi_0(5f^0)|^2|$. [c] Np^{3+} in AmO_2 matrix.

Isomer shifts for neptunium compounds increase regularly with decreasing oxidation state. This increase is a consequence of increased shielding of s electrons from the nucleus as f electrons are added and of a negative fractional change in nuclear deformation for the ^{237}Np Mössbauer γ transition. The trend established by the lower oxidation states is followed by the heptavalent neptunium shifts, which fall approximately in the region to be expected from simple extrapolation, as shown in Figure 2.

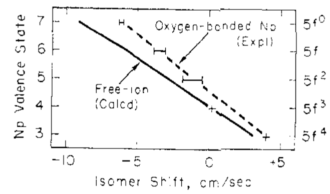

Figure 2.—Correlation of ^{237}Np isomer shifts with oxidation state.

The wave-mechanical calculation of s-electron density at the nucleus, although very approximate, clearly reproduces the shielding effects (mainly on the 6s shell) of additional 5f electrons in the free ions.[12] The regular decrease in the calculated s-electron density at the nucleus can be correlated with the experimentally observed increase in isomer shift. Addition of a 5f electron to neptunium decreases the s-electron density at the nucleus by (1.2–1.4) × 10^{26} cm^{-3} and increases the isomer shift by 2–3 cm/sec. Calibration of the neptunium isomer-shift scale by correlating the theoretical results with experimental shifts must be somewhat subjective because of the approximate nature of the calculation and the lack of data on bonding in neptunium compounds. Nevertheless, it is possible to make an approximate calibration using all available ^{237}Np isomer shifts. A typical calibration obtained by this procedure is given in Table II (calcd IS), also shown as the solid line in Figure 2.

The significant feature of this calibration is that it yields shifts for the free ions Np^{5+}, Np^{6+}, and Np^{7+} that are 1–3 cm/sec more negative than the experimental shifts for the corresponding oxygen-bonded compounds. The neptunyl species NpO_2^+ and NpO_2^{2+} are known to involve some degree of covalency in the Np–O bonding, and their electronic structures would presumably be inadequately represented by Np^{5+} and Np^{6+}; a similar argument would apply to the anionic species present in Np(VII) compounds. The covalent contribution to the Np–O bonding must introduce additional shielding, probably of 5f character, to the central neptunium atom, and thus the shifts for such species should be greater than those for the corresponding free ions.

We conclude that the isomer shift measured for $Co(NH_3)_6NpO_5 \cdot xH_2O$ (and two other materials) is consistent with the presence of an oxygen-bonded Np(VII) species. The measurements presented here represent the largest isomer shifts so far found for any material, extending the span of neptunium shifts to more than 10 cm/sec, or about 3000 natural line widths. Although experimental lines are broad, typically no less than 30 natural line widths, the ^{237}Np Mössbauer resonance is nevertheless one of the most sensitive to chemical effects. The present work demonstrates conclusively the presence of heptavalent neptunium in the solids studied.

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[12] For a more detailed calculation and discussion of 5f-electron shielding effects in heavy elements, see M. Wilson, *Phys. Rev.*, **176**, 58 (1968).