Thus the nmr spectrum is that expected for 1,2-dimethyldisilane and the spectrum demonstrates that methyldisilane was absent.[13] The very weak resonances observed probably were due to 1,1-dimethyldisilane.[14] From the integrated intensities one can estimate that the ratio of 1,2-dimethyldisilane to 1,1-dimethyldisilane was about 60:1.

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CONTRIBUTION FROM THE WILLIAM A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Preparation and Nuclear Magnetic Resonance Spectrum of *cis*-Dichlorobis(bipyridyl)iridium(III) Hexafluorophosphate

BY RICHARD E. DESIMONE AND RUSSELL S. DRAGO

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During our investigations of the nmr contact shifts of several paramagnetic tris-bipyridyl complexes it was necessary for us to prepare the tris(bipyridyl)iridium(III) ion for use as a diamagnetic reference. Following the literature method of preparation,[1] we encountered a product which upon further investigation turned out to be *cis*-dichlorobis(bipyridyl)iridium(III) hexafluorophosphate, a previously unreported compound, and not the tris(bipyridyl)iridium(III) complex as expected. We wish to report the results of our nmr investigations of this complex.

The tris(bipyridyl)iridium(III) ion has been previously reported to be the sole product of the reaction of $IrCl_6^{3-}$ and bipyridyl.[1] It was first reported to be bright orange, but later was shown to be canary yellow[2] upon recrystallization from aqueous solution containing activated charcoal. The orange color was assumed by these authors to be due to contamination with small amounts of *trans*-dichlorobis(bipyridyl)iridium(III) in analogy with the colors noted for the similar phenanthroline complexes.[2] Our preparation yielded only a small amount of orange precipitate and a yellow solution from which the *cis* complex was isolated upon cooling and addition of KPF_6.

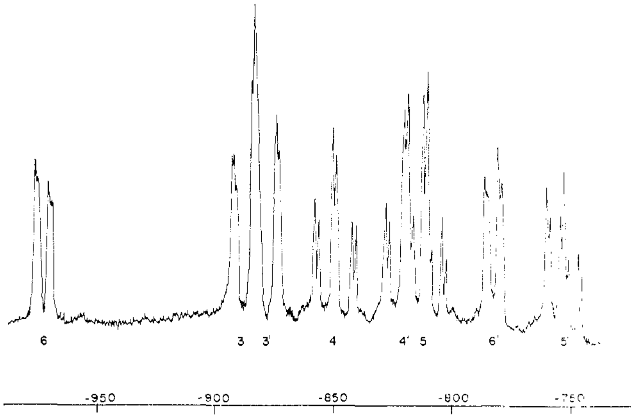

Figure 1.—*cis*-Dichlorobis(bipyridyl)iridium(III) hexaflurophosphate in DMSO at 100 MHz.

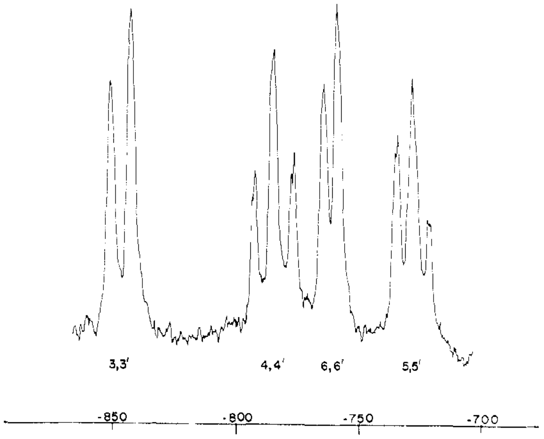

Figure 2.—Tris(bipyridyl)osmium(II) hexafluorophosphate in CD_3CN at 100 MHz.

Examination of the nmr spectrum (Figure 1), indicated immediately that the complex did not contain the desired tris(bipyridyl)iridium(III) ion. In contrast with the usual spectrum of a tris-bipyridyl complex (as illustrated by $Os(bipy)_3^{2+}$ in Figure 2), many more peaks were present than would be expected. In order to interpret the spectrum and to determine which protons belong to equivalent rings of the bipyridyl molecule (in C_{2v} symmetry, both rings of bipyridyl are no longer equivalent), decoupling experiments were carried out and spectra were also recorded at 100°. Room-temperature and 100° spectra were virtually identical except for slight sharpening of the very small couplings. It was assumed, therefore, that the molecule is very stable and does not undergo rearrangement.

In general, what is observed for a tris complex is a spectrum consisting of two doublets from the 3 and 6 protons and two triplets from the 4 and 5 protons (see Figure 3 for the numbering system). The triplets result from overlap of two doublets due to spin–spin splittings of comparable magnitudes from two adjacent protons. Since the 3 and 6 protons experience large couplings to only one other proton, doublets result. Inter-ring coupling is not observed. The spectrum of the iridium complex, while appearing complicated, can be reduced to a series of doublets and triplets indicating eight nonequivalent protons. The results of our analysis are presented in Table I, and a brief summation of the method used to interpret the decoupled spectra follows.

The decoupling experiment provides an easy way to separate the resonances belonging to atoms on the same

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Table I

Nmr Data for *cis*-[Ir(bipy)$_2$Cl$_2$]PF$_6$ in DMSO at 100 MHz

	Proton							
	3	3′	4	4′	5	5′	6	6′
Shift[a]	−891	−882	−850	−820	−815	−751	−965	−785

Coupling Constants[b]

$J_{4,5} \approx J_{3,4} = 8.0$; $J_{3,5} \approx J_{4,0} = 1.5$; $J_{6,5} = 5.0$

[a] In Hz relative to TMS internal standard. [b] In Hz (±0.05 cps). High precision was not attempted.

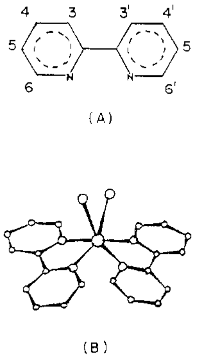

Figure 3.—(A) Numbering system of bipyridyl and (B) structure of the complex, projected perpendicular to a plane containing the C_2 axis.

ring since irradiation of a proton resonance from one ring will affect no proton resonances arising from the other ring. Bearing this in mind, and with the aid of spectra of free bipyridyl[3] and several tris complexes prepared in our laboratory, we have found it possible to assign most peaks unambiguously. Figure 3 will be useful in following our interpretations.

The initial assignment, that of the low-field doublet to the 6 proton, is made on the basis of the observed coupling constant of ~6 Hz which is appropriate to J_{5-6} as can be seen by comparison with the osmium(II) complex in Figure 2. Alternative assignment to H_3 would lead one to expect a coupling constant J_{3-4} of about 8 Hz. The extreme low-field position of this 6 proton, which invariably shifts upfield upon coordination in all tris complexes so far observed, may perhaps be explained by recourse to a model where it can be seen that in a tris complex, all 6 protons lie "over" a pyridyl ring from another bipyridyl molecule and are presumably exposed to a shielding due to ring currents in the benzenoid rings. In the *cis*-dichloro complex, two 6 protons find themselves directed away from any other rings and toward a halide ion, thus experiencing a significantly different environment. Again, making use of the coupling constants, we note that the large triplet at −887 Hz is composed of two overlapping doublets with coupling constants of ~8 Hz. These then must both be 3 protons. The close proximity of the two resonance frequencies is readily understood when looking at a model where it is seen that all 3 protons find themselves in virtually identical environments well removed from the anion.

Upon irradiation of the low-field doublet, the smaller coupling in the triplet at −850 Hz collapses. This therefore must be the 4 resonance and irradiation at −850 Hz should allow us to find 3 and 5. Irradiation at this frequency results in a shift in position and intensity of the two low-field lines in the triplet at −887 Hz with no change whatsoever in the upfield component of this multiplet. Therefore we can assign the 3 proton resonance at −891 Hz and 3′ at −882 Hz. Decoupling noise makes it too difficult to say anything certain about the effect of this irradiation on the large quartet at −818 Hz, but the 5 proton is certainly one of the sets of overlapping triplets present in this region. The two multiplets at highest field belong, therefore, to protons from the "other" ring since they are completely unaffected by decoupling of 6 and 4. Irradiation of the high-field triplet results in a collapse of the adjacent doublet to a singlet and a collapse of the small coupling in the highest field component of the triplet at −887 Hz. Also a shift in the low-field components of the quartet at −818 Hz is obvious, indicating collapse of a large coupling. These results, along with observed multiplicities of the resonances, lead to an assignment of the highest field triplet as 5′, the adjacent doublet as 6′, and the low-field component of the quartet at −818 Hz as the triplet belonging to 4′. Cross-checks on these assignments are possible by other irradiations and these bear out the assignments made above.

It appears, then, that previous reports of the preparation of tris(bipyridyl)iridium(III) are either in error or fail to recognize the existance of more than one product.

After completion of this work, Gillard and Heaton[4] also found that previous reports of the preparation of Ir(bipy)$_3^{3+}$ and Ir(phen)$_3^{3+}$ were erroneous, thus complementing our findings here. They expressed some uncertainty, however, as to the isomeric assignment of the bis complex they prepared but concluded that the bulk of the evidence pointed toward the *cis* configuration. Our work completely rules out the *trans* isomer and explicitly identifies the product as having the *cis* configuration.

Experimental Section

Reagents and Preparation.—Potassium hexachloiridate(III) trihydrate was obtained from Alfa Inorganics, Inc., 2,2′-bipyridyl was obtained from Aldrich Chemical Co., and KPF$_6$ was obtained from Ozark Mahoning Co. $K_3IrCl_6 \cdot 3H_2O$ (0.5 g) and 1.4 g of bipyridyl were heated and fused in a test tube at 270° for 15 min. After cooling slightly, the mixture was extracted with benzene to remove excess bipyridyl. The residue was taken up in a warm 50:50 ethanol-water solution and filtered. This solution was evaporated until slight turbidity was noticed, whereupon it was again filtered and added to a solution of KPF$_6$ in water (50 ml). An orange precipitate forms slowly and this is filtered leaving a yellow solution. Further addition (10 ml) of KPF$_6$ solution and evaporation to small volume yields yellow crystals of the *cis*-dichlorobis(bipyridyl)iridium(III) hexafluorophosphate complex. Recrystallization was from hot CH$_3$CN. The compound was appreciably soluble only in DMSO.

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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.

CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
E. I. DU PONT DE NEMOURS AND CO.,
AIKEN, SOUTH CAROLINA 29801

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

BY J. A. STONE, W. L. PILLINGER, AND D. G. KARRAKER

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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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