

PREPARATION AND MÖSSBAUER SPECTRA OF Np(III) -
ALKALI METAL CHLOROCOMPOUNDS

by

D. G. Karraker and J. A. Stone

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina 29801

MASTER

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ABSTRACT

M_2NpCl_5 , MNp_2Cl_7 ($M = K, NH_4, Rb$) and $NpCl_3 \cdot 4CH_3CN$ were prepared by zinc amalgam reduction of $NpCl_4 \cdot MCl$ in 50:1 acetonitrile-propionic acid solutions. The ^{237}Np Mössbauer spectra of these compounds showed quadrupole interactions, with Mössbauer parameters $\delta = 3.4$ to 3.5 cm/sec and $\frac{1}{2}eqQ = 0.5$ to 0.7 cm/sec. Mössbauer spectra established that preparations analyzing as $MNpCl_4 \cdot CH_3CN$ were mixtures of M_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$.

INTRODUCTION

Drozdzyński has recently reported^{1,2} the preparation and some properties of uranium(III) chlorocompounds of the general formulae M_2UCl_5 and MU_2Cl_7 ($M = K, NH_4, \text{ or } Rb$) by reducing a 50:1 acetonitrile-propionic acid solution of MCl and UCl_4 with zinc

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amalgam. The work reported here involves the preparation of the neptunium analogs, and their investigation by Mössbauer spectroscopy.

EXPERIMENTAL

Reagents

NpCl_4 was prepared by reacting Np(V) hydroxide with hexachloropropene, and was sublimed in vacuum at 600°C for purification.³ Acetonitrile was degassed by nitrogen sparging, and dried by passage through a molecular sieve column. Alkali metal chlorides were of C.P. grade, dried by heating overnight at 110°C , and cooled in an argon atmosphere. Glacial acetic acid and propionic acid (C.P. grade) were degassed with nitrogen and used without further purification. All purifications and reactions were performed in a dry argon atmosphere.

Preparation of Compounds

M_2NpCl_5 , MNpCl_4

The general procedure is described by Drozdzyński³; ca 2g of NpCl_4 and 1-2g MCl were dissolved in 40-50 ml acetonitrile with 5-10 drops of glacial acetic acid or propionic acid added. The solution was filtered and stirred with 2% zinc amalgam until a green precipitate appeared, normally 5 to 15 minutes. The solution was recontacted with zinc amalgam, and a second precipitate was recovered. Repetition of this procedure would yield three or four products with decreasing Cl/Np ratios as the MCl was consumed.

Products that analyzed with Cl/Np ratios of 5 (M_2NpCl_5) and 4 ($MNpCl_4$) were used for Mössbauer studies. All products were washed with acetonitrile and petroleum ether, and dried in vacuum at room temperature. Products with a Cl/Np ratio of 4 still retained some acetonitrile after this treatment.

MNp_2Cl_7

The procedure outlined above was modified to maintain excess $NpCl_4$ before reduction by adding $\sim 0.3g$ $NpCl_4$ dissolved in propionic acid. The reaction yielded a lemon-yellow product.

$NpCl_3 \cdot 4CH_3CN$

$NpCl_4$ was dissolved in acetonitrile and then reduced by zinc amalgam to give the green $NpCl_3 \cdot 4CH_3CN$.

Analyses

Neptunium was determined by alpha counting and corrected for ^{238}Pu from alpha pulse height analysis. Chloride was determined by potentiometric titration with $AgNO_3$ solution. Acetonitrile was identified by gas chromatography. Analytical data for the various products are shown in Table I. Mössbauer spectra were obtained as previously reported.⁴ Attempts to obtain x-ray powder diffraction patterns for the products were unsuccessful.

RESULTS AND DISCUSSION

The Mössbauer spectra of the Np(III) chlorocompounds all show the characteristic five-line pattern resulting from quadrupole splitting. The Mössbauer spectrum of $(NH_4)_2NpCl_5$ (Figure 1a) is

typical of the three M_2NpCl_5 compounds. The Mössbauer parameters (Table II) for the M_2NpCl_5 compounds show a slight increase in isomer shift and quadrupole splitting between K_2NpCl_5 and Rb_2NpCl_5 . These increases probably show the effect of slight changes in structure. The asymmetry parameter (η) is determined from the spacing of the quadrupole-split lines⁵, and may be regarded as a measure of the symmetry of the field on the $Np(III)$ ion. A value of 0 for η requires that the $Np(III)$ ion lie on an n -fold axis, where $n > 2$. The small values of η for the M_2NpCl_5 compounds suggest a near-axial symmetry site for the Np^{3+} ions in these compounds.

The Mössbauer spectra of the " $MNpCl_4$ " ($Cl/Np = 4$) products were similar to the M_2NpCl_5 spectra, but showed either broader lines or splitting of lines. A well-resolved example of these spectra is shown in Figure 1b, for " NH_4NpCl_4 ". Shown also is the Mössbauer spectrum of $NpCl_3 \cdot 4CH_3CN$. The spectrum of " NH_4NpCl_4 " can be reproduced by adding the spectra of $(NH_4)_2NpCl_5$ and $NpCl_3 \cdot 4CH_3CN$. The obvious conclusion is that " NH_4NpCl_4 " is a mixture of $(NH_4)_2NpCl_5$ and $NpCl_3 \cdot 4CH_3CN$. It is still possible that the compound NH_4NpCl_4 exists with Np^{3+} ions in two different sites. Unfortunately, attempts to obtain x-ray powder diffraction patterns on these compound failed. However, from the Mössbauer evidence, the existence of $MNpCl_4$ must be regarded as dubious.

The compound $NpCl_3 \cdot 4CH_3CN$ was found during unsuccessful attempts to synthesize $MNpCl_5$, where M is a divalent metal, such as Co , Ni , Hg , or Zn . $NpCl_3 \cdot 4CH_3CN$ has a slight solubility in

complexing organic solvents and may be useful in syntheses.

The asymmetry parameter of zero determined from the Mössbauer spectrum indicates that Np^{3+} ion in $\text{NpCl}_3 \cdot 4\text{CH}_3\text{CN}$ is in a site with axial symmetry. A possible structure of the $\text{NpCl}_3 \cdot 4\text{CH}_3\text{CN}$ might be one of the several derived from a trigonal prism, with a ligand coordinating through a face of the prism.

ACKNOWLEDGEMENT

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TABLE I

Analytical Data for Chlorocompounds

<i>Compound</i>	<i>Np</i>		<i>Cl</i>		<i>Cl/Np</i> <i>Mole Ratio</i>
	<i>Calc'd</i>	<i>Found</i>	<i>Calc'd</i>	<i>Found</i>	
K_2NpCl_5	48.10	47.21	36.0	35.78	5.06
$(NH_4)_2NpCl_5$	52.61	50.34	39.40	37.59	4.99
Rb_2NpCl_5	40.47	39.83	30.32	29.83	5.01
$KNpCl_4 \cdot CH_3CN$	51.52	51.10	30.93	31.10	4.06
$NH_4NpCl_4 \cdot 2CH_3CN$	49.47	50.0	29.65	30.5	4.07
$RbNpCl_4 \cdot 2CH_3CN$	43.36	41.9	25.98	24.91	3.96
$NpCl_3 \cdot 4CH_3CN$	46.71	47.10	20.96	21.17	3.00

TABLE II

Mössbauer Parameters of Np(III) Chlorocompounds

	<i>Isomer Shift,</i> <i>cm/sec</i>	<i>Quadrupole Coupling</i> <i>Constant, $\frac{1}{2}eQq$, cm/sec</i>	<i>Asymmetry</i> <i>Parameter η</i>
K_2NpCl_5	3.40 \pm 0.04	0.59 \pm 0.04	0.37
$(NH_4)_2NpCl_5$	3.44 \pm 0.04	0.56 \pm 0.04	0.22
Rb_2NpCl_5	3.47 \pm 0.04	0.70 \pm 0.04	0.22
$NpCl_3 \cdot 4CH_3CN$	3.58 \pm 0.04	0.79 \pm 0.08	\sim 0

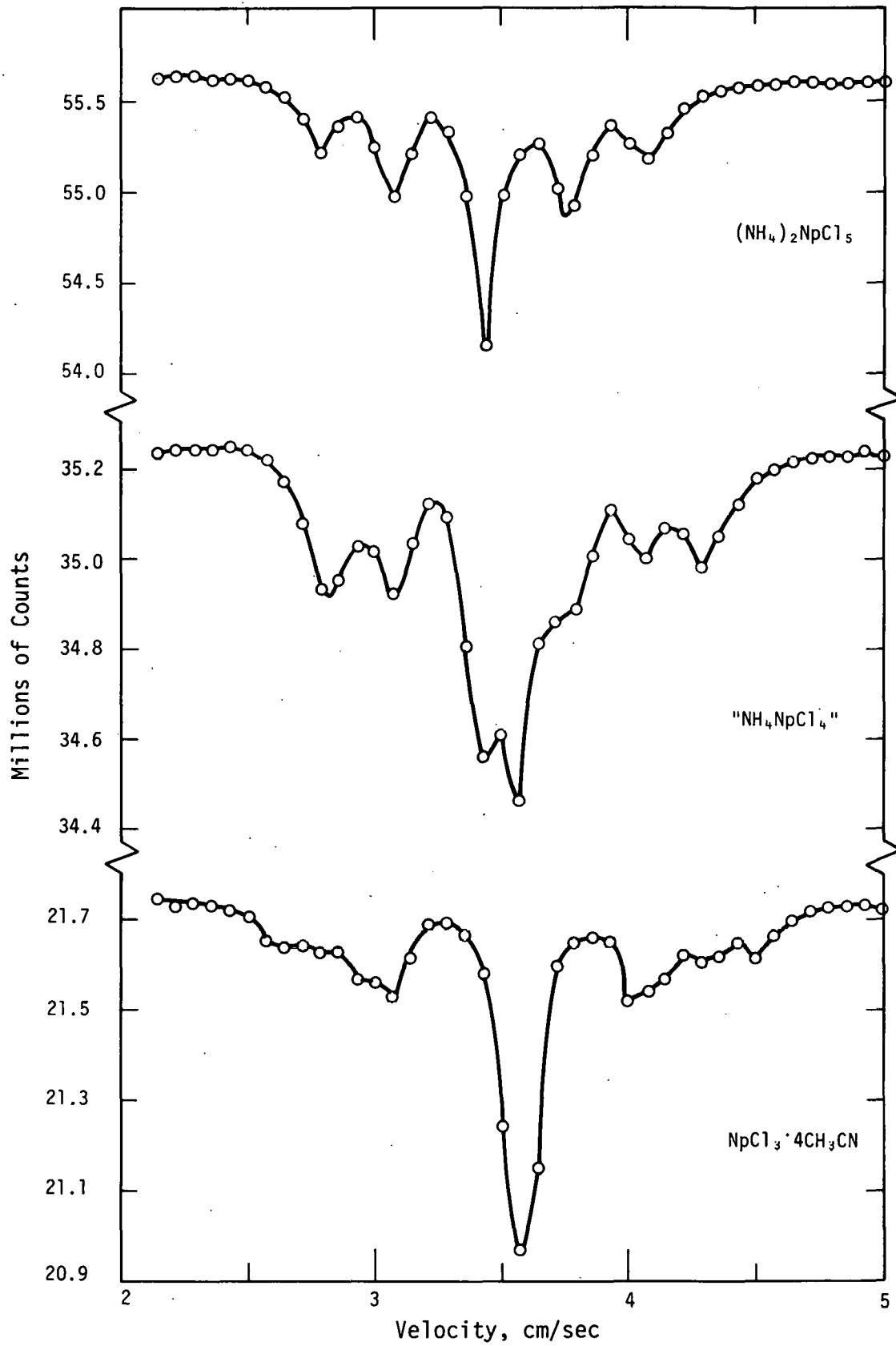


FIGURE 1. Mössbauer Spectra of (a) $(\text{NH}_4)_2\text{NpCl}_5$ (b) $''\text{NH}_4\text{NpCl}_4''$ (c) $\text{NpCl}_3 \cdot 4\text{CH}_3\text{CN}$

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