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MÖSSBAUER SPECTRA AND MAGNETIC SUSCEPTIBILITIES OF
 Cs_2NpCl_6 , $(\text{TMA})_2\text{NpCl}_6$, and $(\text{TEA})_2\text{NpCl}_6$

by

D. G. Karraker and J. A. Stone

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

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A paper proposed for publication in
Physical Review B

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ABSTRACT

Magnetic susceptibility measurements of Cs_2NpCl_6 , $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$, and $[(\text{CH}_3)_4\text{N}]_2\text{NpCl}_6$ from 2.5 to 70 K show that the Γ_8 ground level of the Np^{4+} ion is split by 5-10 cm^{-1} in the first two compounds because of distortions from octahedral symmetry in these crystals. The Γ_8 level in $[(\text{CH}_3)_4\text{N}]_2\text{NpCl}_6$ is not split, and the measurements agree well with first-order theory for $x = 0.39$ and $g_J = 0.60$. The Mössbauer spectra at 4.2 K of $[(\text{CH}_3)_4\text{N}]_2\text{NpCl}_6$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$ are magnetically split, with a small quadrupole interaction. The spectrum of $[(\text{CH}_3)_4\text{N}]_2\text{NpCl}_6$ shows deviations from isotropic magnetic splitting that may be caused by interactions within the degenerate Γ_8 level. The Mössbauer spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$ is consistent with two nonequivalent Np^{4+} sites. The Mössbauer spectrum of Cs_2NpCl_6 is obscured by intermediate relaxation effects.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-765R00001 with the U.S. Department of Energy.

INTRODUCTION

The neptunium(IV) ion in an octahedral field has been studied extensively by optical spectra¹⁻⁴ and electron paramagnetic resonance.^{5,6} The major interest is in the properties of the Γ_8 quartet ground crystal field level that was identified in earlier work.¹⁻⁶ This paper reports additional information obtained from low-temperature magnetic susceptibilities and Mössbauer spectra on Cs_2NpCl_6 , $[(\text{CH}_3)_4\text{N}]_2\text{NpCl}_6$, and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$. The structures of these compounds are inferred from their isostructural uranium and plutonium analogues and the infrared spectral studies.⁷

The Np^{4+} ion is located at the body center of an octahedron of six Cl^- ions in these three compounds. $(\text{TMA})_2\text{NpCl}_6$ [TMA refers to $(\text{CH}_3)_4\text{N}^+$] has a face-centered cubic cell (O_h) with the Np^{4+} ion at a point of full cubic symmetry.⁸ $(\text{TEA})_2\text{NpCl}_6$ has an orthorhombic (D_{3d}) cell that differs from $(\text{TMA})_2\text{NpCl}_6$ by the greater space occupied by the $(\text{C}_2\text{H}_5)_4\text{N}^+$ cations.⁹ Cs_2NpCl_6 has a trigonal cell (D_{3d}), and the NpCl_6^{2-} octahedron is slightly elongated on one axis.^{8,10} The distortions in the structures of Cs_2NpCl_6 and $(\text{TEA})_2\text{NpCl}_6$ may be expected to cause a slight splitting of the Γ_8 quartet into Γ_6 and Γ_7 doublets.^{2,3,7} The splitting can be observed by magnetic measurements.

EXPERIMENTAL

Polycrystalline samples of R_2NpCl_6 and R_2ThCl_6 were prepared by an adaptation of the method of Ryan,¹¹ and the identities of the compounds were confirmed by X-ray powder patterns. Magnetic susceptibilities were measured with a Foner-type vibrating sample magnetometer in a field of 10 kOe over the temperature range of 2.5-70 K, as previously reported in the study of Pu^{4+} analogues.¹² The Mössbauer spectra of the R_2NpCl_6 compounds were taken at 4.2 K with a constant-temperature spectrometer and from 4.2 to 70 K with a variable-temperature spectrometer. The spectrum of Cs_2NpCl_6 at 2.5 K was also recorded. Details of the techniques used for Mössbauer spectra have been published.¹³

RESULTS AND DISCUSSION

Magnetic Susceptibilities

The inverse magnetic susceptibilities of Cs_2NpCl_6 , $(TMA)_2NpCl_6$, and $(TEA)_2NpCl_6$ are shown graphically in Figs. 1-3. The constants were obtained by fitting the data to the Curie-Weiss expression $\chi = C/(T+\theta)$ shown in Table 1. The data for Cs_2NpCl_6 and $(TEA)_2NpCl_6$ exhibit two regions of Curie-Weiss behavior below 70 K; $(TMA)_2NpCl_6$ follows a single Curie-Weiss law from 2.5 to 66 K. From group theory, a Γ_8 quartet must split into two Kramers doublets in any symmetry lower than cubic. Thus, the shapes of the reciprocal susceptibility curves for Cs_2NpCl_6 and $(TEA)_2NpCl_6$ are consistent with each having a Γ_8 ground-level split by a small distortion from octahedral symmetry about the Np^{4+} ion. The

breaks in the curves correspond to splittings of 5-10 cm^{-1} . Additional evidence for splittings of this magnitude is found in the optical³ and infrared spectra⁷ of Cs_2NpCl_6 and $(\text{TEA})_2\text{NpCl}_6$ and is expected from the noncubic crystal structures. In contrast to this behavior, the reciprocal susceptibility of $(\text{TMA})_2\text{NpCl}_6$ is linear down to 2.5 K, indicating that distortions from octahedral symmetry are very small or absent; this observation is consistent with the cubic crystal structure of the compound and with an O_h site symmetry of the Np^{4+} ion. $(\text{TMA})_2\text{NpCl}_6$ is inferred to have an unsplit Γ_8 ground level, from the general similarity of the NpCl_6^{2-} complex in the three compounds.

The low-temperature magnetic properties of the ${}^4I_{9/2}$ ground state of Np^{4+} are determined by the crystal field. For an octahedral field, the magnetic properties can be calculated from the tables of Lea, Leask, and Wolf (LLW)¹⁴ and the analysis of the magnetic properties of Γ_8 levels by Bleaney.¹⁵ The crystal field Hamiltonian for cubic point symmetry¹⁴ is

$$H = A_4 \langle r^4 \rangle \beta (O_4^0 + 5 \cdot O_4^4) + A_6 \langle r^6 \rangle \gamma (O_6^0 - 21 \cdot O_6^4)$$

where $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are the fourth- and sixth-order crystal field parameters; β and γ , the fourth- and sixth-order operator equivalent factors; $\langle r^n \rangle$, expectation values for the 5f electrons; and O_n^m , the equivalent tensor operators. LLW defines the parameter x by

$$\frac{x}{1 - |x|} = \frac{F(4)\beta A_4 \langle r^4 \rangle}{F(6)\gamma A_6 \langle r^6 \rangle}$$

where $F(4)$ and $F(6)$ are constant factors for the matrix elements of the fourth- and sixth-order operators of each J state. The parameter x specifies the ratio of the crystal field parameters, and LLW tabulates eigenvectors for the $J = 9/2$ state of the form

$$A = a_1 |\pm^9/2\rangle + a_2 |\pm^1/2\rangle + a_3 |\mp^7/2\rangle$$

$$B = b_1 |\pm^5/2\rangle + b_2 |\mp^3/2\rangle$$

where $|\pm^\ell/2\rangle$ specifies the $|J_z\rangle$ vector and a_i and b_i depend upon the value of x . For a particular value of x (Reference 15),

$$\mu_{\text{eff}} = [({}^5/6)(A^2+B^2)]^{1/2} g_J$$

Carrying out this calculation for values of x from 0 to 1 shows that the square root factor varies only from 3.66 to 3.82. This variation shows that the value of x has only a minor effect on the magnetic moment. If the free-ion g_J value of $8/11$ is assumed, μ_{eff} ranges from 2.7 to 2.8, compared with the experimental value for $(\text{TMA})_2\text{NpCl}_6$ of $2.28 \mu_B$.

Edelstein, Kolbe, and Bray,⁶ in their analysis of ESR spectra, allowed g_J to vary to obtain best-fit values for g_J , which range from 0.55 to 0.60. For this range of g_J , μ_{eff} is calculated to be from 2.0 to $2.3 \mu_B$, which agrees well with the experimental μ_{eff} .

After a value for x is selected, the experimental value of μ_{eff} can be used to obtain g_J . Menzel and Gruber³ derived

a value of $x = 0.39$ from optical studies. A magnetic study of the Pu^{4+} analogues^{12,16} found $A_4 \langle r^4 \rangle = 3.5 A_6 \langle r^6 \rangle$, which corresponds to $x = 0.34$ for the Np^{4+} ion. (Since the crystal field parameters are determined by the environment of the ion, their variation between analogues Np^{4+} and Pu^{4+} compounds should be small.) If the value $x = 0.39$ is selected, then g_J is 0.60, which agrees well with the value obtained from ESR data.⁶

Mössbauer Spectra

Mössbauer spectra of Cs_2NpCl_6 , $(\text{TMA})_2\text{NpCl}_6$, and $(\text{TEA})_2\text{NpCl}_6$, at 4.2 K, are shown in Fig. 4. The three spectra are markedly different from each other and are characteristic of their respective compounds, as determined by the reproducibility of the spectra from multiple preparations of each compound. The dominant features of the spectra (the spans of the hyperfine patterns and the number of lines) are characteristic of magnetic hyperfine splitting.¹⁷ The magnetic splitting does not result from a ferromagnetic or antiferromagnetic state, since the susceptibility data show that the compounds are paramagnetic at 4.2 K. Instead, the observed splitting at 4.2 K is attributed to slow paramagnetic relaxation rates. This phenomenon is well known in iron and rare earth Mössbauer spectra¹⁸ and has been noted previously for other neptunium compounds.^{19,20} The possibility of relaxation effects is confirmed by spectra at higher temperatures where faster relaxation rates are present. For each of the compounds, the magnetic splitting disappears and is replaced by a broadened

single line above 20 K. The very broad, unresolved spectrum of Cs_2NpCl_6 at 4.2 K is apparently due to an intermediate relaxation rate. For Cs_2NpCl_6 , the spectrum at 2.5 K is practically identical to that at 4.2 K.

The spectrum of $(\text{TMA})_2\text{NpCl}_6$ can be interpreted as magnetically split, with a small quadrupole interaction. The Mössbauer constants for this spectrum analyzed in this fashion are $\delta = -0.66$ cm/sec, $g_0\mu_N H_{\text{eff}} = 7.83$ cm/sec, and $\frac{1}{4} \text{eqQ} = 0.091$. However, detailed examination of the spectrum shows deviations from an isotropic magnetic-splitting pattern. The hyperfine pattern expected for pure isotropic splitting¹⁷ is shown for comparison at the top of Fig. 4. Neither the line spacings nor the intensities of the $(\text{TMA})_2\text{NpCl}_6$ spectrum are consistent with the isotropic splitting patterns, and the deviations cannot be explained by quadrupole splitting. Bleaney¹⁵ has shown theoretically that anisotropic magnetic hyperfine splitting and small quadrupole interactions can be expected in a pure Γ_8 level, particularly when unequal magnetic field splitting occurs. Unequal splitting of the Γ_8 level in the magnetic field may be the cause of the anomalies in the $(\text{TMA})_2\text{NpCl}_6$ spectrum.

The Mössbauer spectrum of $(\text{TEA})_2\text{NpCl}_6$ is quite complex, with about twice the number of lines expected from a magnetically split spectrum. The optical absorption spectrum² at 4.2 K is interpreted as showing Np^{4+} ions in two nonequivalent sites. This interpretation is consistent with the Mössbauer spectrum,

analyzed in terms of two superposed magnetically split spectra with an appreciable quadrupole contribution. The following Mössbauer constants give the most satisfactory fit to the spectrum: for one site, $\delta = 0.75$ cm/sec, $g_0 \mu_N H_{\text{eff}} = 5.78$ cm/sec, and $\frac{1}{4} \text{eqQ} = 0.33$ cm/sec; for the other site, $\delta = 0.71$ cm/sec, $g_0 \mu_N H_{\text{eff}} = 6.26$ cm/sec, and $\frac{1}{4} \text{eqQ} = 0.27$ cm/sec. As with $(\text{TMA})_2\text{NpCl}_6$, the line spacings and intensities are not consistent with the isotropic splitting pattern assumed in the analysis and, therefore, may be modified by a more detailed analysis. However, the spectrum does confirm the presence of two Np^{4+} sites found by optical spectroscopy.²

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total ground state splitting of only 145 cm^{-1} , probably at least a factor of five too small.

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TABLE 1. Magnetic Constants for R_2NpCl_6

Compound	Temperature Range (K)	C^a (emu/mole)	Θ (K) ^a	μ_{eff} (μ_B)
Cs_2NpCl_6	2.5 - 8	0.40	0.65	1.80
	6 - 45	0.66	5.1	2.30
	45 - 75	1.18	40	3.07
	95 - 303 ^b	1.14	65	3.02
$(TMA)_2NpCl_6$	2.5 - 65	0.643	0.25	2.28
$(TEA)_2NpCl_6$	2.5 - 15	0.43	1.1	1.86
	15 - 70	0.73	11	2.41

a. $\chi_m = C/(T + \Theta)$.

b. K. Bagnall and J. B. Laidler, J. Chem. Soc. A 1966, 516 (recalculated).

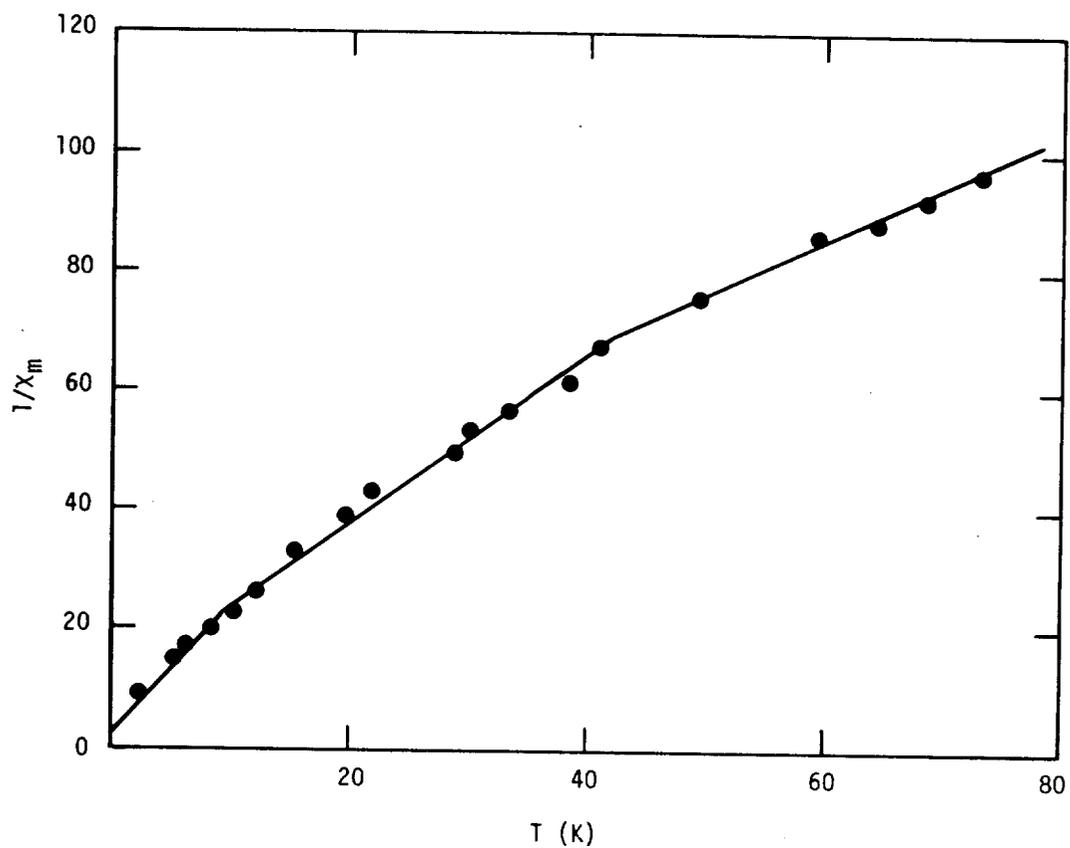


FIGURE 1. Inverse Magnetic Susceptibility of Cs_2NpCl_6

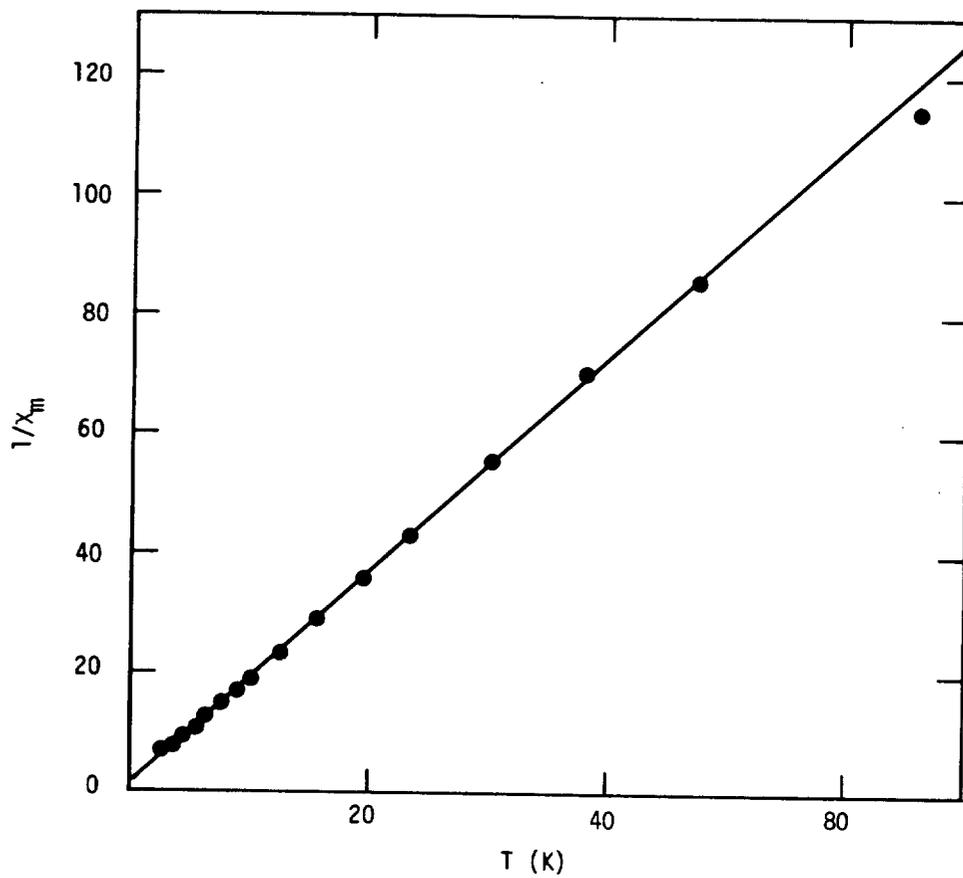


FIGURE 2. Inverse Magnetic Susceptibility of $(TMA)_2NpCl_6$

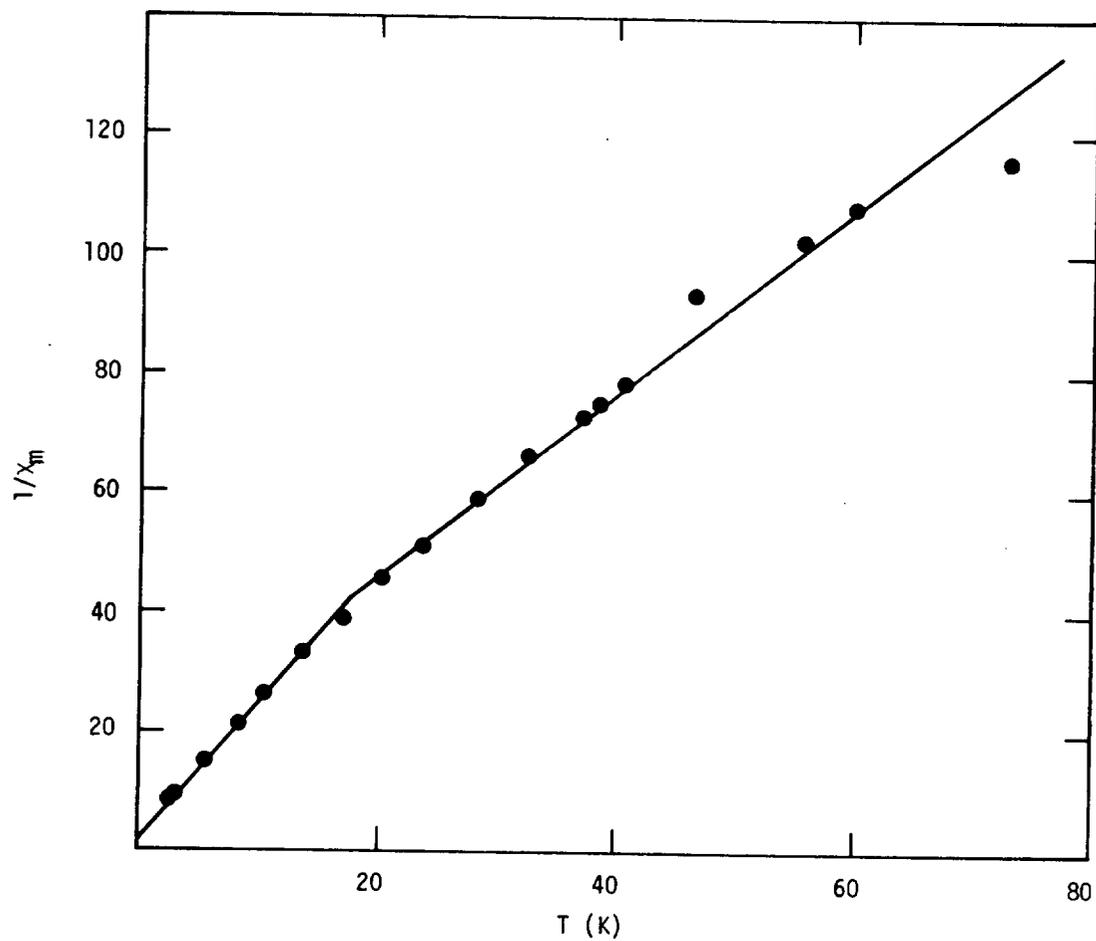


FIGURE 3. Inverse Magnetic Susceptibility of $(\text{TEA})_2\text{NpCl}_6$

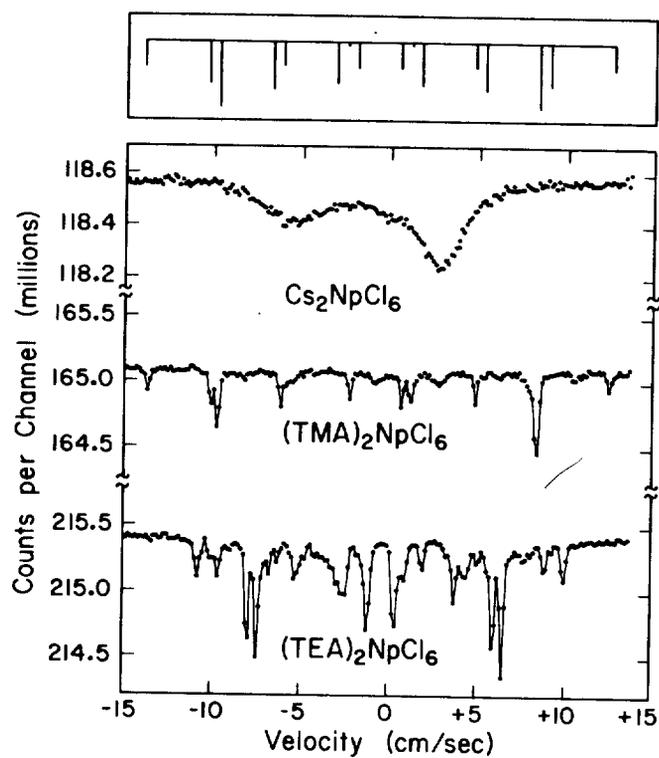


FIGURE 4. Mössbauer Spectra of Cs_2NpCl_6 , $(\text{TMA})_2\text{NpCl}_6$, and $(\text{TEA})_2\text{NpCl}_6$