Inorg. Chem. **1980**, *19*, 3545-3547 **3545**

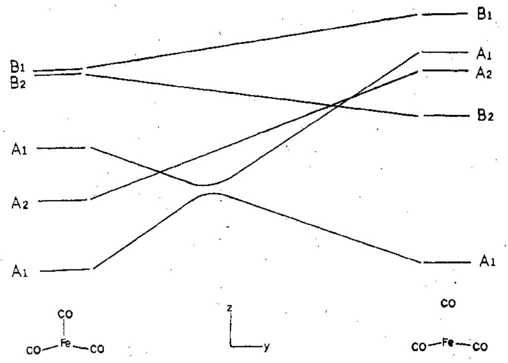

Figure 2. Correlation diagram, C_{2v}, for $Fe(CO)_3^- \rightarrow Fe(CO)_2^-$.

strument parameters and the method of data analysis have been described previously.[8] The low-resolution photodissociation spectra were taken with a 1000-W xenon arc lamp and a Schoeffel Instrument Corp. monochromator; 1.8- and 3.0-nm slits were employed, with 23.8- and 39.6-nm full width at half-maximums, respectively. Results agreed with previous work.[8,10-14] The high-resolution spectra were taken by using a Coherent Radiation Model 590 dye laser, pumped by all lines from an argon ion laser, Coherent Radiation Model CR-12. Rhodamine 6G and Rhodamine 640 were the dyes used to obtain the spectra. Two different electronic transitions and some vibrational structure can be seen in the high-resolution photodissociation spectrum of $Fe(CO)_3^-$ to $Fe(CO)_2^-$ which extends from 440 to 920 nm, with a strong peak at 627.8 nm having a width at half-maximum of 15 nm (Figure 1).

Three vibrational bands can be distinguished within the narrow peak, with maxima at 598, 614, and 627.8 nm. Their spacing corresponds to vibrations of 435 and 359 cm^{-1}, presumably a metal carbonyl stretch. While M–C stretches and M–C–O bends are expected to occur around 650–350 cm^{-1} in metal carbonyls, as observed[15] for $Co(CO)_4$, an exact prediction cannot be made for these ions.[16]

The photodissociation of $Fe(CO)_4^-$ and that of other metal carbonyl anions has been attributed to the metal to ligand charge-transfer transitions that occur at high energies,[13] although the lowest energy bands in $Fe(CO)_5$ itself have been identified as ligand field transitions.[17] Tricoordinate molecules such as $Fe(CO)_3^-$ are predicted to have C_{2v} symmetry while the product ion $Fe(CO)_2^-$ is expected to be linear.[3,4] The lowest optical transition in $Fe(CO)_3^-$, $A_1 \rightarrow A_2$, is forbidden. (See Figure 2.) The lowest *allowed* transition occurs to a level whose energy dependence upon bond angle is quite different from that in the ground state. This $A_1 \rightarrow A_1$ transition therefore has large nondiagonal Franck–Condon factors, causing the transition to be very broad. This is consistent with the photodissociation extending from 440 to 920 nm. The absorption corresponding to the peak at 627.5 nm is the second allowed transition $A_1 \rightarrow B_1, B_2$. It occurs to a level which has an energy–geometry dependence similar to that of the ground state. This band is therefore narrow and higher in intensity.

The A_1 excited state produced by the transition corresponding to the broad absorption connects with the ground state of the products through an avoided crossing, as shown in Figure 2. The B_1, B_2 states do not correlate directly with the ground state of the linear product $Fe(CO)_2^-$ which has A_1 symmetry. These excited states must thus also undergo a radiationless transition before dissociation can take place. The radiationless transitions must be fairly fast, however, since the vibrational bands appear to be broadened. Calculations of the line broadening due to Zeeman splitting and to rotational broadening indicate that the first effect is very small, with the magnitude of the magnetic fields used. The rotational broadening based on C_{2v} geometry, is estimated at 4.4 cm^{-1}, much smaller than that observed.[18]

In an ICR spectrometer it is often possible to observe the direction of the transition moment relative to the direction of dissociation.[19] Thus, a decrease in product signal size change may be observed for different orientations of plane polarized light. The signal for $Fe(CO)_3^-$ *production* has a dependence upon the orientation of polarized light, requiring a nontetrahedral geometry[8] of $Fe(CO)_4^-$. However, the production of $Fe(CO)_2^-$ from $Fe(CO)_3^-$ does not show any additional dependence.

The $A_1 \rightarrow A_1$ transition is allowed for light polarized along the C_2 axis (the z direction). For this transition, a greater loss in ion product signal is expected for light polarized perpendicular to the trapping plates. This is not observed, possibly because in this spectral region the reaction occurs with very little excess translational energy.

The $A_1 \rightarrow B_2$ transition in $Fe(CO)_3^-$ is allowed for y polarized light, while the $A_1 \rightarrow B_1$ occurs with x polarized light. Thus for any orientation of the ion in the cell, dissociation should be isotropic and no polarization dependence would be expected for these transitions, as is observed. This is consistent with the expected C_{2v} geometry of the molecule. The transitions occurring in a C_{3v} molecule would be expected to show a dependence on polarization.

In summary, the photodissociation spectrum for $Fe(CO)_3^- \rightarrow Fe(CO)_2^-$ has been studied at high resolution. A resonance at about 630 nm appears to have vibronic structure and is suggested to be an $A_1 \rightarrow B_1, B_2$ transition embedded in a broad $A_1 \rightarrow A_1$ transition. Assignment of these transitions could be made consistent with expected geometry changes and energy levels on the basis of theoretical predictions. This constitutes one of few direct spectral observations of a highly unsaturated transition-metal complex.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and to Imperial Oil Limited for a Graduate Fellowship. We thank Drs. Burdett and Turner for communicating results before publication.

Registry No. $Fe(CO)_3^-$, 53221-56-0; $Fe(CO)_2^-$, 71701-39-8.

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Preparation and Mössbauer Spectra of Neptunium(III)-Alkali Metal-Chloro Compounds[1]

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Drozdzynski has recently reported[2] the preparation and some properties of uranium(III)–chloro compounds of the

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Table I. Analytical Data for Chloro Compounds

	wt % Np		wt % Cl		Cl/Np mole
	calcd	found	calcd	found	ratio
K_2NpCl_5	48.10	47.2	36.0	35.8	5.06
$(NH_4)_2NpCl_5$	52.61	50.3	39.40	37.6	4.99
Rb_2NpCl_5	40.47	39.8	30.32	29.8	5.01
$KNpCl_4 \cdot CH_3CN$	51.52	51.1	30.93	31.1	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	24.9	3.96
$NpCl_3 \cdot 4CH_3CN$	46.71	47.1	20.96	21.2	3.00

general formulas M_2UCl_5 and MU_2Cl_7 (M = K, NH_4, or Rb) by reducing a 50/1 acetonitrile–propionic acid solution of MCl and UCl_4 with zinc amalgam. The preparation of neptunium(III)–chloro compounds of the compositions M_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$ by the same method and their study by Mössbauer spectroscopy are reported here. Preparations analyzing as $MNpCl_4 \cdot xCH_3CN$ (x = 1, 2) had Mössbauer spectra that could be reproduced by the spectrum of a mixture of M_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$. The $MNpCl_4 \cdot xCH_3CN$ preparations are therefore presumed to be mixtures.

Experimental Section

Reagents. $NpCl_4$ was prepared by reacting neptunium(V) hydroxide with hexachloropropene and was sublimed under 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 CP grade and were dried by heating overnight at 110 °C and cooled in an argon atmosphere. Glacial acetic acid and propionic acid (CP grade) were degassed with nitrogen and used without further purification. All purifications and reactions were performed in a dry argon atmosphere.

M_2NpCl_5, $MNpCl_4$. The general procedure is described by Drozdzynski.[2b] Ca. 2 g of $NpCl_4$ and 1–2 g of MCl were dissolved in 40–50 mL of 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 lemon yellow precipitate appeared, normally 5–15 min. 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 under vacuum at room temperature. Products with a Cl/Np ratio of 4 still retained some acetonitrile after this treatment.

MNp_2Cl_7. Drozdzynski[2b] reports the preparation of MU_2Cl_7 (Cl/U = 3.5) by modifying the previous procedure to have excess UCl_4 present. Attempts to produce an MNp_2Cl_7 (Cl/Np = 3.5) product by following exactly the published procedure[2b] were unsuccessful; the product was still M_2NpCl_5.

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

Analyses. Neptunium was determined by α counting and corrected for ^{238}Pu from α 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; the precision of analyses is about 3% of the value measured. Mössbauer spectra were obtained as previously reported.[4] The source was a 5% ^{241}Am–Th metal alloy. The source and absorber were at 4.2 K for Mössbauer measurements. Attempts to obtain X-ray powder diffraction patterns for the products were unsuccessful.

Results and Discussion

The Mössbauer spectra of the neptunium(III)–chloro compounds all show the characteristic "five-line" pattern resulting from quadrupole splitting. The Mössbauer spectrum of K_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 lines[5] 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.

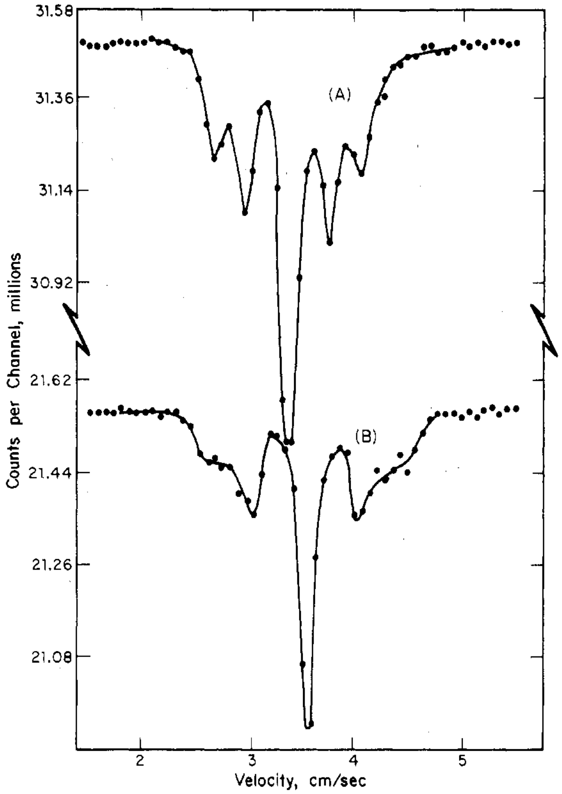

Figure 1. Mössbauer spectra of (A) K_2NpCl_5 and (B) $NpCl_3 \cdot 4CH_3CN$.

Table II. Mössbauer Parameters of Neptunium(III)–Chloro Compounds

	isomer shift, cm/s	quadrupole coupling const, $^1/_4eqQ$, cm/s	asymmetry parameter η
K_2NpCl_5	3.40 ± 0.04	0.59 ± 0.04	0.37 ± 0.04
$(NH_4)_2NpCl_5$	3.44 ± 0.04	0.56 ± 0.04	0.22 ± 0.04
Rb_2NpCl_5	3.47 ± 0.04	0.70 ± 0.04	0.22 ± 0.44
$NpCl_3 \cdot 4CH_3CN$	3.58 ± 0.04	0.79 ± 0.08	0.26 ± 0.10

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 small asymmetry parameter determined from the Mössbauer spectrum (Figure 1B) indicates that Np^{3+} ion in $NpCl_3 \cdot 4CH_3CN$ is in a site with near-axial symmetry. A possible structure of $NpCl_3 \cdot 4CH_3CN$ might be one of the several derived from a trigonal prism, with a ligand coordinating through a face of the prism.

The Mössbauer spectra of the "$MNpCl_4$" (Cl/Np = 4) products were similar to the M_2NpCl_5 spectra but showed

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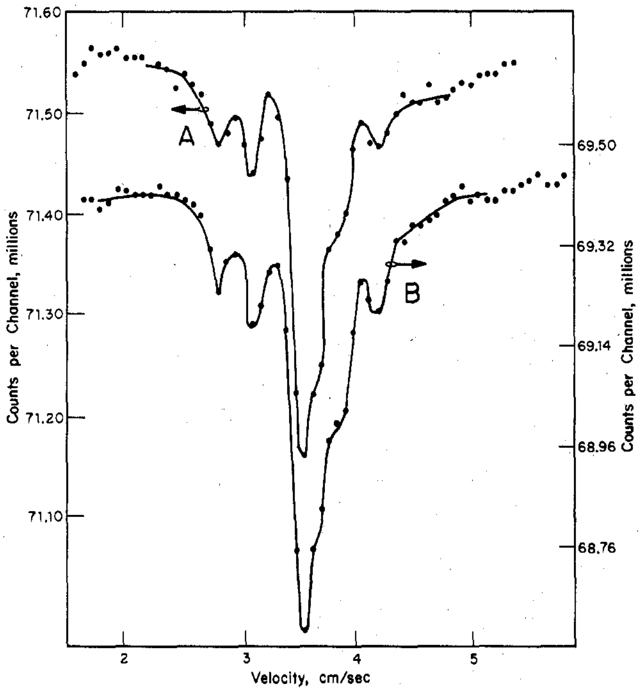

Figure 2. Mössbauer spectra of (A) "$KNpCl_4$" and (B) a mixture of K_2NpCl_5 and $NpCl_3\cdot 4CH_3CN$.

either broader lines or splitting of lines. An example of these spectra is shown in Figure 2A, for "$KNpCl_4$". The spectrum of "$KNpCl_4$" could be reproduced by the spectrum of an equimolar mixture of K_2NpCl_5 and $NpCl_3\cdot 4CH_3CN$ (Figure 2B). The obvious conclusion is that "$KNpCl_4$" is a mixture of K_2NpCl_5 and $NpCl_3\cdot 4CH_3CN$. It is still possible that the compound $KNpCl_4$ exists with Np^{3+} ions in two different sites. Unfortunately, repeated attempts to obtain X-ray powder diffraction patterns on these compounds failed. However, from the Mössbauer evidence, the existence of $MNpCl_4$ must be regarded as dubious.

Acknowledgment. The authors thank B. Tiffany for gas chromatographic analyses.

Registry No. K_2NpCl_5, 73284-55-6; $(NH_4)_2NpCl_5$, 73272-81-8; Rb_2NpCl_5, 73272-82-9; $NpCl_3\cdot 4CH_3CN$, 73272-83-0; $NpCl_4$, 15597-84-9.

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Single-Crystal Magnetic Susceptibility Study of the Linear-Chain Heisenberg Antiferromagnet Copper(II) Pyrazine Nitrate

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There is considerable interest in the magnetic properties of polynuclear and polymeric transition-metal complexes bridged by small diaza heterocyclic molecules[2,3] such as pyrazine. The complex dinitro(pyrazine)copper(II), $Cu(pz)(NO_3)_2$, consisting of linear chains of copper(II) ions bridged by 1,4-pyrazine molecules (Figure 1), is of interest in this context. The bulk magnetic susceptibility of this compound shows a broad maximum at about 7 K[4-6] with no evidence of any long-range interchain interactions down to 0.18 K. This then makes $Cu(pz)(NO_3)_2$ a very suitable system for the study of magnetic exchange interactions in an isolated linear chain of copper(II) ions.[7]

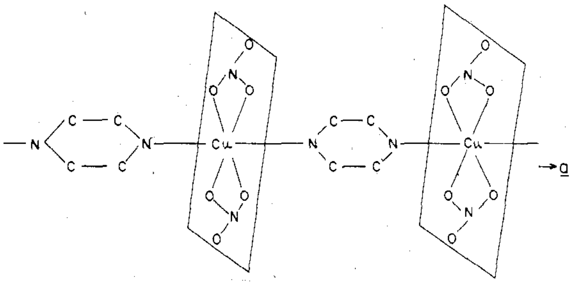

Figure 1. Pyrazine bridging in $Cu(pz)(NO_3)_2$.

In an earlier study the average susceptibility, $\bar{\chi}$, of $Cu(pz)(NO_3)_2$ was reported to 2 K, and the data were analyzed in terms of an antiferromagnetic Ising chain with $J = -6.0$ cm^{-1}.[4] Subsequently a "single-crystal" study was performed by Losee and co-workers[5] on a bundle of crystals all oriented along the a axis but with the b and c axes of the orthorhombic crystal randomly oriented.[8] The a axis of the crystal is also the direction of the linear chain, and so $\chi_{\parallel}$, the susceptibility parallel to the a axis, was χ_a and $\chi_{\perp}$, the susceptibility perpendicular to the a axis, was some average of χ_b and χ_c. The data were shown to be described by the isotropic Heisenberg model.[5] A further study of the bulk susceptibility also showed the behavior expected of an antiferromagnetic Heisenberg chain with $J/k = -5.5$ K.[6]

Single-crystal ESR data[9,10] on $Cu(pz)(NO_3)_2$ gives $g_a = 2.05$, $g_b = 2.27$, and $g_c = 2.06$, showing that the g anisotropy lies between the b axis and the ac plane. On this basis it would then be expected that χ_a and χ_c should be of similar magnitude and differ markedly from χ_b.

In the present work we report the determination of the principal crystal susceptibilities χ_a, χ_b, and χ_c of $Cu(pz)(NO_3)_2$ and analyze the data on the basis of the appropriate exchange model.

Experimental Section

Well-developed needle-shaped crystals of $Cu(pz)(NO_3)_2$ were grown by slow evaporation of an aqueous 1:1 solution of cupric nitrate and pyrazine.[8] Crystal axes were determined by Weissenberg and rotation X-ray photography. The principal crystal magnetic susceptibilities χ_a, χ_b, and χ_c were determined from measurement of the magnetic anisotropies $\chi_b - \chi_a$ and $\chi_b - \chi_c$ of the single crystal and the bulk susceptibility. The magnetic anisotropies of crystals weighing between 2–3 mg were measured by using the Krishan critical torque method, between 4.8 and 100 K, with equipment described earlier.[11] Measurements were made with the a and c axes vertical, giving $\chi_b - \chi_c$ and $\chi_b - \chi_a$, respectively. Measurements on three individual crystals did not show a scatter exceeding 2%. The magnetic fields used for the critical torque experiment ranged between 0.2 and 0.4 T. The

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