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Properties of $NH_4Ni[S_2C_2(CN)]_2 \cdot H_2O$

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Single crystals of $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$ have been grown. The single-crystal resistivity in the high-conductivity direction ($\rho \simeq 20\ \Omega\,cm$) is the lowest observed for salts formed with the anion $\{Ni[S_2C_2(CN)_2]_2\}^-$. A phase transition is observed in both resistivity and magnetic susceptibility in the temperature range $200 > T > 130$ K. This transition is paralleled by several temperature-dependent absorptions in the infrared (IR). Resonance Raman spectroscopy suggests that these absorptions may be associated with A_g modes which become infrared active via a vibronic interaction. These observations are consistent with a dimerization on the anion stack with decreasing temperature.

I. INTRODUCTION

The properties of transition-metal dithiolene complexes have been studied extensively since their discovery in 1962.[1,2] The bis(dithiolene) complexes of the form $\{M[S_2C_2(CN)_2]_2\}^-$ (M = Ni, Pd, Pt) have been the subject of a number of experimental studies. X-ray results[3,4] show that the $\{Ni[S_2C_2(CN)_2]_2\}^-$ anions form stacks, which in all cases studied consist of dimers of anions. The molecular structure of the $\{Ni[S_2C_2(CN)_2]_2\}^-$ anion is shown in Fig. 1. The dimerized structure is consistent with the low electrical conductivity [σ_{RT} (compressed powder) $< 10^{-4}\ \Omega^{-1}\,cm^{-1}$] and the magnetic properties.[2] Although several highly conducting salts have been synthesized containing bis(dithiolene) complexes as the anion,[5,6] in every case the dominant charge transport was likely to occur along the cation stack. Recently, the synthesis of several high-conductivity salts of bis(dicyanoethylene dithiolate) complex monoanions was reported.[7] We present here a more detailed study of one of these salts, $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$. The single-crystal resistivity of this salt, $\rho(295\ K) \sim 20\ \Omega\,cm$, is the lowest single-crystal value reported for the bis(dithiolene) complex salts. Measurements of single-crystal electrical resistivity, static magnetic susceptibility, preliminary crystal-structure data, and infrared absorption measurements have been used to characterize this material. Resonance Raman spectroscopy was used to study the $\{Ni[S_2C_2(CN)_2]_2\}^-$ anion in solution.

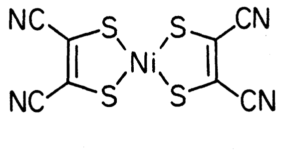

FIG. 1. Molecular structure of $\{Ni[S_2C_2(CN)_2]_2\}^-$.

II. EXPERIMENTAL

The dianion salt $(NH_4^+)_2\{Ni[S_2C_2(CN)_2]_2\}^{-2}$ was synthesized according to published procedures.[7] Single crystals of $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$ (I) were grown by electrodeposition. Two platinum electrodes were placed in an aqueous solution of 2×10^{-2} M $(NH_4^+)_2\{Ni[S_2C_2(CN)_2]_2\}^{-2}$ and 0.1 M urea. A voltage of 1.0 V was applied between the two electrodes. The desired compound (I) grew as crystals at the positive electrode, presumably according to the reaction

$$\{Ni[S_2C_2(CN)_2]_2\}^{-2} \rightarrow \{Ni[S_2C_2(CN)_2]_2\}^{-} + e^-$$

occurring at the platinum electrode. Typical elemental analysis agrees with the formula $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$ within experimental uncertainty. Preliminary x-ray-structure data and measured density to be discussed later are in excellent agreement with the formula of I. Crystals were stored in a moist (75% relative humidity) atmosphere to prevent dehydration.

Static magnetic susceptibility was measured by using a conventional Faraday balance apparatus. Low-temperature data were obtained by using an Air Products Helitran unit. Temperature at the sample was obtained by a direct calibration run during which a sensor located at the sample position was used to calibrate the GaAs sensor attached to the Air Products Helitran cold tip. This calibration was checked by measuring the magnetic susceptibility of $CuSO_4 \cdot 5H_2O$ and comparing data with published measurements on this compound.[8] Single-crystal resistivity measurements were made by using standard four-probe techniques. In both the magnetic susceptibility and resistivity measurements, samples were cooled in a moist atmosphere to prevent dehydration.

The infrared spectrum was recorded from 4000 to 500 cm^{-1} with a Perkin-Elmer model 521 spectrophotometer to an accuracy of about ± 2 cm^{-1}. The infrared spectral region from 500 to 130 cm^{-1} was studied using a Perkin-Elmer model 301 spectrophotometer in the double-beam mode. Under typical conditions the spectral resolution in this region was ~ 2 cm^{-1} and the frequency accuracy about ± 1 cm^{-1}. All infrared spectra were obtained using Nujol or perfluorocarbon mulls of the polycrystalline samples. Variable-temperature measurements were made on samples mounted in a Spectrim II closed-cycle cryostat (Cryogenic Technology).

The Raman measurements were made on a Spex Ramalog spectrometer equipped with photon-counting detection and an argon-ion laser excitation source. Dilute solutions of the sample were prepared using methanol, acetonitrile, and acetone-d_6 (deuterated acetone). Laser radiation at 4880 Å of about 200-mW power was used, together with a rotating sample cell. A substantial resonance Raman effect was observed under these conditions, and the solutions showed no evidence of photodecomposition. All of the Raman bands observed were strongly polarized (i.e., A_g modes).

III. RESULTS

A. Crystal structure

Preliminary crystal-structure information has been obtained on I.[9] The structure is orthorhombic ($a = 12.10$ Å, $b = 29.26$ Å, $c = 3.92$ Å, $d_{\text{calc}} = 1.795$ g/cm^3, and $d_{\text{obs}} = 1.79$ g/cm^3). The short c axis suggests that translationally equivalent anions are stacked plane to plane along c. The plane-to-plane separation of the $\{Ni[S_2C_2(CN)_2]_2\}^-$ planes is probably decreased from 3.92 Å by rotation out of the ab plane. Although this information is rather limited, two very important points emerge. The first is the uniform spacing of the anions along the c axis. The second is the likelihood that in the orthorhombic structure the anions stack forming a Ni-Ni chain. The Ni-Ni distance (3.92 Å) is unusually large for a nickel chain compound. Typical Ni-Ni distances in nickel chain compounds are in the range 3.15 to 3.55 Å,[10] so it is likely that Ni—ligand and ligand—ligand bonding, as well as nickel—nickel bonding, are important in stabilizing this structure.

B. Resistivity

A compressed-powder measurement of the resistivity at room temperature gave a value of ρ (powder) ~ 200 Ω cm. This is a considerably higher value than claimed in Ref. 7, but still a very small resistivity when compared with previously reported data.[2,3] Single-crystal resistivity was measured for current flow along the c axis. The temperature dependence of the c axis resistivity is shown in Fig. 2. As might be expected, the conductivity is activated at all temperatures. In addition, an unusual transition is indicated between ~ 220 and ~ 180 K. For $T > 230$ K, $\rho = \rho_0 e^{+\Delta_\rho/T}$ yields $\Delta_\rho = 2170$ K; for $T \leqslant 165$ K, $\Delta_\rho = 1390$ K. From Fig. 2, in the intermediate region 165 K $\leqslant T \leqslant$ 230 K, Δ_ρ is continuously changing and considerably smaller than at either higher or lower temperatures. A similar anomalous dependence of resistivity on temperature has been observed in $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$, where the resistivity is nearly temperature independent for 160 K $> T >$ 80 K.[11]

C. Magnetic susceptibility

Figure 3 shows the magnetic susceptibility of I corrected for $\sim 3\%$ spin-$\frac{1}{2}$ impurities. Fitting the

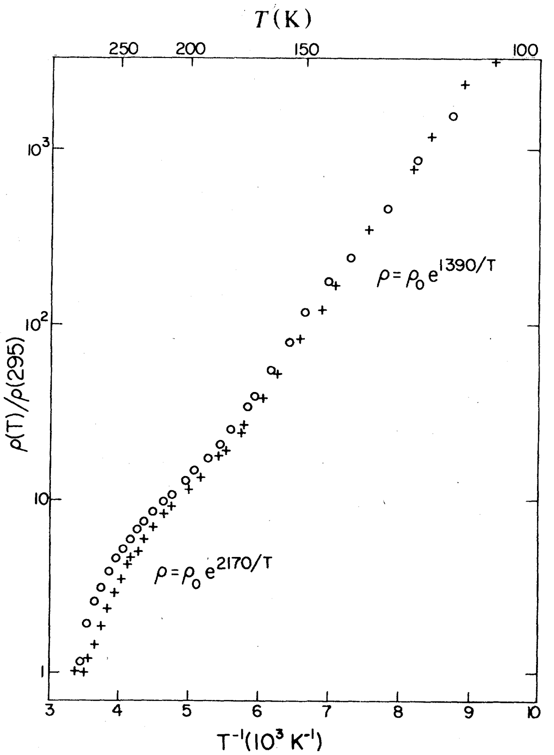

FIG. 2. Temperature dependence of the c-axis resistivity of $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$ normalized to ρ(295 K).

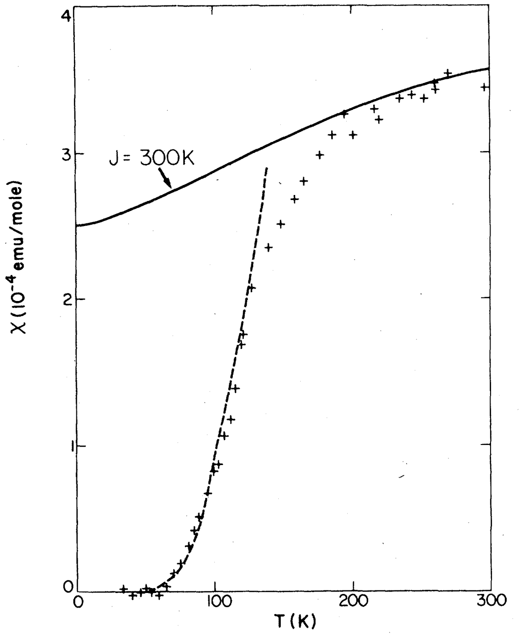

FIG. 3. Temperature dependence of the static magnetic susceptibility of $NH_4Ni[S_2C_2(CN)_2]_2\cdot H_2O$. The data have been corrected for contributions due to spin-$\frac{1}{2}$ impurities and corrected for core-level diamagnetism as explained in text. The magnetic susceptibility of the Bonner-Fisher calculation for the Heisenberg antiferromagnetic chain with $J = 300$ K is shown as the solid curve. The dashed curve is the fit to data using $\chi = Ce^{-\Delta/T}/T$ with $C = 2.40$ emu/mole and $\Delta = 570$ K.

low-temperature ($T < 25$ K) data to $\chi = \chi_0 + C/T$ also yields $\chi_0 = -1.34 \times 10^{-4}$ emu/mole, in good agreement with the value calculated from Pascal's constants ($\chi_{\text{dia}} = -151 \times 10^{-6}$ emu/mole).

The impurities produce a $1/T$ Curie tail in the low-temperature data, which has been removed. The strength of the $1/T$ Curie tail varied randomly from preparation to preparation, ranging from 1.5% to 3% spin-$\frac{1}{2}$ impurities; such a variation is consistent with the assignment of this term to impurities and crystalline imperfections. A description of the magnetic susceptibility over the entire temperature range will be presented later. It is clear from Fig. 3 that the susceptibility is activated, at least below ~ 130 K. The susceptibility is described quite well by $\chi = 2.4e^{-\Delta_m/T}/T$ (in emu/mole) with $\Delta_m = 570$ K.

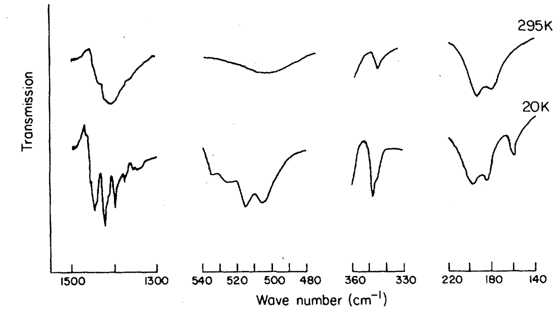

FIG. 4. IR absorption spectra of $NH_4Ni[S_2C_2(CN)_2]_2\cdot H_2O$ at 295 K (top curve) and 20 K (bottom curve).

D. IR absorption and Raman spectroscopy

The observations of a phase transition in the resistivity and magnetic-susceptibility measurements have been supplemented by a study of the temperature dependence of the infrared (IR) absorption spectrum. Figure 4 shows the measured absorption spectra of I at 295 and 20 K. The measured temperatures are accurate to ± 10 K or better. The appearance of new absorptions at 515, 347, and 160 cm^{-1} is clearly seen. The structure of the absorption near 1400 cm^{-1} also changes, developing considerable fine structure. The temperature dependence of the strength of the absorption at 1420 cm^{-1} is plotted in Fig. 5. The temperature dependence of the absorption at 1420 cm^{-1} was obtained by fitting the absorption spectra in the 1400-cm^{-1} region to four Gaussians. The relative strength of the 1420-cm^{-1} absorption was then defined as the fraction of the total absorption due to the 1420-cm^{-1} absorption. The observed temperature dependences are consistent with a phase transition occurring over a broad range of temperature.

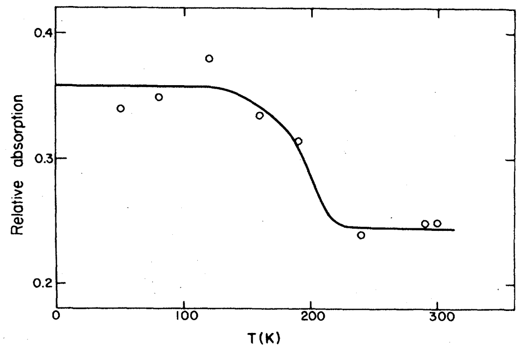

FIG. 5. Temperature dependence of the peak intensity of the 1420-cm^{-1} absorption in $NH_4Ni[S_2C_2(CN)_2]_2\cdot H_2O$.

TABLE I. Correlation between observed Raman modes (A_g) and those infrared modes found to have a strong temperature dependence. Frequencies are in cm^{-1}.

Raman modes	IR modes	Assignment
2215	...	$\nu(\mathrm{C{\equiv}N})$
1467	1420	$\nu(\mathrm{C{=}C})$
1057	...	$\nu(\mathrm{C{-}S})$
532	517	$\nu(\mathrm{Ni{-}S})$
497	...	$\nu(\mathrm{Ni{-}S})$
353	347	$\nu(\mathrm{Ni{-}S})$
180	160	Ring bend

The resonant Raman bands found in the various dilute solutions of $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^-$ are listed in Table I. The normal coordinate analysis of a similar anion indicates a large amount of mixing between the various molecular vibrational motions[12]; hence, for convenience we approximate the assignment of the observed bands by noting only the predominant mode. Accordingly, the 2215-cm^{-1} band is assigned to the symmetric C≡N stretching mode, the 1467-cm^{-1} band to the symmetric C=C stretching mode, the 1057-cm^{-1} band to the symmetric C–S stretching mode, the 532-, 497-, and 353-cm^{-1} bands to modes involving symmetric Ni–S stretching motions, and the 180-cm^{-1} band to a symmetric ring bending mode.

IV. DISCUSSION

A. Phase transition

One-dimensional systems consisting of stacks or chains exhibit well-known instabilities to phase transitions[2]—usually referred to as the Peierls transition. The tendency for $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^-$ anions to exist as dimers in other compounds makes it likely that I will exhibit a lattice instability with a transition to a dimerized chain at reduced temperatures.

Bozio and Pecile[13] have studied the temperature dependence of the IR absorption in a series of alkali-metal (7,7,8,8-tetracyanoquinodimethane) (TCNQ) salts in which phase transitions to dimerized chains are known to occur. Their interpretation of the temperature-dependent bands which grow in intensity in parallel with the phase transition is that (in the TCNQ salts) these bands are due to vibronic activation of totally symmetric A_g modes. The D_{2h} symmetry of $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^-$ gives 33 normal modes. The calculated infrared-active modes[12] account for all the observed absorptions in the IR at room temperature except for absorptions which are assigned to the cation or H_2O.

The A_g modes in $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^-$ have been identified by resonance Raman spectroscopy and are given in Table I. As indicated in Table I, the additional IR modes which are strongly temperature dependent can be correlated with observed A_g modes. The detailed theory of the vibronic activation in one-dimensional solids has been developed by Rice.[14] For a linear chain undergoing a charge-density wave (CDW) distortion, the A_g modes are predicted to produce absorptions polarized along the chain axis at a frequency $\tilde{\omega}_n$ shifted from the bare frequency ω_n according to

$$\tilde{\omega}_n = \omega_n \left[1 - \frac{\lambda_n}{\lambda}\left(1 - \frac{V}{\Delta}\right) - \lambda_n \left(\frac{\omega}{2\Delta}\right)^2 f\left(\frac{\omega}{2\Delta}\right)\right]^{1/2},$$

where $2V$ is the gap in the electron density of states in the absence of electron-phonon coupling, 2Δ is the gap with electron-phonon coupling, λ_n is the dimensionless electron-phonon coupling constant, $\lambda = \sum_n \lambda_n$ (where the summation is over the A_g modes), and $f(X) = \tan^{-1}[X/(1-X^2)^{1/2}]/[X(1-X^2)^{1/2}]$. Thus, in the absorption spectra, the absorption is shifted to lower frequency from that observed for the A_g mode in the Raman spectra, in agreement with the observations of Table I. The magnitude of the vibronic effect depends upon the magnitude of the λ_n for each mode. From this, one infers that the λ_n for the A_g modes at 2215, 1057, and 497 cm^{-1} are very small.

B. Electrical and magnetic properties

In a discussion of the electrical and magnetic properties, I will be considered to be a one-dimensional solid. This may be a poor approximation since the observed anisotropy in the conductivity at room temperature is quite small (~10–20). The phase transition and the marked tendency of $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^-$ anions to stack in dimerized chains suggest, however, that I is dominated by one-dimensional interactions.

It has been shown that at low temperatures $\chi = 2.40 e^{-\Delta_m/T}/T$ with $\Delta_m = 570$ K. The activation energy for conductivity $\Delta_\rho = 1390$ K so that a simple semiconductor model cannot be applied. This suggests that electron-electron correlation may be important and that some form of the one-dimensional Hubbard model might be a good starting point for describing I.

For a description of the low-temperature properties of I, a reasonable starting point is the dimerized Hubbard chain. The susceptibility of $\frac{1}{2}N$ dimers[15] at low temperature ($kT << 4t^2/U$, $4t << U$) is

$$\chi = \frac{1.50}{T} \exp\left(\frac{-4t^2}{(kTU)}\right) \qquad (1)$$

expressed in units of emu/mole, where t is the electron-transfer integral and U is the on-site electron-electron repulsion, so that this is of the correct form to describe the low-temperature magnetic susceptibility.

It was mentioned previously that the low-temperature magnetic susceptibility of I was described by $\chi = 2.4e^{-570/T}/T$ emu/mole, so that in comparison with Eq. (1) there is a significant difference in the pre-exponential factor. This can be handled empirically by defining an effective triplet magneton $\mu_T = g\sqrt{s(S+1)}$ so Eq. (1) is rewritten

$$\chi = \frac{1.50}{T}\left(\frac{\mu_T}{2\sqrt{2}}\right)^2 \exp\left(\frac{-4t^2}{(kTU)}\right) \qquad (1')$$

again in emu/mole, since for the "ideal" dimer $S = 1$ and $g = 2$. The data from I at low temperature yield $\mu_T \simeq 3.6$, which is nearly equal to the value $\mu_T = 3.7$ obtained by Weiher *et al.*[16] for (tetraethylammonium)$^+$ $\{Ni[S_2C_2(CN)_2]_2\}^-$.

In this model the activation energy of the resistivity (Δ_ρ) is given by $\Delta_\rho = \frac{1}{2}U$. Thus, this model is consistent with the experimental result that $\Delta_m < \Delta_\rho$. The high-temperature phase should be described by an undimerized Hubbard chain with $U >> 4t$ and one electron per site.

In the limit $U >> 4t$, the magnetic part of the Hubbard model can be described by a Heisenberg linear chain,[17] and the magnetic susceptibility is given by the Bonner-Fisher result.[18] For the half-filled-band case appropriate for I, the effective antiferromagnetic exchange interaction $J = 2t^2/U$. As shown in Fig. 3, a value of $J = 300$ K gives good agreement with the magnitude of the magnetic susceptibility at high temperatures and its temperature dependence for $T \geqslant 200$ K.

V. CONCLUSIONS

Some of the properties of the organometallic conductor $NH_4Ni[S_2C_2(CN)_2]_2 \cdot H_2O$ (I) have been discussed. Preliminary crystal-structure data indicate that the properties of I may be dominated by the close packing of planar $\{Ni[S_2C_2(CN)_2]_2\}^-$ anions along a stacking axis and thus have a quasi-one-dimensional nature. A broad phase transition occurring between 200 and 150 K is observed in magnetic susceptibility and electrical resistivity.

The observation of IR absorptions associated with the vibronic activation of A_g modes observed in resonance Raman spectroscopy is consistent with a picture in which I undergoes a phase transition involving CDW formation and lattice dimerization which is stabilized by electron-phonon interaction involving intramolecular modes. Further work on the polarization of the infrared absorption and the crystal structure as a function of temperature is required to substantiate this hypothesis.

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