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ISOTOPE EFFECT STUDY OF κ-(BEDT-TTF)$_2$Cu(NCS)$_2$: LABELING IN THE ANION

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Abstract Isotopic labeling in the anion of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, with ^{13}C and ^{15}N isotopes in the thiocyanate groups, has been carried out. This labeling does not lead to an isotope effect on the superconducting transition temperature (T_c).

INTRODUCTION

Since the initial discovery of organic superconductivity in 1979, a large number of organic superconductors have now been synthesized, with T_cs approaching *ca.* 13 K. However, the mechanisn of electron-pairing in these novel superconductors has remained largely unresolved. During the last few years, several studies have been carried out to gain important insights into this problem. They include NMR, μSR, infrared reflectivity, Raman, dc magnetization, specific heat, and isotope effect studies. Among these, the isotope effect studies constitute an important experimental tool for the investigation of whether or not the electron-pairing mechanism in organic superconductors is phonon-mediated, as in conventional superconductors. Recent isotope effect studies in our laboratory, involving *seven* different isotopically labeled BEDT-TTF (or ET) derivatives, have demonstrated the following: (i) *intra*molecular phonon modes involving C=C and C–S stretching vibrations in the ET donor molecule are *not* the dominant mediators of electron-pairing,[1] and (ii) in κ-(ET)$_2$Cu(NCS)$_2$, there exist two competing isotope effects—a normal mass effect, i.e., lowering of T_c upon isotopic labeling, when the ET molecular mass is increased by concurrent ^{13}C and ^{34}S labeling, in addition to an inverse isotope effect upon deuterium labeling in ET.[2] The inverse isotope effect of various magnitudes ranging from +0.3 to +0.8 K was previously reported by others.[3–6] Our recent measurements involving a large sampling of crystal specimens have confirmed this inverse isotope effect and have shown this isotope shift to be *ca.* +0.3 K.[2] The presence of two different isotope effects of opposite sign in the same material is intriguing from the point-of-view of the electron-pairing mechanism, since it suggests a conventional, phonon-mediated mechanism within the conducting layer where the normal isotope effect is observed, and an unconventional mechanism in the non-conducting layer containing the hydrogen/deuterium atoms of the donor molecules. Therefore, it is of great interest to investigate if there is an isotope effect when the charge-compensating *anions*, which are also located within the non-conducting layer in the superconducting cation-radical salts, are isotopically labeled. The existence of an isotope effect when the anions are labeled would be indicative of electron-pairing with the mediation of vibrational frequencies associated with the anions. In this paper, we present the results of the *first* isotope effect study in which isotopic labeling in the anion portion of κ-$(ET)_2Cu(NCS)_2$ is carried out. We find *no* isotope effect when the carbon and nitrogen atoms of the thiocyanate groups in the anion are replaced with ^{13}C and ^{15}N isotopes.

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

Two different approaches were adopted for incorporating ^{13}C and ^{15}N isotopes in the thiocyanate groups in the superconducting salt κ-$(ET)_2Cu(NCS)_2$. Initially, we synthesized $Ph_4PCu(^{15}N^{13}CS)_2$ from commercially available $KS^{13}C^{15}N$ (99% enriched in both ^{13}C and ^{15}N, Isotec Inc., Miamisburg, Ohio), CuCl and Ph_4PCl, according to a modified procedure of Bowmaker and Rogers[7]. A batch of unlabeled $Ph_4PCu(NCS)_2$ was also synthesized in a parallel experiment by use of corresponding unlabeled precursors. The crystal samples of the κ-$(ET)_2Cu(NCS)_2$ superconductor prepared by electrocrystallization with the use of the pre-formed electrolyte were not only very small in size, but also exhibited very broad superconducting transitions, thus making the determination of isotope effect difficult and unreliable. Therefore, we resorted to the well-known crown ether route.[8,9] The starting material $CuS^{13}C^{15}N$ was prepared from $CuSO_4.5H_2O$, Na_2SO_3 and $KS^{13}C^{15}N$ (and the unlabeled CuSCN in strictly parallel synthesis), in a manner analogous to the literature method for the preparation of CuCl.[10] The superconducting crystal samples of both labeled and unlabeled κ-$(ET)_2Cu(NCS)_2$ were prepared by electrocrystallization by use of the crown ether method in strictly parallel experiments.

Infrared and Raman spectroscopies were employed to monitor the frequency shifts in the thiocyanate stretching vibrational modes upon isotopic labeling. Infrared spectra of unlabeled $Ph_4PCu(NCS)_2$ revealed two strong peaks at 2107 and 2079 cm^{-1}, which were shifted to 2029 and 2001 cm^{-1} respectively in the labeled $Ph_4PCu(^{15}N^{13}CS)_2$ material, corresponding to a frequency shift of 78 cm^{-1}. Frequency shifts of similar magnitude (75 cm^{-1}) were observed in the Raman spectra of the superconducting salt κ-

$(ET)_2Cu(NCS)_2$, with the unlabeled salt exhibiting two peaks at 2104 and 2065 cm^{-1}, and the labeled salt at 2029 and 1990 cm^{-1}, as shown in Figure 1.

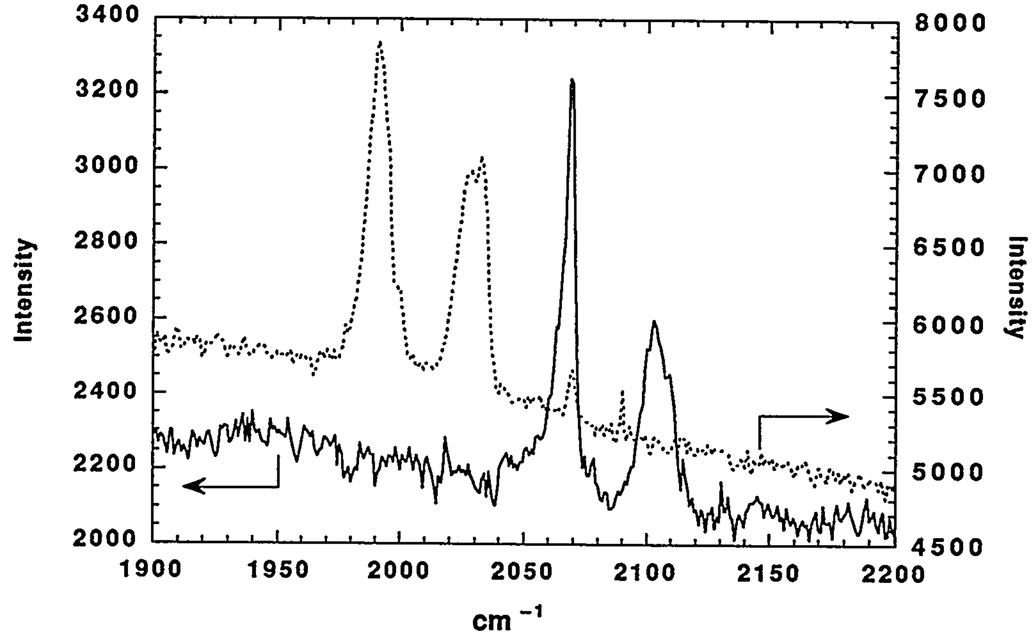

FIGURE 1 Raman spectra of κ-$(ET)_2Cu(NCS)_2$: solid line (unlabeled) and broken line (labeled with ^{13}C and ^{15}N in the thiocyanate group).

ISOTOPE EFFECT MEASUREMENTS

The superconducting transition temperatures were determined with the use of an ac susceptometer (Lake Shore Cryotronics, Inc., Model 7221) operating with a modulation field of 1 Oe and frequency of 125 Hz. Full details of the measurement methods and data analysis have been described elsewhere.[2] For each sample, we recorded the following: the onset transition temperature, T_{co} (temperature at which the first diamagnetic signal appears); mean-field transition temperature, T_{cl} (temperature corresponding to the intercept of the linear extrapolations of the susceptibility at $T < T_c$ and $T > T_c$); the transition mid-point, T_{cm}; the temperature at the maximum in the peak of the imaginary component of the susceptibility, $T_{c\chi''}$; and the 10–90% transition width, ΔT. To provide an adequately large sampling, we collected data for 12 crystal specimens each of both unlabeled and labeled superconductor samples. Based on our previous experience, the large sampling is crucial for the determination of statistically meaningful isotope shifts, because organic superconductors typically show sample-to-sample variations in T_c as much as ± 0.2 K, even for samples within the same electrocrystallization synthesis batch.

The superconducting transition temperatures of the 12 samples each of both labeled and unlabeled superconducting salts from the above measurements are listed in Table I. These data are without corrections for demagnetization, and both sets cover essentially the same range of transition widths and saturation signals (related to demagnetization factors, which are not listed in the Table for clarity). Table I also lists the average T_cs and standard deviations for each set, and at the bottom of the Table, the isotope shift $\Delta T_c = T_c(\text{labeled}) - T_c(\text{unlabeled})$. A perusal of these values clearly suggests the *absence* of an isotope effect when the $Cu(NCS)_2^-$ anion is labeled with ^{13}C and ^{15}N isotopes, since the isotope shifts are much smaller than the standard deviations for every definition of T_c. Moreover, the standard deviations are more a reflection of sample-to-sample variations in T_c than the uncertainties in the measurements, as we have pointed out previously.[1,2] It is also to be noted that the mean-field transition temperatures (T_{cl}) show the smallest standard deviations and are the most reliable measure of isotope effect since T_{cl} is defined by the intercept of susceptibilities in the normal and superconducting states covering extended temperature regions.

A graphical representation of the absence of an isotope effect is given in Figure 2. In this Figure, we compare the curves in the temperature region of 8–10 K of four crystals each in the labeled and unlabeled sets. The four crystals were chosen (among the 12 crystals) such that they cover the entire range of observed saturation magnetization values (lowest, highest, and two intermediate values), and demagnetization corrections were applied to all the curves to yield unit shielding at 5 K. It can be seen that the curves for both unlabeled (open symbols) and labeled (filled symbols) samples are spread over a temperature region of *ca.* 0.1–0.15 K indicative of the sample-to-sample variations in T_c. The curves of both sets also overlap over the same temperature region indicating the *absence* of an isotope effect.

TABLE I Superconducting transition temperatures (T_c) for unlabeled and labeled κ-$(ET)_2Cu(NCS)_2$ crystals.

Crystal	T_{co} (K)	T_{cl} (K)	T_{cm} (K)	$T_{c\gamma''}$ (K)	ΔT
		κ-$(ET)_2Cu(NCS)_2$			
1	9.34	8.96	8.50	8.56	0.86
2	9.48	9.13	8.81	8.87	0.74
3	9.22	9.04	8.89	8.88	0.36
4	9.15	8.90	8.69	8.72	0.41
5	9.48	9.14	8.87	8.86	0.64
6	9.75	9.19	8.90	8.75	0.59
7	9.97	9.19	8.95	8.95	0.47
8	9.23	9.07	8.72	8.74	0.67
9	9.33	9.07	8.73	8.76	0.61
10	9.18	8.96	8.78	8.79	0.49
11	9.56	9.15	8.95	8.95	0.47
12	9.64	9.16	8.88	8.81	0.63
Mean	9.44±0.25	9.08±0.10	8.81±0.13	8.80±0.11	0.58±0.14
		κ-$(ET)_2Cu(^{15}N^{13}CS)_2$			
1	9.61	9.20	8.90	8.84	0.74
2	9.99	9.10	8.76	8.81	0.92
3	9.24	9.09	8.74	8.73	0.75
4	9.35	9.12	8.87	8.88	0.58
5	9.62	9.14	8.99	8.99	0.32
6	9.44	9.17	8.94	8.88	0.45
7	9.50	9.21	8.87	8.79	0.73
8	9.20	9.05	8.84	8.87	0.41
9	9.53	9.20	8.85	8.79	0.68
10	9.25	9.19	9.06	9.07	0.32
11	9.30	9.09	8.94	8.95	0.31
12	9.39	9.03	8.82	8.84	0.47
Mean	9.45±0.22	9.13±0.06	8.88±0.09	8.87±0.10	0.58±0.14
ΔT_c	0.01±0.33	0.05±0.12	0.07±0.16	0.07±0.15	

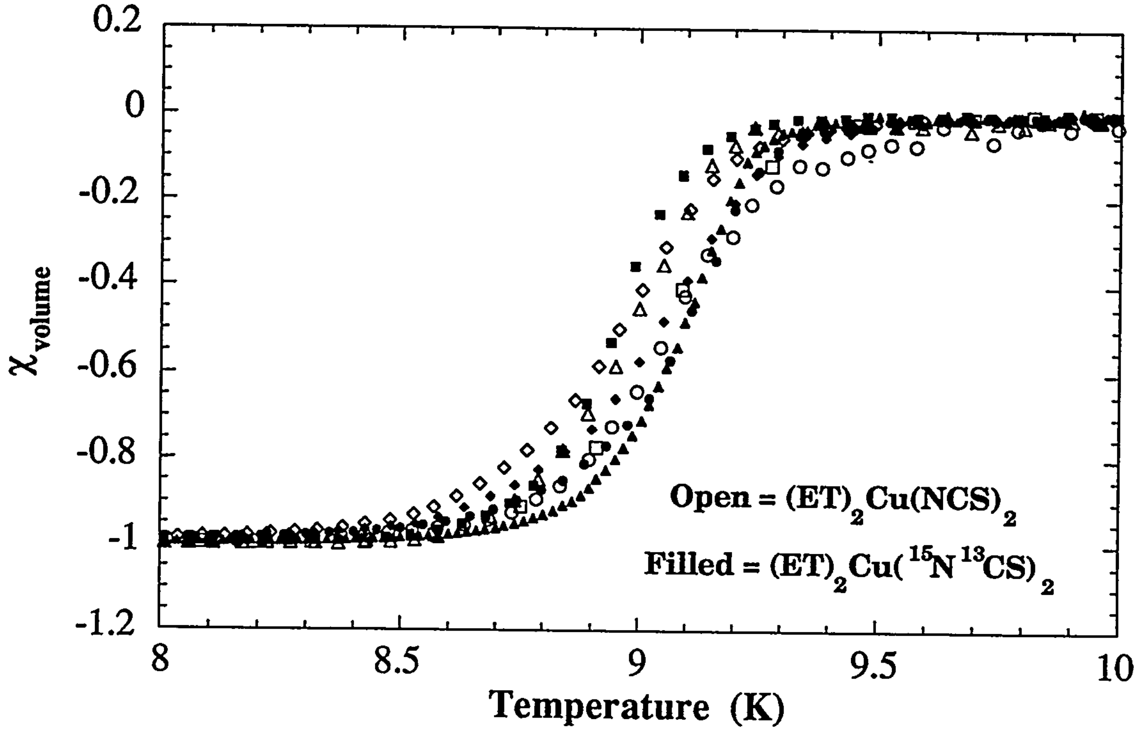

FIGURE 2 Volume susceptibility χ' (corrected for demagnetization) of four crystals each of labeled and unlabeled κ-$(ET)_2Cu(NCS)_2$.

CONCLUDING REMARKS

The isotopic labeling in the anion of the superconductor κ-$(ET)_2Cu(NCS)_2$ now rounds out our comprehensive isotope effect studies. The anion labeling, despite producing large frequency shifts in the thiocyanate stretching vibrational modes (*ca.* 75 cm^{-1}), does not lead to any appreciable isotope shift, suggesting the anion vibrational modes do not contribute in any significant way towards the electron-pairing mechanism in the κ-$(ET)_2Cu(NCS)_2$ superconductor. This is not too surprising considering the high energy (*ca.* 2000 cm^{-1}) associated with these modes relative to the Fermi energy (E_F). We have previously shown that the high-energy, *intra*molecular C=C and C–S vibrational modes of BEDT-TTF, which are also of higher energy with respect to the Fermi energy, are not the principal mediators of superconductivity.[1] Furthermore, the mass change (4 amu per formula unit) associated with this labeling is too small to produce a BCS-like mass isotope shift, which would be indiscernible in our measurements.

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