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Static Polycrystalline Magnetic Susceptibility and Four-Probe Single-Crystal Conductivity Studies of $[Ru(bpy)_3]^0$

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Abstract: Magnetic susceptibility measurements of polycrystalline samples of electrochemically grown $[Ru(bpy)_3]^0$ show a low-temperature sub-Curie law tail and a broad maximum at about 300 K. The data are consistent with an alternating linear-chain spin-$^1/_2$ Heisenberg antiferromagnetic system, with $|J|/k = 238(3)$ K, the alternation parameter $\alpha = 0.40(3)$, and $g = 2.20(4)$. The stronger coupling is probably intermolecular between ligand-localized electrons on adjacent molecules with significant π^* overlap. Four-probe single-crystal conductivities of needle-shaped crystals show the material to be moderately conducting ($\sigma \approx 1.5 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$ at 297 K) along the long axis. Fittings of the temperature dependence of the conductivity suggest that variable-range three-dimensional hopping is responsible for the observed conductivity.

Introduction

The synthesis of crown ethers[1] by Pedersen in 1967 and cryptands[2] by Lehn in 1969 ignited the still-exploding field of macrocyclic host–guest chemistry. These complexants and those synthesized subsequently have been used to make a myriad of expanded metal cations and entirely new classes of salts. Two such salts, alkalides and electrides, consist of complexed alkali metal cations charge-balanced by alkali metal anions or trapped electrons, respectively.[3] The anionic electrons in electrides range from weakly coupled, localized electrons to strongly interacting electrons with itinerant behavior. Closely related to electrides are electropositive metals that are complexed by organic complexants with low-lying molecular acceptor levels. The charge-transferred electrons are localized in these orbitals rather than in lattice vacancies. If the complexant allows for delocalization of the electron(s) over the complexant molecule, the charge-neutral entity can be considered an "expanded atom".[4] This type of molecular species holds the promise of bridging the gap between electrides and the closely related alkali metal doped fullerenes (M_xC_{60}), which have the highest recorded superconducting critical temperatures of any known molecular material.[5,6] Electrides and M_xC_{60} differ mainly in that electrides have no low-lying π^* orbitals into which the reducing electrons can delocalize. Bridging this gap with "expanded atoms" holds the promise of new and exciting electronic properties in view of the properties of the extreme members.

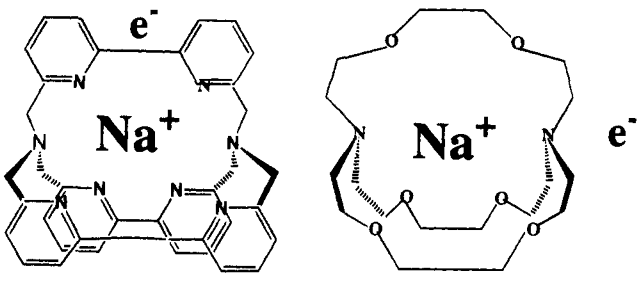

Figure 1. Schematic diagram of (a) sodium cryptatium, with (b) a sodium cryptate electride included for comparison.

A compound which comes close to this description, referred to as a *cryptatium* and depicted in Figure 1, has been synthesized, and its crystal structure has been determined.[7] Its complexant, tris(bipyridine) cryptand,[8] can be considered to be three bipyridine ligands tethered at both ends. The electron released from the complexed sodium cation is localized in one of the bipyridine ligands. Complexation of a trivalent cation might result in a crystalline species of "expanded atoms" in which each "cryptand" captures three electrons.

The success of controlled-current electrocrystallization of cryptatium led to the subsequent crystallization of single crystals of $[Ru(bpy)_3]^0$.[9,10] Powder or microcrystalline samples of this material had been previously reported and studied by EPR methods,[11-13] but no previous attempts to grow single crystals had been reported. $[Ru(bpy)_3]^0$ is of interest to us due to the obvious relationship of its ligands to *cryptatium* and its bireduced state. Numerous attempts to solve the structure by X-ray diffraction failed, presumably because of disorder,

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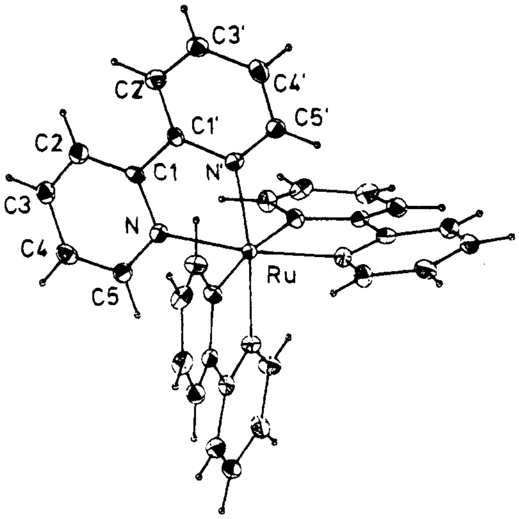

Figure 2. The local structure of [Ru(bpy)$_3$]$^{3+}$. This structure is virtually indistinguishable from the dipositive species. Reproduced with permission from ref 14. Copyright 1992 American Chemical Society.

although it was possible to determine that the material possesses hexagonal symmetry. The molecular nature of the material leads us to assume that the *local* structure about the Ru^{2+} ion is similar to that determined for [Ru(bpy)$_3$](PF$_6$)$_2$ (Figure 2),[14] with a propeller-like, six-coordinate arrangement of the ligands and nearly octahedral coordination of the nitrogen atoms. However, the absence of space-filling counterions suggests that the molecules might be packed in the solid state with good intermolecular π^* overlap. If so, this material might be a good model for crystallized "expanded atoms". This article reports the results of four-probe single-crystal conductivity and powder static magnetic susceptibility measurements.

Experimental Section

Crystals of [Ru(bpy)$_3$]^0 were grown by reductive electrocrystallization methods described fully elsewhere.[7,9,10] Two Pt wires were used, one as the cathode and one as the anode. The solvent vapor pressure was maintained during the controlled-current process ($I = 4$ μA/cm^2), and 0.1 M tetrabutylammonium tetrafluorophosphate in acetonitrile was used as the solvent. Since the crystals are air sensitive, manipulations of the harvested dark black-blue needle-shaped crystals were always performed under inert atmosphere or vacuum.

The magnetic susceptibility was measured from 1.5 to 390 K with a S. H. E. Corp. model 800 variable-temperature SQUID susceptometer. The sample was pulverized into a fine powder with an agate mortar and pestle and loaded into an aluminum–silicon alloy holder in a helium-filled glovebox. The sample was then transferred to the SQUID under a helium atmosphere and cooled to 2 K in a zero applied field. The temperature dependence of the susceptibility was measured in a 7 kG applied field. The small, nearly temperature independent paramagnetic susceptibility of the holder was subtracted after running the empty holder under the same conditions.

The dc conductivity was obtained by using a previously described crystal holder.[15] Measurements were made on a well-formed single crystal with hexagonal outer morphology (cross section). Results with other crystals were qualitatively similar. The length of the crystal was 1.30(3) mm, and its face-to-face width was 0.91 (3) mm (numbers in parentheses are uncertainties in the final digits). The crystal was selected in a helium-filled glovebox and transferred under helium to a pair of nitrogen-filled glovebags. One of the glovebags was set up inside the other; separate nitrogen gas supplies purged each glovebag so that the outer bag served as an antechamber. A dewar of liquid nitrogen was maintained inside the inner bag to minimize the humidity.

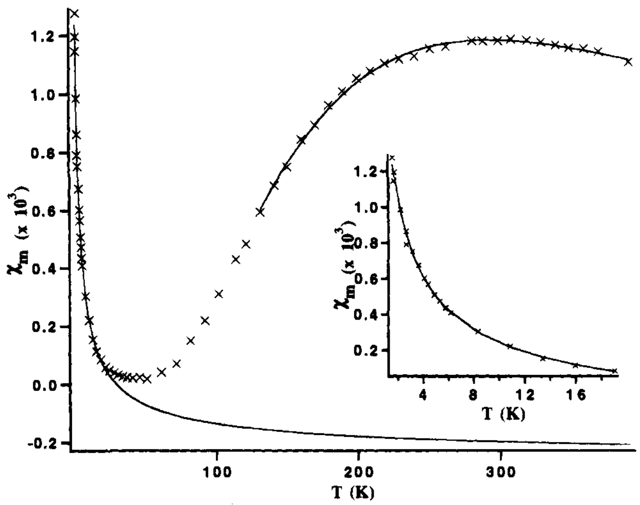

Figure 3. Temperature dependence of the magnetic susceptibility of [Ru(bpy)$_3$]^0 (×). The solid line extending from the low-temperature data is the "sub-Curie" tail and diamagnetic correction. The solid line extending from the high-temperature data is the best fit to eq 6. The low-temperature "sub-Curie" tail (×) is shown in the inset. The solid line represents the best fit to eq 1.

Four gold wire leads (0.0127 mm diameter) were attached in a linear arrangement along one face of the crystal under a microscope with silver paint. The temperature was controlled by suspending the cell in a liquid nitrogen dewar above the liquid level. A positive pressure of flowing nitrogen was maintained in the dewar at all times. The temperature was measured with a copper–constantan thermocouple mounted in contact with the sample platform. After the sample was allowed to come to thermal equilibrium, a dc current of 100 μA was supplied to the outermost leads, and the voltage between the innermost leads was measured. The leads were then reversed, and the measurement was repeated. The two readings were averaged when the resistivity was determined. Ohmic behavior was confirmed at each temperature by measurements at 10 μA. Two Keithley 617 electrometers were employed as the current source and voltameter.

Results and Discussion

The measured molar susceptibility is shown in Figure 3. The low-temperature rise in susceptibility is qualtitatively similar to that expected for uncorrelated impurities (a "Curie tail"). However, a Curie law fit is far from satisfactory. A much better fit of the 1.5–19 K data can be obtained by using

$$\chi_m = CT^{-n} + D \qquad (1)$$

where $C = 0.002\,00(4)$ (which could be accounted for by ≈0.5% of the total spins) and $n = 0.59(5)$. The bulk diamagnetic correction, D, is $-0.000\,27(6)$, which is reasonable when compared to that obtained from Pascal's constants (≈$-0.000\,338$), especially if one considers the possibility of a small temperature-independent paramagnetic component.[16,17] This fit is shown in the inset of Figure 3. We are aware of only two theoretical explanations for such a sub-Curie law tail; the random-exchange Heisenberg antiferromagnetic coupling (REHAC) model[18] and the interspersion of variable-length paramagnetic odd and diamagnetic even chain segments.[19] The REHAC model results in a sub-Curie temperature dependence due to random, weak exchange between paramagnetic sites. The chain segmentation model results in the same behavior but is

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due to the presence of paramagnetic, odd-length segments. The probability of the occurrence of the weakly interacting spin subsystems required for sub-Curie law behavior is negligibly small in two- and three-dimensional systems.[18] This behavior strongly suggests a one-dimensional exchange pathway. It should be noted that one-dimensional exchange does not necessarily imply a linear chain structure. All that is required is that each Ru(bpy)$_3$ molecule interact magnetically with two and only two neighboring molecules. This could result in a myriad of different molecular packing arrangements, including linear, zig-zag, helical, circular, etc.

After subtraction of the sub-Curie law tail, the susceptibility rises from 0 as the temperature is increased and displays a broad maximum at about 300 K. Attempts were made to fit the higher temperature susceptibility to simple spin-pairing models.[17,20] Neither $S = 1$ nor $S = {}^1/_2$ models could satisfactorily fit the data. The low-temperature sub-Curie law tail and broad maximum in the susceptibility both strongly suggest one-dimensional chain behavior. Qualitatively, however, the behavior does not determine whether an effective spin of 1 or ${}^1/_2$ is more appropriate.

DeArmond and co-workers have suggested, on the basis of EPR data, that the two electrons in the HOMO of $[\mathrm{Ru(bpy)_3}]^0$ are localized in the ligand π^* orbitals (Lπ^*) when the molecule is in solution and in the two metal dσ^* orbitals in the solid state.[11-13] They make the assignment in the solid state based on a choice of the three configurations they see as most likely, assuming no significant orbital mixing: $(\mathrm{L_1}\pi^*)^1(\mathrm{L_2}\pi^*)^1$, $(\mathrm{L_1}\pi^*)^1(\mathrm{d_1}\sigma^*)^1$, and $(\mathrm{d_1}\sigma^*)^1(\mathrm{d_2}\sigma^*)^1$. They rule out the first configuration on the basis of its lack of a reasonable mechanism to account for a large g-shift from 1.995 (solution) to 2.23 (solid). The second configuration, while accounting for the broad (250 G) signal in the solid state, is dismissed; it was concluded that spin–spin and spin–orbit coupling would have an uncertain effect on the EPR spectrum. They argue that the third, metal-based, configuration is correct since the isoelectric Ni(II) species with strong exchange interactions displays similar g-values and line widths. The change from a ligand-based HOMO in solution to a metal-based one in the solid, they conclude, is due to the small energy separation between the ligand π^* and the metal dσ^* orbitals and to solvent stabilization of the former. This would mean that $[\mathrm{Ru(bpy)_3}]^0$ would be best represented as an $S = 1$ species in the solid state.

The conclusions of DeArmond and co-workers yield a d^8 ground-state configuration. A pseudooctahedral environment is expected, leading to a $^3\mathrm{A}_{2g}$ single-ion ground term and quenching of the orbital angular momentum. The general spin Hamiltonian, assuming a one-dimensional chain and neglecting all terms except single-ion and nearest neighbor interactions, would be

$$H = H_{\mathrm{zee}} + H_{\mathrm{D}} + H_{\mathrm{HDVV}} + H_{\mathrm{D-M}} + H_{\mathrm{A}} + H_{\mathrm{bi}} \quad (2)$$

or

$$H = \sum_i (g_i \beta \hat{S}_i \vec{H} + \hat{S}_i \cdot D \cdot \hat{S}_i - 2J_{i,i+1} \hat{S}_I \cdot \hat{S}_{i+1} + D_{i,i+1} \cdot [\hat{S}_i \times \hat{S}_{i+1}] + \hat{S}_i \cdot \Gamma_{i,i+1} \cdot \hat{S}_{i+1} + J_{i,i+1} (\hat{S} i \cdot \hat{S}_{I+1})^2) \quad (3)$$

where the terms represent the field-dependent Zeeman perturbation, the local distortion, the Heisenberg–Dirac–Van Vleck isotropic exchange, the Dzyaloshinsky–Moriya antisymmetric exchange, *the* anisotropic exchange, and the biquadratic splitting, respectively.[17] The high temperature at which the maximum in susceptibility is reached strongly suggests that the isotropic exchange term dominates. The biquadratic splitting only affects the excited-state terms of an exchange-coupled ground-state singlet; since these excited states are only populated at rather high temperatures in this system, kT is expected to be much larger than the interaction parameter. The magnitude of the anisotropic exchange can be approximated by $(1-2/g)^2J$.[17] This interaction, using $g = 2.23$, is approximately 1% of the isotropic exchange and thus is negligible at high temperatures. The antisymmetric exchange is similarly negligible, typically dominated even by the anisotropic exchange.[20] Local anisotropy is typically on the order of a few kelvins. Neglecting the contributions of these terms should not significantly affect the determination of the isotropic exchange interaction if only the high-temperature data are included in the fitting procedure.

The resulting Hamiltonian from the above analysis is simply that of a linear-chain Heisenberg antiferromagnet (LCHA). The temperature dependence of the susceptibility of LCHAs has not been solved as a closed-form analytical expression, except in the case of the classical spin ($S = \infty$) in a zero magnetic field.[21] Extrapolations of infinite-chain behavior from finite-size ring calculations have been published for the case of $S = {}^1/_2$.[22] The results of these calculations are qualitatively similar; the susceptibility displays a broad maximum and a nonzero intercept at 0 K. For a number of years, it was assumed that LCHAs with other spin values would be qualitatively similar as well. It was further assumed that the quantitative behaviour would vary systematically with spin, excluding the classical spin. More recently, Haldane[23] has published a conjecture which states that half-integer spin systems should be qualitatively similar to the spin-${}^1/_2$ case, but that all even-integer spin systems will diverge from this behavior near $T = 0$. Half-integer systems exhibit a finite 0 K susceptibility, arising from their lack of an excitation gap between the ground-state singlet and triplet excited states.[24] On the other hand, integer systems, according to Haldane, should have a gap in their energy spectra resulting in a susceptibility which vanishes exponentially as T approaches 0. The existence of the Haldane gap has been confirmed in the $S = 1$ case by both experimental and numerical methods.[25,26] In addition to the exponential decrease in susceptibility as T approaches 0, expected of $S = 1$ chains, low-temperature Curie-type behavior has been observed experimentally. This was attributed to the finite length of the chains in the systems studied.[27-30]

The temperature dependence of the susceptibility of $S = 1$ LCHAs has been studied by finite-ring extrapolation methods.[31] The study did not extend to temperatures low enough to observe the effects of the Haldane gap.[32] The results were fitted by the analytical expression[33]

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$$\chi = \frac{N\beta^2 g^2}{kT}\left(\frac{2 + 0.0194X + 0.777X^2}{3 + 4.346X + 3.232X^2 + 5.834X^3}\right) \qquad (4)$$

where $X = 2|J|/kT$, and the expression is valid for $X \leq 5$ (note that the factor of 2 difference in the definition of X between this paper and the published expression derives from the conventions used in the formulation of the respective Hamiltonians). This expression has been successfully used to fit the temperature dependence of $S = 1$ LCHAs which show the effects of the Haldane gap.[30,33] Nonlinear least-squares fits of this expression to the $[Ru(bpy)_3]^0$ data proved to be unsatisfactory. Even fitting only data below $X \approx 1$ ($T > 239$ K) resulted in systematic errors as shown in Figure 4. Although eq 4 was derived for infinite $S = 1$ chains, we would expect it to apply in the present case if the chains were of the $S = 1$ type, since the average chain length is about 200 molecules. We have assumed in our analysis that the low-temperature sub-Curie tail is caused by chain ends; however, neither the exact form of the temperature dependence nor the origin of this tail is important in the analysis, since its contribution is negligible in the high-temperature fitting region. It is clear from the high-temperature behavior that the $S = 1$ chain model does not agree with the magnetic properties of $[Ru(bpy)_3]^0$.

An alternative model of $[Ru(bpy)_3]^0$ is as a system with two ligand-localized, nominally unpaired electrons on each molecule at high temperatures. Voltammetric results support such an assignment.[34] However, the electrons would probably have significant dσ^* character as suggested by DeArmond et al.[35] A one-dimensional chain structure could result from an antiferromagnetic *intermolecular* interaction of the ligand π^* orbitals. Thus, the $[Ru(bpy)_3]^0$ system could be considered one in which each electron is coupled both *intramolecularly* to the electrons on one of the other ligands and *intermolecularly* to an electron on a neighboring molecule's ligand. This model is equivalent to that of a spin-$^1/_2$ alternating linear-chain Heisenberg antiferromagnet (ALCHA), whose Hamiltonian (excluding the Zeeman term) is

$$H = -2J\sum_{i=1}^{n/2}[\hat{S}_{2i}\hat{S}_{2i-1} + \alpha\hat{S}_{2i}\hat{S}_{2i+1}] \qquad (5)$$

where J is the exchange parameter between a spin and one of its nearest neighbors along the chain, and αJ is the exchange parameter between a spin and its other nearest neighbor. Although this model has not been solved analytically, infinite-limit extrapolations of numerical calculations of finite-size rings and convenient fitting expressions based on these calculations have been published.[36] The published expression is

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{[A(\alpha)] + [B(\alpha)]X + [C(\alpha)]X^2}{1 + [D(\alpha)]X + [E(\alpha)]X^2 + [F(\alpha)]X^3}\right] \qquad (6)$$

where $X = |J|/kT$, and the expression is valid for $X < 2$. The constants A through F are given functions[36] of α and take on values which depend on whether α is larger than or less than 0.4. Nonlinear least-squares fitting of the susceptibility data resulted in excellent agreement (see Figure 3) with $\alpha = 0.40(3)$, $|J|/k = 238(3)$ K, and $g = 2.20(4)$. Note the excellent agreement between the fitted magnetogyroscopic ratio (g) and that determined by DeArmond and co-workers from EPR spectra.[13] The intermolecular exchange parameter, $|J|/k$, refers to the *intermolecular* coupling while the *intramolecular* coupling (between the two ligand-localized electrons on each $[Ru(bpy)_3]^0$) is αJ. This assignment was chosen because, in the case of stronger intermolecular coupling, the finite lengths of the spin chains would result in one weakly coupled electron at each end of every chain. These "random defects" would give rise to the observed sub-Curie law behavior due to the random nature of their intermolecular coupling.[37] On the other hand, if the stronger coupling were intramolecular, the random distribution of exchange parameters required by the REHAC model would not be present, and intramolecular spin dimerization as temperature decreased would result in a single ground state, even for the chain ends. Therefore, the stronger coupling must be intermolecular in order to give rise to the observed sub-Curie tail.

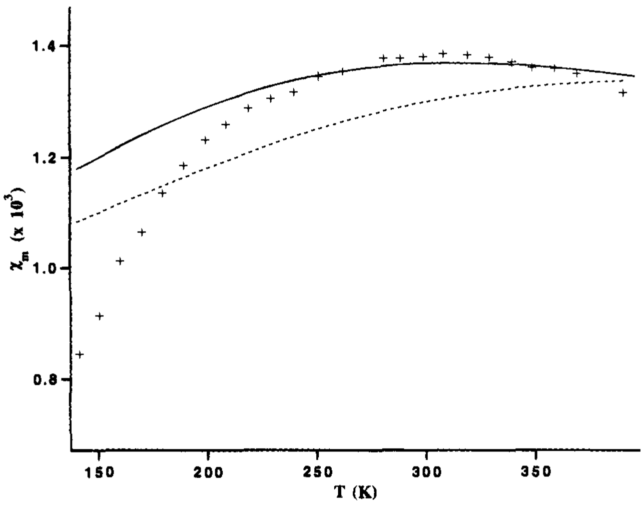

Figure 4. Best fits to the high-temperature susceptibility data to a $S = 1$ chain model (eq 4). The solid line was generated from a fit of the data between 239 and 390 K, showing systematic errors even over a limited temperature range. Theoretically, the line should fit the entire temperature range shown. However, as demonstrated by the dashed line, fitting this larger temperature range resulted in a much poorer fit due to the inability of the model to incorporated the necessary curvature.

In solution, $[Ru(bpy)_3]^0$ EPR results have been interpreted in terms of the spatially isolated orbital model.[11-13,35,38] Within this model, the ligand π^* orbitals are electronically isolated and filled independently upon successive reduction. DeArmond and co-workers suggested that loss of solvent stabilization of these orbitals in the solid state results in the reordering of the orbitals such that the metal dσ^* orbitals become the HOMO orbitals. They based their assignment of metal-based HOMOs and the resulting $S = 1$ configuration on the assumption that there was no significant orbital mixing. This was probably not a good assumption, especially in light of the small energy separation between the metal dσ^* and ligand π^* *orbitals*.[39,40] The loss of solvent stabilization may be responsible for reducing the energy gap between the metal dσ^* and ligand π^* orbitals, but the susceptibility data presented here strongly suggest that the orbitals are not reordered. The observed g shift is probably due to additional dσ^* character introduced into the ligand-localized orbitals as they suggested in a later review.[35] This could be due to the loss of solvent stabilization resulting in

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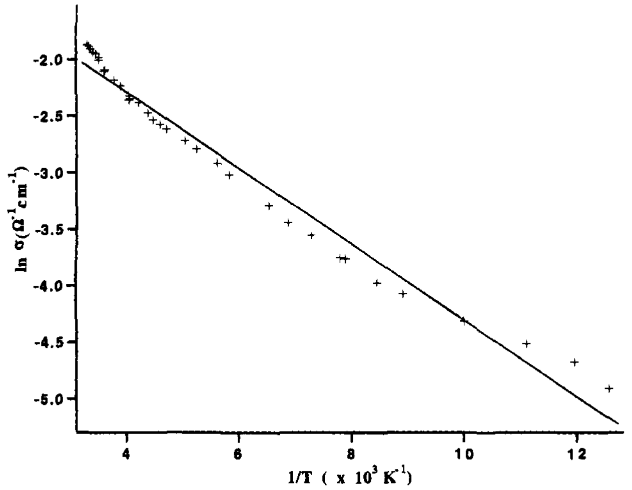

Figure 5. Best fit (solid line) of the temperature dependence of the conductivity with a conventional semiconductor expression (eq 7).

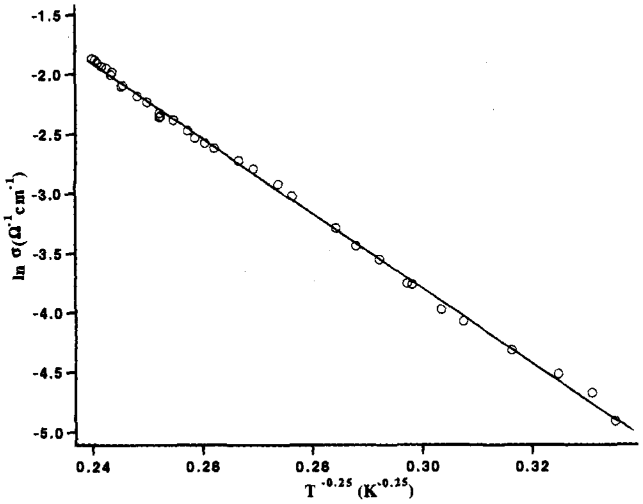

Figure 6. Best fit (solid line) of the temperature dependence of the conductivity to a 3-D variable-range hopping mechanism (see text).

narrowing of the energy gap or to crystal lattice interactions. The broad EPR lines[13] are due to the strong spin–spin coupling in the solid state, a mechanism which can be especially effective in one-dimensional systems.[41,42] Despite repeated attempts, we were unable to observe an EPR signal, suggesting that, in the crystalline material studied here, the EPR signal is broadened beyond detection. Thus, $[\text{Ru(bpy)}_3]^0$ is best considered under the spatially isolated orbital model even in the solid state.

The conductivity along the long axis (the 6-fold symmetric axis) of the crystals is displayed in Figures 5 and 6. It is about 2 orders of magnitude less conductive than n-doped silicon at room temperature. Its conductivity increases with temperature as one might expect for a semiconductor. Fitting the data with a conventional semiconductor expression

$$\sigma = \sigma_0 \exp(-E_a/2kT) \qquad (7)$$

where E_a is the bandgap and all other symbols have their usual meanings, proved to be highly unsatisfactory, as shown in Figure 5 ($E_a/2 = 0.029(1)$ eV). We therefore fitted the data by the more general expression

$$\sigma = \sigma_0 \exp[-(T_0/T)^n] \qquad (8)$$

where the definition of T_0 depends on the conduction mechanism, and the value of $0 < n < 1$ is indicative of this mechanism. This resulted in an excellent fit with fitting parameters of $\sigma_0 = 4(1) \times 10^3\ \Omega^{-1}\ \text{cm}^{-1}$, $T_0 = 5.44(5) \times 10^7$ K, and $n = 0.19(4)$. The value of n suggests that the conduction is due to a variable-range three-dimensional hopping mechanism.[43,44] In this model, the theoretical value of n is 0.25, and T_0 is inversely proportional to the localization length of the electronic states responsible for the conductivity. This model was derived from materials with localized states near the Fermi level which are randomly distributed in energy and space. The fit of the data by this model and our repeated failures to solve the structure of these seemingly well formed crystals by single-crystal X-ray diffraction imply a certain degree of disorder. Fitting the data with the value of n held constant at the theoretical value of 0.25 resulted in an excellent fit with $\sigma_0 = 278(3)\ \Omega^{-1}\ \text{cm}^{-1}$ and $T_0 = 9.75(7) \times 10^5$ K as shown in Figure 6.

Hopping conductivity could result from jumps from occupied to unoccupied Lπ^* and/or metal dσ^* orbitals. Hopping between the ligands is expected; in solution fast electron hopping is responsible for broadening of the EPR line.[13] In the solid state, the alternating nature of the exchange path results in a splitting of the half-filled Lπ^* band, creating a gap about the Fermi level with a filled lower band and an unfilled upper band.[45] The hopping mechanism invoked to explain our results assumes that this gap is much larger than kT and that the disordered localized states (the unoccupied Lπ^* or dσ^* orbitals) are near the Fermi level. Both conditions seem reasonable.

The difference in the dimensionality of the hopping conduction and the magnetic exchange paths is in no way contradictory. As stated above, the hopping is probably not between occupied sites in the chain. Even if the hopping conductivity is largely one-dimensional, if the total distance of all interchain hops is comparable to the length of a single chain, the system would behave as a 3-D system.[43]

Within the ALCHA model of $[\text{Ru(bpy)}_3]^0$, we can speculate on the nature of the disorder which is indicated by both our single-crystal X-ray and conductivity results. Localization of the two reducing electrons in two of the ligands should break the 3-fold symmetry, resulting in two of the three ligands having bond lengths that are shorter than the third. A similar reduction of molecular symmetry was seen in the case of cryptatium.[7] Such asymmetry might result in disorder in the crystal as the molecules may pack with occasional random orientation of the three ligands.

Conclusions

The results of static magnetic susceptibility measurements on $[\text{Ru(bpy)}_3]^0$ are consistent with a model of ligand localization of the reductant electrons, although these HOMO orbitals are probably hybrids with significant metal dσ^* character. While we could not solve the structure through single-crystal X-ray diffraction methods, it seems likely that it can be characterized as "complexed" ruthenium cations whose ligand-localized reductant electrons are moderately antiferromagnetically coupled. This interaction is probably mediated by the cation's e_g^* orbitals since the ligand–ligand angle is expected to be ~120° allowing

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for a nonorthogonal component of the overlap through the metal $d_{x^2-y^2}$ and d_{z^2} orbitals. These neutral molecules pack in close proximity, allowing for strong intermolecular antiferromagnetic $\pi^*-\pi^*$ overlap. This nearest neighbor interaction is unique so that each reductant electron is intermolecularly coupled strongly to only one other electron. Thus, the intra- and intermolecular interactions repeat through the lattice in a chainlike fashion, with, of course, breaks in the chain due to the occasional molecular misalignment.

Conductivity measurements with a four-probe dc method show that the crystals are highly conducting along the needle axis. Conduction is probably through a variable-range three-dimensional hopping mechanism. The conduction path may be composed of the empty $L\pi^*$ and/or metal $d\sigma^*$ orbitals.

This material represents another step toward the production of crystalline solids composed of "expanded atoms". The electrons released from the cation are localized in two of the bipyridine ligands rather than delocalized over the entire "complexant" so the neutral species does not truly represent an "expanded atom". It would be interesting to synthesize compounds in which all of the $L\pi^*$ orbitals were singly occupied. Delocalization of these electrons over the extended π^* orbital system would represent a bridge over the gap between electrides and alkali-doped fullerenes.

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