Picosecond Events in Magnetic Resonance Spectroscopy of the Bacteriochlorophyll Special Pair Cation

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Abstract: The various time domain limits of EPR, ENDOR, and ESE magnetic resonance studies of the primary donor free radical of photosynthesis are discussed. Both incoherent monomer cation jumping and coherent supermolecule dimer delocalization of the unpaired electron within the special pair chlorophyll dimer cation are considered. EPR and ENDOR are associated with time scales of nanoseconds and do not give any information about the picosecond nature of the special pair. In contrast, the ESE time scale can easily be in the subpicosecond range. As a consequence, the primary donor free radical of bacterial photosynthesis is shown by electron spin echo experiments to be a dimeric species in the picosecond time domain.

The primary photochemistry of photosynthesis has been shown to occur within a few picoseconds.[1,2] One of the products resulting from the initial picosecond electron transfer is the free radical[3] of the special pair,[4] a dimeric form of chlorophyll. Once formed, this paramagnetic species, presumably a cation, is sufficiently long lived to be studied by many spectroscopic techniques including electron paramagnetic resonance (EPR). This special pair of chlorophylls has been invoked as a primary donor of photosynthesis both in green plant photosystem I[4,5] and in purple photosynthetic bacteria.[4,6] Most of the direct evidence for the existence of the special pair has been provided by magnetic resonance (MR) studies of photosynthetic bacteria. The special pair was originally proposed in order to explain that the inhomogeneous EPR line width in vivo is smaller than the line width of the in vitro monomeric chlorophyll cation by a factor of $\sim 2^{1/2}$.[4] For bacteria, this explanation was supported by electron nuclear double resonance (ENDOR) studies showing that the in vivo hyperfine splittings are ~ 2 times smaller than the corresponding splittings in the monomer cation.[7,8] The factor of $2^{1/2}$ in the EPR width and the corresponding factor of 2 in the ENDOR splittings can be explained easily by a special, dimeric in vivo species. By using the existing ENDOR data[9-12] from selective isotopic labeling experiments, it can be shown that at least a dimeric species is demanded and a role for trimers, tetramers, etc., can reasonably be ruled out. Thus, the fundamental assumption in this work is the existence of the special pair in photosynthesis bacteria.

However, for a species to appear dimeric in an EPR experiment does not necessarily mean the species is dimeric on a time scale of a few picoseconds, i.e., on a time scale of the primary photochemistry of photosynthesis. Thus, the picosecond nature of this cation is of great interest. We now discuss some of the various limits on the time domain of magnetic resonance, including EPR and the two related techniques of ENDOR and ESE. In the case of the special pair $Bchl_{sp}$, we will show that while EPR and ENDOR are associated with time scales of nanoseconds or longer, the ESE time scale can be subpicosecond.

Although some emphasis is to be placed on the advantages of the ESE time scale, the central question is whether or not the Bchl special pair cation is a picosecond species. We define a picosecond dimer (or a nanosecond dimer) as a species in which an experimental method with an inherent resolving time of picoseconds (or nanoseconds) will find the hole (or spin) divided between the two halves of the dimer. We emphasize that the inherent resolving time of an experimental method as defined here is not necessarily the instrumental integrating or response time. For example, high-resolution EPR spectra may be taken with an instrumental integration time of 30 s even though the spectral line shape reflects events occurring on a nanosecond time scale.

Theory

In principle, the techniques of optical spectroscopy can provide information about the special pair cation with a resolution of less than picoseconds.[13] Unfortunately, the optical spectroscopy of the pigments participating in the primary photochemical act in bacteria is not sufficiently well understood to provide reliable information on the time scale of delocalization of the unpaired electron in the special pair cation.

We treat the problem of unpaired electron delocalization within the chlorophyll special pair dimer from two extreme viewpoints.[14] In one, the unpaired electron is localized on one molecule at a time but "hops" between the two monomers fast enough to show some dimeric properties. This is the incoherent monomer jumping model for the $Bchl_{sp}$. In the second view the two components of the $Bchl_{sp}$ are correlated to form a supermolecule which is assumed to exist at *all* times and is characterized by a "coherent" lifetime T_c. This is the coherent $Bchl_{sp}$ supermolecule model. In this model, the special pair is a dimer on any MR time scale, including a picosecond time scale. We emphasize that this second interpretation is not the only valid explanation for the EPR data since the incoherent jumping model can explain the EPR data equally well but does not necessarily indicate a dimer exists on the picosecond time scale.

According to the first viewpoint, we consider the random jump model in which delocalization is a random, incoherent process. Specifically, the dimeric species is viewed as the following chemical equilibrium:

$$(Bchl_I^{+}\cdot Bchl_{II}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (Bchl_I Bchl_{II}^{+}\cdot)$$

where $k_1 = k_2 \equiv k$, and the correlation time for "hole jumping" $\tau_c \equiv 1/k$. We note that $k = 0$ corresponds to "complete monomer" while $k = \infty$ approximates complete delocalization into a "supermolecule". In actual fact the case of the supermolecule is more correctly treated by the coherent delocalization discussed later. When the unpaired electron (hole) is on $Bchl_I$, its EPR frequency is determined by the local magnetic environment pri-

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marily from hyperfine interactions with the nuclear spins of $Bchl_I$; similarly, the electron on $Bchl_{II}$ has an EPR frequency determined by the environment from $Bchl_{II}$. With high probability, the magnetic environments are different and are only infrequently identical. Thus, in general, when the hole "jumps" back and forth from $Bchl_I$ to $Bchl_{II}$ the resonance frequency changes rapidly and some "average" of the resonance frequencies is observed. If the distributions of environments of $Bchl_I$ and $Bchl_{II}$ are known, then the resulting "average" magnetic resonance spectrum can be used to determine the jump time τ_c (see eq 1 below).

The distribution of magnetic environments of the chlorophylls is primarily due to magnetic nuclei, mostly the hydrogen nuclei in the chlorophyll molecules themselves. The hydrogen nuclei produce a Gaussian distribution of EPR frequencies characterized by a well-understood width. Thus, not only is this distribution well-known, but the width can be easily manipulated by replacement of ^1H with ^2H, i.e., H with D. The question of the dimer time scale can be answered by the determination of τ_c. In EPR, ENDOR, and ESE, an appropriate version of the following equation of the fast motional regime[15] can be employed

$$\tau_c = 2\overline{\Delta\omega_{ic}}/\overline{\Delta\omega_{iT}^2} \qquad (1)$$

where i = H, D (H = ^1H and D = ^2H) and $\overline{\Delta\omega_{ic}}$ is effectively the average contribution to the homogeneous line width due to the incoherent jumping of the electron between $Bchl_I$ and $Bchl_{II}$, and $\overline{\Delta\omega_{iT}^2}$ is the total second moment of the monomer cation $Bchl^{+}\cdot$. The right-hand side of eq 1 differs from the normal textbook fast limit formula by the factor 2; this factor of 2 in eq 1 arises because $\overline{\Delta\omega_{ic}}$ is an average value for all possible dimers. Because the magnetic environment of the chlorophyll radicals has a Gaussian distribution, $\overline{\Delta\omega_{iT}^2}$ is easily measured for the chlorophyll cations (eq 2 below); thus, in order to determine the jump time τ_c associated with the special pair cation, only $\overline{\Delta\omega_{ic}}$ must be measured. In cases where spectra with good resolution allow complete EPR line-shape analysis, $\overline{\Delta\omega_{ic}}$ can be measured. However, in the chlorophyll radical spectra of very low resolution, EPR and ENDOR cannot measure $\overline{\Delta\omega_{ic}}$ directly, and only limits can be placed on the value of $\overline{\Delta\omega_{ic}}$ resulting in corresponding limits on the value of τ_c. Whereas EPR and ENDOR probe the inhomogeneous line width, $\overline{\Delta\omega_{iT}}$, ESE measures a homogeneous line width and more accurately determines $\overline{\Delta\omega_{ic}}$. In the case of ESE two short but intense microwave pulses separated in time by τ_p produce an echo $\sim\tau_p$ after the second pulse. The echo is the resonant magnetization of the sample probed by the first pulse and "refocused" by the second pulse. The echo intensity as a function of τ_p provides an accurate time-domain measurement of the homogeneous line shape even when the external magnetic field is inhomogeneous and/or when the sample's spectrum is inhomogeneously broadened. In fact, the technique requires inhomogeneously broadened spectra before echoes can be directly observed. ESE is superior to EPR and ENDOR in determining limits on τ_c.

Thus far, we have treated delocalization within the Bchl special pair as a random, incoherent jumping process. In the second viewpoint the special pair is viewed as a supermolecule with coherent and roughly equal spin delocalization. The equal amplitudes for spin delocalization on the two halves of the pair is required by the ENDOR data.[7-12] By this description, the coherence time T_c is a measure of the lifetime of the supermolecule in a given set of energy levels (eigenstates). In contrast to the incoherent interpretation, no significant spectroscopic homogeneous line broadening is directly associated with the coherent delocalization process. Instead, one can place a useful minimum on the coherence time, T_c, determined by the inverse of the homogeneous line width consistent with the application of the uncertainty principle. For the MR signals associated with photosynthesis, only the inhomogeneous line width of the cation can be determined by EPR or ENDOR. Since ESE can measure the approximate homogeneous line width, again ESE is the experimental method of choice to determine the time scale of delocalization.

The models represent two extremes in interpreting the magnetic resonance experiments. Each viewpoint can explain the experimental results, and each approach is valid within certain limits. The incoherent picture begins with a monomer cation where the cation jumps randomly between the sites of a special pair. The characteristic jump time τ_c is approximately the time that the cation retains the properties of a specific monomer. For inherent resolving times longer than approximately the jump time, the cation appears to be a dimer, and for inherent resolving times shorter than τ_c, the cation appears to be a monomer. Later we will show that the experimentally determined value of the jump time, τ_c', represents the maximum "monomer time"; in other words, the true τ_c could be less than the maximum limit set by the magnetic resonance experiments.

In contrast, the coherence model begins with a supermolecule dimer. The experimentally determined coherence time T_c represents the minimum time that the cation appears to be a coherent dimer in the magnetic resonance (MR) experiments. Coherence lifetime is a quantum mechanical distinction for the preservation of some "phase" between two dimer eigenstates.[14] A simple description of coherence is neither possible nor required for our purposes here. What is important is that for all MR observations times shorter or longer than the coherence lifetime, the cation appears to be a dimer. Thus in all MR cases, the coherent model can be interpreted in terms of a picosecond dimer.

In order to establish the picosecond nature of the $Bchl_{sp}$ using MR, it must be shown that either the coherent model is the only correct viewpoint or alternatively the τ_c' of the incoherent model must be determined with picosecond time resolution. At present, experiments have not been performed by MR to distinguish these two extreme viewpoints of the $Bchl_{sp}$. Thus traditional MR as interpreted in the incoherent regime can lead to a dimer cation with a "nonpicosecond" nature, since the jump time τ_c' is the longest time that the system can appear monomer-like and still explain the magnetic resonance data. In previous MR experiments the incoherent model is compatible with a picosecond monomer and demands only a nanosecond dimer. Please note that an incoherent picosecond dimer is also possible, just not demanded. In the next section, we reject any possibility of a picosecond monomer cation by using ESE as the experimental probe. (Although the incoherent model is the most relevant to establish experimentally the picosecond nature of the chlorophyll special pair cation, we favor the coherent model as the more accurate description of the chlorophyll special pair).

Results and Discussion

A. Incoherent "Jumping" Monomer Model. We first treat the EPR measurement of $\overline{\Delta\omega_{ic}}$ for chlorophyll-like radicals. We have mentioned that the EPR spectrum of the chlorophyll cations can be accurately described by a Gaussian line shape whose width is primarily determined by hyperfine interactions between the protons and the unpaired electron. Regardless of origin of the width, for Gaussian line shapes the total second moment $\overline{\Delta\omega_{iT}^2}$ is given by

$$\overline{\Delta\omega_{iT}^2} = 1/4\ \overline{\Delta\omega_{iTPP}^2} \qquad (2)$$

and

$$\overline{\Delta\omega_{iT}^2} = \overline{\Delta\omega_i^2} + \overline{\Delta\omega_x^2} \qquad (3)$$

for i = H, D where $\Delta\omega_i^2$ is the average second moment due to protons or deuterons, $\Delta\omega_x^2$ is that part of the total second moment due to all other sources, and $\Delta\omega_{iTPP}$ is the observed first derivative line width of the Gaussian line. Second-moment contributions are additive for lines which are convoluted together. Using the fact that

$$\overline{\Delta\omega_H^2} = C_0\overline{\Delta\omega_D^2} \qquad (4)$$

where $C_0 = 15.9097 = (3/8)(\gamma_H/\gamma_D)^2$, one can derive from eq 3 the relationship

$$\overline{\Delta\omega_X^2} = \frac{1}{(C_0 - 1)4}(C_0\Delta\omega_{DTPP}^2 - \Delta\omega_{HTPP}^2) \qquad (5)$$

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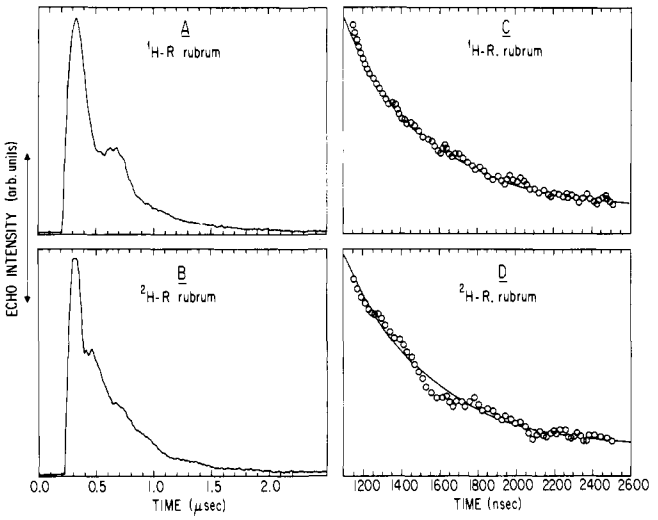

Figure 1. Phase memory decay of special pair cations at 4 K in oxidized whole cells of (A) protonated and (B) deuterated *Rhodospirillium rubrum*. Nonlinear least-squares fits of a exponential decay to data from (C) protonated and (D) deuterated special pair cations in vivo. Data recorded and analyzed on a home-built ESE spectrometer interfaced to a Nicolet 1180 computer.

Since the special pair cation in vivo has a Gaussian line shape, the fast motional limit holds for all nuclear spin combinations and

$$\overline{\Delta\omega_X{}^2} \geq \overline{\omega_c{}^2} \tag{6}$$

It follows from eqs 5, eq 6, and eq 1 that

$$\tau_c \leq \frac{4}{\Delta\omega_{H7PP}}\left[\frac{C_0}{C_0-1}\left(\frac{\Delta\omega_{D7PP}{}^2}{\Delta\omega_{H7PP}{}^2}\right)-\frac{1}{C_0-1}\right]^{1/2} \tag{7}$$

Using the values $\Delta\omega_{H7PP} = X_1$ (12.8 G) where $X_1 = 2\pi \times 2.83 \times 10^6$ rad/(s G) and $\Delta\omega_{D7PP} = X_1$ (5.4 G) according to eq 7, the EPR experiment requires $\tau_c \leq 6.2$ ns. Six nanoseconds is 3 orders of magnitude slower than the initial picosecond photochemistry, and we emphasize that the EPR experiment does not require the special pair cation to be delocalized on a time scale comparable to the primary act. Thus we conclude a serious problem exists when comparing the EPR observations on the special pair to the initial picosecond photosynthesis act. Similar arguments hold for the ENDOR experiments.

The question arises as to whether the magnetic resonance time scale can be shortened significantly by use of ESE. The advantage of ESE primarily originates in its ability to measure homogeneous line shapes since one can then utilize a more precise equation involving the average total homogeneous line width. The phase memory time τ_m is the characteristic time for echo decay in a two-pulse echo experiment. Typical phase memory decays in vivo of the special pair radical are given in Figure 1 for both protonated and deuterated organisms. The relationship between τ_m and $\overline{\Delta\omega_{ic}}$ is given by[17]

$$\overline{\Delta\omega_{ic}} \leq 1/\tau_{im} \tag{8}$$

for i = H, D. A nominal τ_m value is about 3 μs in the absence of the jump process of interest here; i.e., Chl monomeric free radicals exhibit phase memory times of about 1 μs. In the case of ESE the hole jumping randomly within the special pair results in an additional decrease in the phase memory time. Since the decrease in τ_m due to jumping is sensitive to inhomogeneous broadening from hyperfine, it can be altered by the use of isotopes. Thus, again the isotopes H and D are useful in lowering the limit placed on the jump time τ_c. For the homogeneous line shapes that occur in the chlorophyll cations the following relationship is sufficient[17]

$$k_{im} = \tau_{im}{}^{-1} = \overline{\Delta\omega_{ic}} + \overline{\Delta\omega_{ix}} \tag{9}$$

where $\overline{\Delta\omega_{ix}}$ represents all contribution to k_{im} other than that due to the jumping process represented by $\overline{\Delta\omega_{ic}}$.

Subtracting eq 9 for D from eq 9 for H and combining the difference with eq 1 and eq 2 result in

$$\tau_c = \frac{8(\Delta k_m - \Delta\omega_{HDX})}{\Delta\omega_{H7PP}{}^2 - \Delta\omega_{D7PP}{}^2} \tag{10}$$

where $\Delta k_m = k_{Hm} - k_{Dm}$ and $\Delta\omega_{HDX} = \Delta\omega_{HX} - \Delta\omega_{DX}$. Since $\Delta\omega_{HDX}$ cannot be measured independently, only the following can be determined:

$$\tau_c \leq 8\ \Delta k_m/(\Delta\omega_{H7PP}{}^2 - \Delta\omega_{D7PP}{}^2) \tag{11}$$

The difference in phase memory decay rates has been measured to be 0 ± 40 kHz (see Figure 1). Thus, by using the same values for $\Delta\omega_{H7PP}$ and $\Delta\omega_{D7PP}$ as in the EPR experiment, 40 kHz results in $\tau_c \leq 7$ ps.

A reasonable estimate for $\Delta\omega_{HDX}$ based on similar isotope experiments in monomer Chl radicals suggests that τ_c is significantly less than 7 ps. Such considerations strongly support the view that the special pair cation will appear dimeric when a technique with an inherent resolving time of a few picoseconds or longer is used. Thus we conclude that magnetic resonance spectroscopy can study reversible picosecond events in random, solid solutions or single crystals. In energy terms, 7 ps represents about 5 cm^{-1} of minimum exchange interaction, and again the interaction is likely much greater. Five reciprocal centimeters suggests that the members of the special pair are at least within ~6 Å of each other,[16] and much closer distances are likely more realistic. Thus, all evidence suggests that the special pair is a dimer on a time scale of a few picoseconds and certainly is dimeric on a 7-ps time scale.

B. Coherent Dimer Lifetime Supermolecule Model. In this model each dimer energy level and corresponding eigenfunction is split into two levels separated by the interaction energy V_{AB} provided by the supermolecule structure. The upper level is thus no longer a ground state and is populated at equilibrium to the extent that thermal energy is comparable to the interaction energy V_{AB}. The coherence time T_c is a measure of the lifetimes of these two energy levels. In particular, we consider the lifetime of the lower ground-level level in the supermolecule. The coherence model utilizes the inverse of the homogeneous line width as a limit on the coherence time T_c, in other words, rate equations of the slow motional regime.

EPR of the chlorophyll cations determines only the inhomogeneous line width which sets limits on the homogeneous line widths. Thus, for the normal EPR experiment, eq 7 is still appropriate (except that the left-hand side is called T_c, not τ_c) and by EPR the minimum coherence time T_c is 6.2 ns. The 6.2 ns represents a minimum duration of dimer coherence. The measurement provides only a minimum value because other contributions to the second moment of the EPR spectra such as nitrogen hyperfine have not been taken into account. From the coherent model viewpoint, the supermolecule dimer also exists at shorter times, namely on a picosecond time scale. By itself, the EPR experiment can be interpreted in the two following extremes: (1) a supermolecule exists and is coherent for at least 6.2 ns (i.e., a picosecond species must exist); or (2) an incoherent dimer exists but it may be necessary to observe it for times longer than the 6.2-ns maximum average jump time to see the dimeric nature (i.e., a picosecond species is neither required nor eliminated).

Thus, EPR alone (or ENDOR) cannot establish the picosecond nature of the special pair.

We can also measure a limit T_c' for the coherent lifetime of the supermolecule by using ESE. Because the coherence decay contributes directly to the phase memory decay, one can place

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a minimum of ~ 1 μs on the supermolecule coherent lifetime T_c in using ^1H or ^2H reaction centers. Again, ESE is the advantageous method in comparison with EPR, ENDOR, or optical spectroscopy. According to ESE, the supermolecule dimer is coherent for at least 1 μs and again the coherent picture requires a picosecond dimeric species.

Summary and Conclusions

All measurements can be interpreted by considering the special pair as a symmetrical dimer on the picosecond time scale. The coherent delocalization interpretation of the magnetic resonance data demands a picosecond dimer in all cases. (We note in passing that the picosecond transient optical spectrum can still appear to be that of a nonstationary state monomer). The incoherent delocalization model can be interpreted in all cases in terms of a picosecond special pair, although only a nanosecond species is required by EPR or ENDOR. However, ESE results show the special pair cation must be a picosecond species for both incoherent or coherent models. This last statement is possible only because the ESE experiment on reversible processes provides spectroscopic data relevant to the subpicosecond time scale. Thus, from ESE measurements, we conclude that the chlorophyll special pair cation is a picosecond dimer.

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Resonance Raman Spectra and Vibrational Assignments of "Red" and "Black" Forms of Potassium Bis(dithiooxalato)nickel(II)

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Abstract: The infrared and Raman spectra of the red form of potassium bis(dithiooxalato)nickel(II) have been measured and complete vibrational assignments made on the basis of the ^{58}Ni-^{62}Ni isotope data and normal coordinate calculations. Resonance Raman spectra of the red form have provided two overtone series of the totally symmetric modes; $n_1\nu_1$ and $n_1\nu_1 + \nu_2$ where ν_1 is the C-C coupled with the C-S stretch and ν_2 is the C=O coupled with the C-C stretch. The calculated harmonic wavenumber and anharmonicity constant from the former series are 1088.5 ± 0.8 cm^{-1} and -1.74 ± 0.05 cm^{-1}, respectively. The differences in infrared and Raman spectra between the red and black forms have been interpreted in terms of molecular orbital and valence bond theories. Excitation profile studies of two totally symmetric vibrations (ν_1 and ν_4(Ni-S stretch)) of both forms reveal the presence of three electronic transitions in the visible region. The origin of these transitions has been discussed on the basis of previous molecular orbital calculations.

Potassium bis(dithiooxalato)nickel(II), $K_2[Ni(dto)_2]$, was first prepared and investigated by Robinson and Jones in 1912.[1] The salt which they obtained as dark red crystals from aqueous solution was first characterized via X-ray analysis by Cox et al.[2] Later Coucouvanis and his colleagues[3] refined the data and established that the red crystals were monoclinic (space group C_2/c) with $a = 22.52$ Å, $b = 7.86$ Å, $c = 11.09$ Å, and $\beta = 143.92°$. The dithiooxalate ion (dto^{2-}) is a versatile ligand that forms O,O-; S,S-; and O,S-bonded complexes where the coordination sites employed depend upon the "hardness" or "softness" of the metal.[4,5] In addition, it has the desirable property of being able to delocalize charge density throughout its relatively extensive π-orbital system. This latter property was one of the reasons that dto^{2-} ion was an early choice of Latham et al. in their quest for square-planar complexes of transition metals.[6] Following the discovery of the highly one-dimensional conducting system consisting of partially oxidized bis(oxalato)platinum[7,8] and unsuccessful attempts to synthesize similar Pt systems with the dto^{2-} ion as the ligand, Gleizes et al.[9] substituted Ni for Pt and attempted to obtain a partially oxidized form of $[Ni(dto)_2]^{2-}$. Although they claimed to be able to detect a partially oxidized species in acetone solution, they were unable to isolate it. However, when using $K_2Cr_2O_7$ as an oxidant they obtained a black, crystalline material which was subsequently shown to correspond to the formula $K_2[Ni(dto)_2]$. X-ray analysis revealed that the crystals have monoclinic symmetry (space group $P2_1/n$) with $a = 11.04$ Å, $b = 4.19$ Å, $c = 12.72$ Å, and $\beta = 111.78°$. In both cases, the $[Ni(dto)_2]^{2-}$ moiety is planar, but in the black crystals it is tilted with respect to the stacking axis.

In this paper we report the results of a detailed IR and Raman investigation of these two fascinating compounds. Included in the above are complete band assignments obtained from a normal coordinate analysis of the red form of $K_2[Ni(dto)_2]$, calculated values for the anharmonicity constant of the ν_1 mode (C-C coupled with C-S stretch), obtained from overtone progressions in resonance Raman spectra as well as verification of earlier MO calculations[6] through the use of Raman excitation profiles.

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