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Electron Spin Echo Envelope Modulation (ESEEM) Study of $\mathrm{Cu^{II}}$(dien)–Pyrazole (dien = Diethylenetriamine) and –Pyridazine Complexes[1]

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Electron spin echo envelope modulation spectroscopy (ESEEM) was used to study the nuclear quadrupole interactions of the remote nitrogen of pyrazole and pyridazine in $\mathrm{Cu^{II}}$(dien)–heterocycle complexes. The quadrupole parameters were obtained by field-dependent ESEEM spectral simulations for the amino nitrogen of pyrazole ($e^2qQ = 2.86$ MHz and $\eta = 0.74$) and for the imino nitrogen of pyridazine ($e^2qQ = 5.35$ MHz and $\eta = 0.02$). The values obtained for pyridazine are comparable to those for metal-free solid pyridazine (Schempp, E.; Bray, P. J. *J. Chem. Phys.* **1967**, *46*, 1186). Since the quadrupole parameters for the amino nitrogen in metal-free solid pyrazole have not been reported, a comparison is made with the values obtained in the gas-phase measurement using microwave spectroscopy ($e^2qQ = 3.02$ MHz and $\eta = 0.52$: Nygaard, L.; et al. *J. Mol. Struct.* **1974**, *22*, 401). Although the difference in quadrupole parameters for pyrazole in the $\mathrm{Cu^{II}}$(dien) complex as compared to values for pyrazole in the gas phase is small, a hydrogen-bonding effect can be attributed to the change observed. An explanation for the differences in quadrupole parameters between the amino nitrogen of imidazole and of pyrazole complexed to $\mathrm{Cu^{II}}$(dien) as a consequence of cross-substitution of nitrogen and carbon in the five-membered heterocycle is given.

Electron spin echo envelope modulation spectroscopy has been used to determine the nuclear quadrupole interaction of weakly coupled ^{14}N near paramagnetic centers.[2–6] For Cu(II)–imidazole complexes in crystalline solids,[4] in solution,[2,3,5] and in proteins,[7] it is the remote or nonbonded ^{14}N that gives rise to the ESEEM spectrum, the directly coordinated nitrogen being too strongly coupled to have effect.[8] At X-band under conditions where the electron–nuclear coupling is nearly equivalent to twice the ^{14}N Zeeman interaction,[2] the so-called condition of exact cancellation,[9] the spectrum is dominated by four lines. The three sharp low-frequency lines, $\nu_\pm$ and ν_0, that arise from one of the electron spin manifolds are related to the nuclear quadrupole interaction, so that

$$\nu_\pm = {}^3/_4 e^2qQ(1 \pm \eta/3) \qquad (1)$$

$$\nu_0 = {}^1/_2 e^2qQ\eta \qquad (2)$$

where e^2qQ is the nuclear quadrupole coupling constant and η is the asymmetry parameter. For the second electron spin manifold, where the electron–nuclear coupling and the Zeeman interaction are additive, typically one obtains a broad spectral feature, a so-called "$\Delta M = 2$" or double-quantum transition, at a frequency approximately equal to the sum of twice the ^{14}N nuclear Zeeman frequency plus the electron nuclear hyperfine coupling.[3a] The correspondence between nuclear quadrupole parameters obtained from ESEEM measurements for imidazole, *N*-methylimidazole, and *N*-benzylimidazole, complexed to $\mathrm{Cu^{II}}$(dien) in frozen solution with those obtained from nuclear quadrupole resonance (NQR) studies of the metal-free solids is quite good,[3a,4a] indicating that the coordination of Cu(II) at N3 of imidazole has little effect on the electric field gradient at N1 and therefore on the nuclear quadrupole interaction.

A structural isomer of imidazole is pyrazole. The cross-substitution for carbon and nitrogen at the 2- and 3-positions of the five-member heterocycle has a profound effect on both nitrogen atoms. For N1, the pK_a is dropped by about 4 pH units, from 6.9 for imidazole to 2.5 for pyrazole.[10] Concomitant with this weakening in basicity is a marked reduction in affinity for metal ions.

In this investigation, we have carried out an ESEEM study of pyrazole complexed to $\mathrm{Cu^{II}}$(dien) in order to determine the effect on the nuclear quadrupole interaction of moving the nitrogen from the 3-position in imidazole to the 2-position in pyrazole. In an analogous ESEEM study, we have also examined the $\mathrm{Cu^{II}}$(dien) complex of pyridazine, which is an analog of pyrazole but in a six-member ring. Unlike pyrazole or imidazole, no hydrogen atom is attached to either nitrogen in pyridazine. As for $\mathrm{Cu^{II}}$(dien)–imidazole, those directly coordinated nitrogen atoms, N2 of pyrazole and pyridazine, as well as those from diethylenetriamine, are spectroscopically silent to ESEEM measurements. The spectral features obtained arise from the remote nitrogen (N1) of the coordinated heterocycle.

The nuclear quadrupole parameters obtained for the protonated ^{14}N of pyrazole complexed to $\mathrm{Cu^{II}}$(dien) in frozen-solution samples are far closer to the values for pyrazole in the gas phase[11] than

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(1) Abbreviations: ESEEM, electron spin echo envelope modulation; dien, diethylenetriamine; CW, continuous wave; NQR, nuclear quadrupole resonance; ENDOR, electron–nuclear double resonance.

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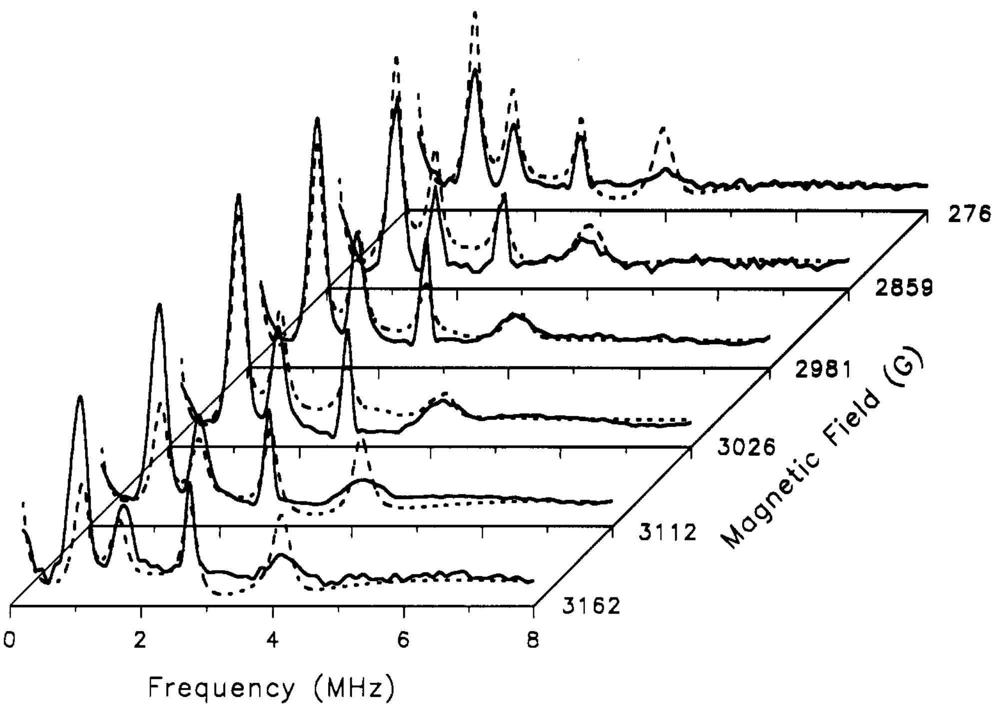

Figure 1. Three-pulse ESEEM spectra and spectral simulations for Cu^{II}(dien)–pyrazole at six different magnetic field settings within the EPR absorption: solid line, experimental data; dashed line, simulation. Measurement conditions: microwave frequency 8.7355 GHz; temperature 4.2 K. The magnetic fields at which the spectra were collected are indicated, and the τ value for each spectrum is equal to twice the proton periodicity at the corresponding magnetic field. Simulation parameters are listed in Table 1.

the comparable values for the protonated nitrogen of imidazole complexed to Cu^{II}(dien). An explanation for the structural differences between pyrazole and imidazole which affect nuclear quadrupole parameters as well as hydrogen-bonding properties of the N–H bond in pyrazole is discussed. The effect of the coordination of Cu(II) to pyridazine on the quadrupole parameters of the noncoordinated nitrogen is also explored.

Experimental Section

Sample Preparation. A complex of Cu(II) and dien using 20% excess ligand was prepared by combining cupric acetate (Sigma) with dien (Sigma) to a final concentration of 5 mM Cu(II). It was then titrated optically with pyrazole (Eastman; recrystallized from petroleum ether) at pH 8.3–8.4. The binding constant, pK_a, obtained by a least-squares fit[3a] of the absorption at 590 nm, is −2.20 mM^{-1}, more than 2 orders of magnitude lower than that of Cu^{II}(dien) with imidazole.[3a]

The sample prepared for an ESEEM study contained a 50-fold molar excess of pyrazole (pH = 8.3). An equal volume of ethylene glycol was added to ensure good glass formation. The final concentration of Cu(II) was 2 mM. The Cu^{II}(dien)–3-methylpyrazole complex (Eastman) was prepared in the same way as that with pyrazole.

Cu^{II}(dien)–pyridazine (Sigma) was prepared using a 200-fold molar excess of the heterocycle ligand, rather than a 50-fold excess, reflecting the weaker basicity of the ligand. The pH of the complex was 9.0 before ethylene glycol was added.

Spectroscopy. X-band CW EPR spectra of Cu^{II}(dien)–pyrazole and –pyridazine at 77 K were obtained with a Varian E-9 spectrometer equipped with a Varian gaussmeter and a Systron-Donner frequency counter. The spectrum of the pyrazole complex ($g_\parallel$ = 2.215, $A_\parallel$ = 595 MHz, $g_\perp$ = 2.045, $A_\perp$ = 70 MHz) and that for the pyridazine complex ($g_\parallel$ = 2.210, $A_\parallel$ = 591 MHz, $g_\perp$ = 2.04, $A_\perp$ = 70 MHz) were simulated with the computer program QPOWA, supplied by Dr. Linn Belford.[11]

Spectral Simulation. ESEEM spectra were obtained by Fourier transformation of stimulated echo (90°–τ–90°–T–90° pulse sequence) data as described previously.[6,12] Spectral simulations were carried out using the density matrix formalism of Mims[12] together with an angle-selection scheme originally developed for ENDOR spectroscopy.[13] Under favorable conditions, the electron–nuclear coupling constants and the nuclear quadrupole parameters, as well as the orientation of the principal axes of these two tensors with respect to those of the g tensor, have been obtained.[3b,6a] In addition to the principal values of the nuclear quadrupole interaction, $e^2qQ(1-\eta)/2$, $e^2qQ(1+\eta)/2$, and e^2qQ, which can be derived directly from the quadrupole frequencies by spectral observation, and the Euler angles α, β, and γ, the rotations required to align the principal axes of the quadrupole tensor and the g tensor, are obtained in the spectral simulation procedure. As before,[3] the electron–nuclear coupling tensor is taken to be axial, with principal values $A_{iso} - F$, $A_{iso} - F$, and $A_{iso} + 2F$, where A_{iso} is the isotropic component and F the anisotropic component. Assuming a point dipole–dipole interaction between the unpaired electron of copper and the coupled ^{14}N of the heterocycle, the magnitude of F is related to the effective distance r_{eff} by $F = g_e\beta_e g_N\beta_N/r_{eff}^3$, where g_e and g_N are the electron and nuclear g factors and β_e and β_N are the Bohr and nuclear magnetons. The angles θ_N and ϕ_N, which specify the apparent spherical polar coordinates of the interacting ^{14}N, are sufficient to describe the orientation of the principal axes of the electron–nuclear coupling tensor and the g tensor for the axial system. These four parameters are also obtained from spectral simulations.

Results and Discussion

ESEEM of Cu^{II}(dien)–Pyrazole and –Pyridazine. The CW EPR spectra for Cu^{II}(dien)–pyrazole and for Cu^{II}(dien)–pyridazine are very similar to that for Cu^{II}(dien)–imidazole,[3a] suggesting that the heterocycle in each case binds equatorially to Cu(II) in a $d_{x^2-y^2}$ ground-state complex. Axial coordination of heterocycle is also possible as a large excess of ligand is used to form each complex. However, axially coordinated ^{14}N makes little spectral contribution and is not expected to interfere with the measurement for an equatorially coordinated ^{14}N-containing ligand, especially under conditions of exact cancellation. For equatorially coordinated pyrazole and pyridazine, the coupling to the directly coordinated ^{14}N is expected to be too large to give rise to the ESEEM.[14] It is the remote ^{14}N that is responsible for the modulations we observe, as it is in the case for Cu^{II}(dien)–imidazole.

The ESEEM spectrum for Cu^{II}(dien)–pyrazole, studied at 8.74 GHz and 3026 G, consists of four lines (1.04, 1.67, 2.73, and 4.19

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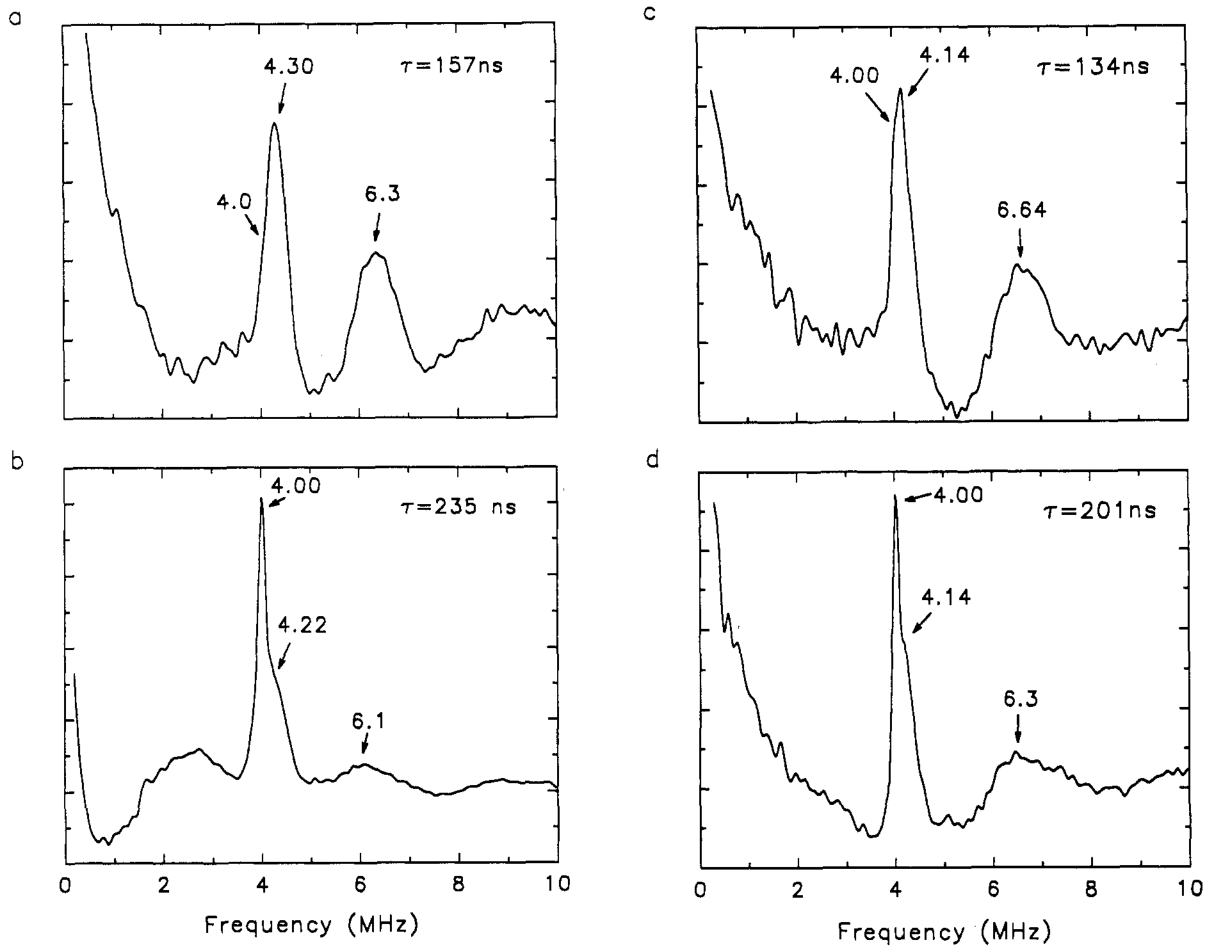

Figure 2. Three-pulse ESEEM spectra of Cu^{II}(dien)–pyridazine studied at different τ values at two different microwave frequencies. Measurement conditions: microwave frequency (a, b) 8.6455 GHz and (c, d) 10.0970 GHz; magnetic field (a, b) 3000 G and (c, d) 3502 G; temperature 4.2 K; τ value (a) 157 ns, (b) 235 ns, (c) 134 ns, and (d) 201 ns. The $1/\tau$ value is 6.36 MHz for (a) and 4.26 MHz for (b). The suppression effect can be clearly seen for the 4.0-MHz line in (a) and the 6.3-MHz line in (b), suggesting that they arise from transitions from different electron spin manifolds. The same effect is seen at 10.0970 GHz in (c) and (d).

MHz), characteristic of a magnetically coupled ^{14}N (Figure 1). As noted for spectra obtained at distinct positions across the EPR absorption envelope (Figure 1), the frequencies of the three low-frequency lines are virtually field independent and the lower two add to give the third, indicative of the satisfaction of the exact cancellation condition. The higher frequency feature scales with approximately twice the Zeeman interaction for ^{14}N. The three low-frequency lines are the quadrupole lines, and the higher frequency feature is the double-quantum line.[3a] Similarly, a four-line spectrum (1.21, 1.60, 2.82, and 4.22 MHz at 3026 G) with differences in the quadrupole frequencies is obtained for the 3-methylpyrazole complex. From the field dependence of frequencies and the relative intensities of the quadrupole and double-quantum lines in the ESEEM spectrum, one can accurately assess, for Cu^{II}(dien)–pyrazole and 3-methylpyrazole, the nuclear quadrupole parameters, the relative orientation of the nuclear quadrupole tensor with respect to the g tensor, and the magnitudes of the isotropic and anisotropic hyperfine interactions.

In the case of the pyridazine complex, only two major features are obtained at 8.6 GHz. The first is a line at 4.3 MHz, with a poorly resolved shoulder at 4.0 MHz (Figure 2a), whose frequency is nearly field independent across the EPR absorption. The second is a broader line at a frequency of 6.32 MHz (at 3000 G), which scales with approximately twice the Zeeman interaction. However, the four-line spectrum, normally seen for ^{14}N, is not observed.

When examined at a higher microwave frequency, 10.1 GHz, it was found that the 4.3-MHz feature moved slightly to 4.14 MHz, while the 6.3-MHz line moved to 6.6 MHz when the magnetic field was increased by 502 G (Figure 2c).[15] The high-frequency line again scaled with twice the Zeeman interaction for ^{14}N, suggesting that the modulations observed are attributed to this nucleus.

Further, with a judicious use of τ value, one can suppress one or the other spectral components. For example, in three-pulse studies at 8.64 GHz, when τ, the spacing between the first and second microwave pulses, was set at 157 ns, approximately the periodicity of the 6.3-Mhz line, the 4.0-MHz line was suppressed and appeared only as a shoulder on the 4.3-MHz line (Figure 2a). Conversely, by applying the second pulse at 235 ns subsequent

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(14) The spectrum was also obtained for Cu^{II}(dien)–pyrimidine and Cu^{II}-(dien)–pyrazine, in which the two nitrogens of the six-member ring are separated by one and two carbon atoms, respectively. In both complexes, 200-fold excess of heterocycle ligand was used. No resolvable modulations were observed, either for nitrogen atoms directly coordinated to Cu^{II} from equatorial and axial ligands or for those from noncoordinated ligands.

(15) The frequencies of the three quadrupole lines are not exactly the same as the "zero-field" NQR frequencies, especially when the ^{14}N nuclear Zeeman and the electron–nuclear coupling do not satisfy the exact cancellation condition. A field-dependent term must be introduced so that $\nu_0 = 2(\nu_N - a/2) + {}^1/_2e^2qQ\eta$, $\nu_- = -(\nu_N - a/2) + {}^3/_4e^2qQ(1 - \eta/3)$, and $\nu_+ = (\nu_N - a/2) + {}^3/_4e^2qQ(1 + \eta/3)$, where the ν_N is the ^{14}N Zeeman frequency and a is the electron–nuclear coupling. For the double-quantum line, $\nu_d = 2(\nu_N + a/2) + {}^1/_2e^2qQ\eta$. When the spectrum is obtained at a higher microwave frequency, therefore, at a higher magnetic field, the ^{14}N Zeeman frequency also increases. The frequencies, ν_0, ν_+, and ν_d increase, while the frequency of ν_- decreases. The 4.3-MHz line is assigned to ν_-. As can be seen later, the 4.0-MHz line can be assigned to ν_+, which exhibits the suppression effect[12b] with ν_d from the other electron spin manifold (see below).

Table 1. ^{14}N Superhyperfine Parameters for Cu^{II}(dien)–Heterocycle Complexes Obtained by ESEEM Spectral Simulations

	e^2qQ (MHz)	η	α, β, γ^a (deg)	A_{iso} (MHz)	r_{eff} (Å)	θ_N, ϕ_N (deg)
pyrazole	2.86 ± 0.02	0.74 ± 0.02	0, 75, 0	1.37 ± 0.05	3.2 ± 0.1	75, 0
3-methylpyrazole	2.88 ± 0.02	0.86 ± 0.02	0, 75, 0	1.40 ± 0.05	3.2 ± 0.1	75, 0
pyridazine	5.3 ± 0.1	0.02 ± 0.05	0, 30, 0	2.7 ± 0.1	2.5 ± 0.3	75, 0
imidazole^b	1.43 ± 0.03	0.94 ± 0.05	0, 90, 0	1.65 ± 0.05	3.2 ± 0.1	90, 0

^{a} The uncertainty for the angles in simulation is 15°. ^{b} The parameters for imidazole for comparison are from refs 3a,c.

to the first pulse, approximately the periodicity of the 4-MHz feature, the 4.0-MHz line appeared much stronger than the 4.3-MHz line and the 6.3-MHz line was suppressed (Figure 2b). This suppression effect,[12b] also seen at 10.1 GHz (Figure 2c,d), suggests that the 4.0- and 6.3-MHz lines in the spectrum arise from ^{14}N ENDOR transitions in different electron spin manifolds. The nature of the shift of the 6.3-MHz line with field is indicative of a $\Delta M = 2$ transition, while the relative invariance of frequency of the 4-MHz feature suggests that it primarily arises from the nuclear quadrupole interaction. The alteration of τ and field changes the line shape of the 4-MHz feature so that the 4.0-MHz shoulder has variable intensity. If this feature indeed consists of two nearly resolved nuclear quadrupole lines, then the third would be expected at or below 0.3 MHz, beyond the resolution limit of the spectroscopic measurement. Therefore, the first feature observed in the spectrum consists of two unresolved quadrupole lines at 4.0 and 4.3 MHz, and the second feature at 6.3 MHz represents the double-quantum transition. The electron–nuclear coupling in Cu^{II}(dien)-pyridazine, then, approximately satisfies the exact cancellation condition. However, because of the missing lowest quadrupole line and the poor resolution of the other two, the nuclear quadrupole and electron–nuclear coupling parameters cannot be as well determined as for pyrazole where a complete four-line spectrum is obtained.

Spectral Simulation. The approach to spectral simulation was described in detail previously.[3c,5] As the EPR spectra for all three complexes are typical of axial $d_{x^2-y^2}$ complexes,[16] the three amine nitrogen atoms from the dien moiety and N2 from pyrazole or pyridazine approximately form the equatorial plane. Two principal axes of the g tensor, g_x and g_y, lie arbitrarily in this plane, and g_z is perpendicular to the plane. Therefore, θ_N and ϕ_N, the azimuthal angles, can be first reasonably assumed as 90 and 0°, respectively. Values for quadrupole parameters, e^2qQ and η, and for the electron–nuclear coupling constants, A_{iso} and r_{eff}, were estimated on the basis of frequencies of the quadrupole lines (eqs 1 and 2) and of the double-quantum line at different magnetic fields. The Euler angles were then varied to simulate the relative intensities of the quadrupole lines at the field setting where the largest echo was obtained. It was found that variations of α and γ had little effect, while variations of β produced a significant change. The range for β giving reasonable fits to the relative intensities of quadrupole lines in experimental data was determined. Quadrupole parameters were then readjusted to give a good agreement of frequencies of quadrupole lines. Subsequently, all the other parameters were refined to give reasonably good fits for all the spectra obtained across the EPR absorption. The best values for the quadrupole and electron–nuclear parameters obtained for pyrazole, 3-methylpyrazole, and pyridazine are listed in Table 1.

Microwave spectroscopic studies[17] and ab initio calculations for pyrazole[18] show that the axis with the largest principal value for the quadrupole tensor lies perpendicular to the pyrazole plane.

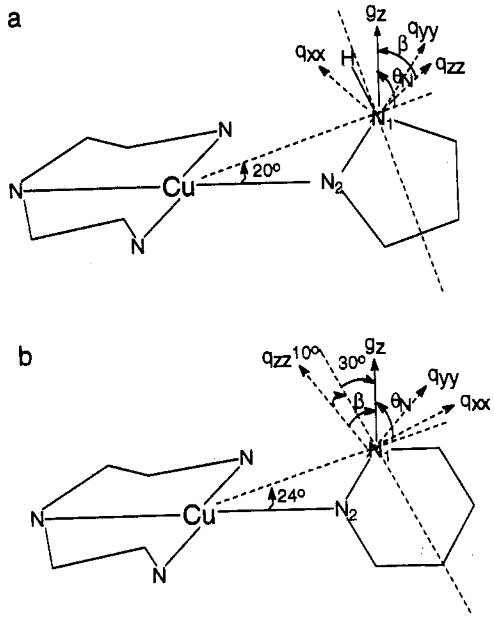

Figure 3. Schematic drawings of Cu^{II}(dien)–pyrazole (a) and Cu^{II}(dien)–pyridazine (b), showing the principal-axis systems of the **g** tensor and of the electric field gradient tensor, **q** (from gas-phase microwave studies[17,21]). The direction of g_z is perpendicular to the equatorial plane formed by the three amino nitrogen atoms from dien and N2 of pyrazole or pyridazine. The direction of q_{zz} is perpendicular to the heterocycle plane for pyrazole (a) and in the heterocycle plane, nearly along the bisector of the N2N1C angle (about 10° toward N2), for pyridazine. The directions of q_{xx} and q_{yy} are shown respectively with $|q_{zz}| > |q_{yy}| > |q_{xx}|$.

The same orientation is assumed for pyrazole when bound to Cu^{II}(dien). Were the pyrazole to assume an orientation perpendicular to the equatorial plane, defined by Cu(II) and the three nitrogen ligands of dien, the value for β would be 90° and the value for θ_N would be 70° (Figure 3).[19] It was found that best fits of ESEEM data were obtained with β equal to 75° and θ_N equal to 75°, suggesting structures where the pyrazole plane lies essentially perpendicular to the plane formed by Cu^{II}(dien). Such an orientation would prevent steric interference from the proton on N1 of pyrazole with the protons of dien.

For comparison, the quadrupole and electron–nuclear parameters obtained in an earlier study of Cu^{II}(dien)–imidazole[3a,c] are also shown in Table 1. Although the anisotropies in the electron–nuclear couplings are the same for pyrazole and imidazole, the magnitude of A_{iso} for pyrazole, 1.37 MHz, is significantly smaller than the value obtained for imidazole, 1.65 MHz. Further, a much larger value for e^2qQ and a smaller value for η, 2.86 MHz and 0.74, respectively, are obtained for pyrazole as compared to the values, 1.43 MHz and 0.94, for the imidazole. This difference in the quadruple parameters represents a sig-

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(19) Assuming the coordination of pyrazole to Cu(II) is similar to that in poly[bis(μ-pyrazolato-*N,N'*)copper(II)],[20] the N1–Cu–N2 angle is about 20°. Therefore, θ_N is about 70°. The value for θ_N can be calculated similarly for pyridazine. Assuming that the Cu–N–N angle is 120°, the N–N bond length is taken to be the same as that of pyridazine in the gas phase,[21] 1.22 Å; the Cu–N bond is 1.96 Å, and the N1–Cu–N2 angle is about 24°. Therefore, θ_N is 66°.

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nificant difference in the bonding environment of N1 of pyrazole and imidazole (see below).

For pyridazine, a microwave spectroscopic study[21] and ab initio calculations[18] show that the principal direction of the largest quadrupole value is aligned approximately along the lone pair of N1. Were the pyridazine to assume an orientation perpendicular to the equatorial plane, the value for β would be about 40° and the value for θ_N would be 66° (Figure 3). In this case, the closest fits of simulated spectra to the experimental data are obtained with $\beta = 30°$ and $\theta_N = 75°$. Therefore, similar orientations of heterocycle are found for pyridazine and for pyrazole bound to Cu^{II}(dien).

The values of e^2qQ for pyridazine are within the regime of values obtained by NQR spectroscopy for the compound in the solid phase[22] and by microwave spectroscopy in the gas phase,[21] consistent with our assignment of the modulations seen for a noncoordinated ^{14}N. Metal coordination usually reduces e^2qQ, as, for example, in a comparison of values obtained by NQR for pyridine nitrogen ($e^2qQ = 4.58$ MHz) and for Zn^{II}–pyridine ($e^2qQ \approx 3$ MHz).[23] Rather surprising is the fact that the A_{iso} value is considerably greater for the pyridazine complex than for the pyrazole complex. This is accompanied by greater anisotropy as indicated by a smaller value for r_{eff}. It is interesting to speculate that the larger coupling could arise from increased π interaction with Cu(II) in the pyridazine complex, where the hydrogen on the ^{14}N adjacent to the copper docking point as found in pyrazole is absent.

Coordination of Cu(II) to Pyridazine. The nuclear quadrupole interaction for ^{14}N is the interaction of the nitrogen nucleus with its local electric field gradient, which is a direct measurement of the electron distribution and, therefore, the bonding properties at this nitrogen. Two methods have been commonly used for the determination of nuclear quadrupole parameters, nuclear quadrupole spectroscopy for samples in the solid state, and microwave spectroscopy for samples in the gas phase. Due to a change of internal electrostatic field and introduction of the torsional vibration by the crystal lattice, an average decrease of 5% in the quadrupole coupling constant is normally observed by NQR measurement in the solid state as compared to that observed by microwave spectroscopy in the gas phase, while η is almost unaffected.[24] For many ^{14}N-containing compounds, the differences between measurements obtained by both methods are within the expected range whereas, for others, much larger changes are seen. For example, e^2qQ for pyridine decreases by 6% from gas phase[25] to solid phase[23a] measurements (Table 2), while η decreases by 2%. However, the quadrupole parameters obtained for imidazole show much more profound changes from the gas-phase values ($e^2qQ = 2.573$, $\eta = 0.1175$)[26] as compared to the solid-state values ($e^2qQ = 1.4098$, $\eta = 0.98$).[27] These differences were attributed to structural alterations in the solid state that are not found in the gas, such as the hydrogen bonding at N1 of imidazole, which occurs in the solid but cannot occur in the gas phase (see below).[27]

Another method for obtaining nuclear quadrupole parameters is through the use of ESEEM spectroscopy.[2-6] Under certain conditions, the coupling of ^{14}N to a paramagnetic center elicits a spectrum from which nuclear quadrupole parameters can be derived. For Cu(II)–imidazole complexes, both in model compounds[2-5] and in proteins,[7] the quadrupole parameters for N1 are comparable to those obtained by NQR spectroscopy for the metal-free solid.[27] The coordination of Cu(II) to N3 of imidazole has very little effect on the quadrupole parameters of N1. In the case of pyridazine, an 8% decrease in the quadrupole constant is seen for N1 due to the phase change from the gas[21] to solid[22] (Table 1). The quadrupole parameters obtained by ESEEM studies for N1 of pyridazine, when coordinated to Cu^{II}(dien) are comparable to those obtained by NQR studies for the metal-free solid (Tables 1 and 2). As is the case for Cu^{II}–imidazole, the coordination of Cu(II) to N2 of pyridazine also appears to have little effect on the quadrupole parameters of N1.[28]

Table 2. Comparisons of Nuclear Quadrupole Parameters of Diazoles and Diazines Obtained by Microwave Spectroscopy in the Gas Phase and Nuclear Quadrupole Resonance Spectroscopy in the Solid State

	gas phase				solid state		
	e^2qQ (MHz)	η	φ[c] (deg)	ref	e^2qQ (MHz)	η	ref
imid							
N1[a]	2.57	0.1175	17	26	1.4098	0.98	27
N3	4.032	0.12	4		3.267	0.129	
pyrazole							
N1	3.02 ± 0.10[d]	0.52	28	17			27a
N2	4.48 ± 0.10	0.65	17		3.995	0.657	
pyridine	4.88 ± 0.04	0.405 ± 0.006		25	4.5845	0.396	23
pyridazine[b]	5.65 ± 0.1	0.16 ± 0.02	10	21	5.1877	0.0854	22

[a] The amino nitrogen is refered as N1 and the imino nitrogen as N3 for imidazole and N2 for pyrazole. [b] Two nitrogen atoms of pyridazine are equivalent. [c] The angle between the principal axis of the quadrupole tensor and the bisector of the CNC or CNN angle. [d] Unless indicated, errors are not reported.

No quadrupole parameters for N1 of solid pyrazole have been reported. Therefore, comparison cannot be made for N1 of this compound as complexed to Cu^{II}(dien) with metal-free solid in order to assess the effect of Cu(II) coordination to N2. On the basis of the ESEEM study of Cu^{II}(dien)–pyridazine and Cu^{II}(dien)–imidazole, it is clear that values of e^2qQ and η for metal-free solid and those for the Cu^{II}(dien) complexes are within a few percent of each other. Therefore, for N1 of metal-free pyrazole, one would predict that the quadrupole parameters should be in the ranges 2.86 ± 0.1 MHz and 0.74 ± 0.05 for e^2qQ and η, respectively.

Pyrazole vs Imidazole. Both amino and imino nitrogen atoms in pyrazole and imidazole are sp^2 hybrids, with three sp^2 orbitals forming σ bonds with N or C, and H atoms, or accommodating a lone pair of electrons. The p orbital perpendicular to the heterocycle plane engages in the aromatic π bond. However, due to the difference in the bonding environment of amino or imino nitrogens between pyrazole and imidazole, significant differences are seen for the principal values and the principal-axis directions of the quadrupole tensor of corresponding nitrogens of the two heterocycles. For the amino nitrogen, the $p\pi$ orbital has the highest electron occupancy so that the largest quadrupole coupling (q_{zz}) for N1, the protonated nitrogen of both pyrazole and imidazole, occurs perpendicular to the heterocycle plane in the gas phase (Figure 4).[17,18,26] However, there is much less electron occupancy at the N–N σ orbital of pyrazole as compared to the

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(28) Once pyridazine is bound to Cu^{II}(dien), the structural degeneracy is removed. The quadrupole parameters are expected to be different from those for the metal-free solid, since the electron distribution of the directly coordinated N2 is altered, and thus would affect the electron distribution of N1. Also, Cu(II) is much closer to N1 in pyridazine than to N1 in imidazole. However, the incomplete ESEEM spectrum of Cu^{II}(dien–pyridazine precludes a more accurate determination of these parameters. Therefore, within the limit of our measurement for pyridazine (Δe^2qQ + 0.1 MHz and $\Delta\eta$ ± 0.05), the coordination of Cu(II) to N2 of pyridazine appears to have little effect on the quadrupole parameters of N1.

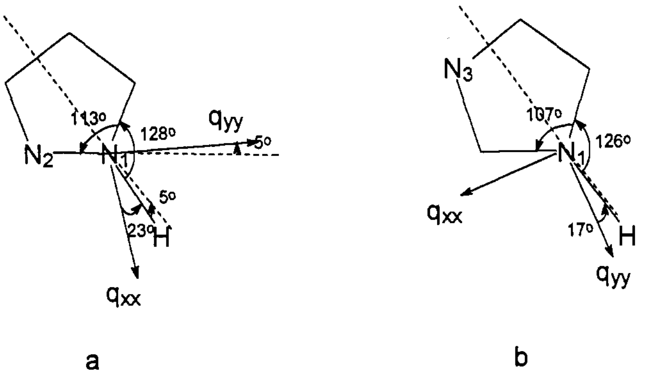

Figure 4. Schematic drawings of the principal-axis systems of the nuclear quadrupole tensors for N1 of pyrazole and imidazole in the gas phase. The direction of q_{zz} is out of the ring plane. The directions of q_{xx} and q_{yy} are from refs 17c and 26a, with $|q_{zz}| > |q_{yy}| > |q_{xx}|$.

N–C σ orbital of imidazole, due to the higher electronegativity of the bonding atom, a N as compared to a C. This makes the inequivalency of the N–H bond and the N–C bond of pyrazole N1 less significant so that the principal direction of the second largest quadrupole coupling, q_{yy}, is almost along the N2–N1 bond direction (5° off) and that of the weakest quadrupole coupling, q_{xx}, lies 23° away from the N1–H bond direction (Figure 4a).[17c] In imidazole, the near-equivalency of the two N–C bonds at N1, however, brings the direction of q_{yy} closer to the N–H bond direction (17° away) and that of q_{xx} 20° away from the N1–C2 bond direction (Figure 4b).[26] As a consequence of the higher asymmetry in electron distribution at the three bonding sp^2 orbitals in the pyrazole plane, a larger quadruple coupling constant and a larger asymmetry parameter are observed for pyrazole than for imidazole (Table 2).[29]

The quadruple coupling constant e^2qQ obtained for N1 of pyrazole by ESEEM is larger than the value for N1 of imidazole, while the asymmetry parameter η is smaller. It is noteworthy that the nuclear quadrupole values we obtain for pyrazole by ESEEM are not very different from the values determined for pyrazole in the gas phase[17] whereas, for imidazole, the gas-phase value and the ESEEM value are quite different from each other. In the case of imidazole, solid- and gas-phase differences go beyond expectations for physical-state change and, as noted above, have been interpreted as arising from hydrogen bonding in the solid that cannot occur in the gas phase.[3a,27] Structural adjustments in accord with hydrogen-bonding effects in the solid (among which is an N–H bond length increase of 0.05 Å) are obtained from neutron diffraction measurements.[30] As shown by microwave studies in the gas phase, one of the quadrupole principal axes, q_{yy}, in imidazole is directed close to the N–H bond direction. Thus, the quadruple parameters are sensitive to alteration in N–H bond polarization brought about by hydrogen bonding. As a consequence, in the solid or in the Cu^{II}(dien) complex, there is a significant change of the quadrupole coupling along the N–H bond and the principal direction of the smallest quadrupole coupling, q_{xx}, is now along the N–H direction at N1 of imidazole. The principal direction with the largest quadrupole coupling, q_{zz}, has switched from being perpendicular to the imidazole plane to being within the plane.[3a,4b]

In pyrazole, the N–H bond direction is away from the principal axis of the quadrupole tensor,[17] so that any change of N–H bond polarization has less effect on the principal values of the quadruple coupling. The principal directions are nearly retained. Although a decrease of e^2qQ and an increase of η are observed for pyrazole in the Cu^{II}(dien) complex as compared to the gas-phase measurement, the hydrogen-bonding effects on quadrupole parameters as profound as might be found in imidazole are not expected.

The placement of a methyl group on C3 of pyrazole changes the electron distribution around N1, thereby affecting the quadrupole parameters. Such effects have been observed earlier for Cu^{II}(dien)–imidazole.[3a] An analysis based on the Townes–Daily model[3a,31] suggested that the electron occupancy at the three sp^2 hybrid σ orbitals of N1 of imidazole has been altered by the change of the electron distribution at a ring C through an induction effect brought about by methyl substitution. A similar effect is observed here as well.

In summary, we have demonstrated that one can measure the nuclear quadrupole parameters using ESEEM spectroscopy for the remote ^{14}N of pyrazole and pyridazine when complexed to Cu(II). For pyridazine, the nuclear quadruple parameters of the remote (noncoordianted) imino nitrogen are comparable to those obtained by NQR for metal-free pyridazine and are larger than for the imino nitrogen atoms of pyridine and imidazole. For pyrazole, the nuclear quadrupole coupling constant of the remote amino nitrogen is larger than that of the amino nitrogen of imidazole. Clearly, the presence of an adjacent, more electronegative nitrogen atom, rather than a carbon, bound to the nitrogen under investigation leads to the change. Our investigation further shows that the study of electron–nuclear coupling using ESEEM of metal heterocycle complexes need not be relegated to studies with imidazole exclusively and that the study of other nitrogen-containing heterocycles may be a fruitful investigative endeavor.

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(29) A larger quadrupole coupling constant and a larger asymmetry parameter are also observed for N2 of pyrazole than for N3 of imidazole for the same reason (Table 2). There is a higher asymmetry present in the electron distribution among the three sp^2 orbitals within the heterocycle plane at the imino nitrogen of pyrazole as compared to imidazole.

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