it increases when the σ-donor power is modified by electron-withdrawing groups (compounds **12**, **13**, and **15**).

Though the delocalization on the macrocycle can be a possible explanation of the high Δ value of FePcL$_2$ compared with the parameters of porphyrin homologues, it cannot account for its detailed variation along the series. The position of the substituent on the pyridine ring determines mainly the σ and π properties of the ligand;[13,23] this would explain the differences observed between complexes with meta- and para-substituted pyridines. We single out the Δ values of the species FePcXCO (X = piperidine, dimethylformamide, tetrahydrofuran, methanol, dimethyl sulfoxide, tetrahydrothiophene, or H$_2$O), which are lower than those of FePcX$_2$.[35] In that case, the authors assume that the reduction of d$_{xz}$ and d$_{yz}$ electron population by π bonding to CO is overcompensated by the strong σ component along the z axis, which increases the d$_{z^2}$ population. This must be related to the Δ value of 0.51 mm s^{-1} for K$_2$FePc(CN)$_2$.[8] This shows that the question of the precise origin of Δ is still open; no absolute model is proposed, but our results give an example of useful comparisons of data along homogeneous families of compounds. No crystal structure exists for most of the examined complexes, but we assume a strictly constant geometry about iron when L varies. Changes in η values arising from distortions in the Fe–L region would not account for the changes in Δ, which are reasonably related to variations in π-overlap populations.

Conclusion

Our results concur to reveal that if the complexes of phthalocyanine, particularly FePc, can be taken as analogues of complexes of porphyrins or dimethylglyoxime in view of their planar and rigid structure, they are different enough to forbid hasty generalization of their properties.

We have shown the following: (i) The CT at ~410 nm is a L → Pc CT, and a Fe → L CT appears in the spectrum of FePcL$_2$ only when L has enough evident acceptor properties, as shown by correlation with pK_a values and electron population values. (ii) δ is almost constant along the series of studied compounds while Δ varies. δ values appear to be differently correlated with pK_as and CT optical absorptions for compounds with electron-withdrawing substituted pyridines and for complexes with donor substituents. No marked correlation is observed between δ and Δ for all the compounds. (iii) The high Δ value of FePcL$_2$ may be related to the L → Pc CT. More effective equatorial π type delocalization in the case of Pc complexes than for any other tetrapyrrolic macrocycle appears to be the main factor for EFG.

(35) F. Calderazzo, G. Pampaloni, and D. Vitali, *J. Organomet. Chem.*, **191**, 217 (1980).

Contribution from the Department of Chemistry,
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Temperature Dependence of ^{63}Cu and ^{14}N Nuclear Quadrupole Resonance Frequencies in Potassium Dicyanocuprate(I)

HIROKAZU NAKAYAMA, NOBUO NAKAMURA, and HIDEAKI CHIHARA*

^{63}Cu and ^{14}N nuclear quadrupole resonance frequencies were measured as functions of temperature between 77 and 300 K for potassium dicyanocuprate(I), KCu(CN)$_2$. Four ^{14}N resonance frequencies at 3.1382, 2.9658, 2.5253, and 2.3947 MHz were observed at 77 K. These four resonance frequencies were assigned on the basis of the Zeeman effect on a powdered specimen. These four nitrogen lines showed normal temperature dependence, whereas the ^{63}Cu resonance frequency showed a large, positive temperature dependence. These experimental results were interpreted in terms of the vibrational effect on d–π* bonds between Cu atom and C atoms. Electron distribution over various bond and lone-pair orbitals is discussed.

Introduction

Potassium dicyanocuprate(I), KCu(CN)$_2$, crystallizes in a monoclinic system with a space group $P2_1/c$ (C_{2h}^5), and its unit cell contains four formula units.[1] The complex anions form spiral polymer chains composed of [Cu(CN)$_2^-$]$_\infty$, in which a slightly distorted trigonal coordination of copper is recognized as shown in Figure 1. Each Cu atom forms three coordination bonds with two carbon atoms from two different cyanide ions (cyanide 1 and cyanide 2) and one nitrogen atom from another cyanide 2. This structure is entirely different from those of analogous silver and gold complexes, in which discrete linear 2-fold coordination has been found.

Krüger and Meyer-Berkhout[2] reported in 1952 that there is only one ^{63}Cu nuclear quadrupole resonance (NQR) line in polycrystalline KCu(CN)$_2$ and that the frequency is much higher at 300 K than at about 100 K. They ascribed the unusual, positive temperature coefficient to elongation of the bond in a discrete [NC–Cu–CN]$^-$ complex, which they assumed forms the anion. The crystal structure determined later did not substantiate their model.

McKown and Graybeal determined the directions of the principal axes of the electric field gradient (EFG) tensor and the asymmetry parameter at the Cu nucleus by a Zeeman study of the NQR.[3] They attempted to explain their experimental results on the basis of sp^2-hybrid σ bonds and d–π* bonding between copper and ligands but did not explain the positive temperature coefficient of the ^{63}Cu resonance frequency.[6]

The present paper presents the experimental results of ^{63}Cu and ^{14}N NQR frequency measurements as functions of temperature. The ^{14}N data would not only supplement the ^{63}Cu

(1) Cromer, D. T. *J. Phys. Chem.* **1957**, *61*, 1388.
(2) Krüger, H.; Meyer-Berkhout, U. *Z. Phys.* **1952**, *132*, 171.

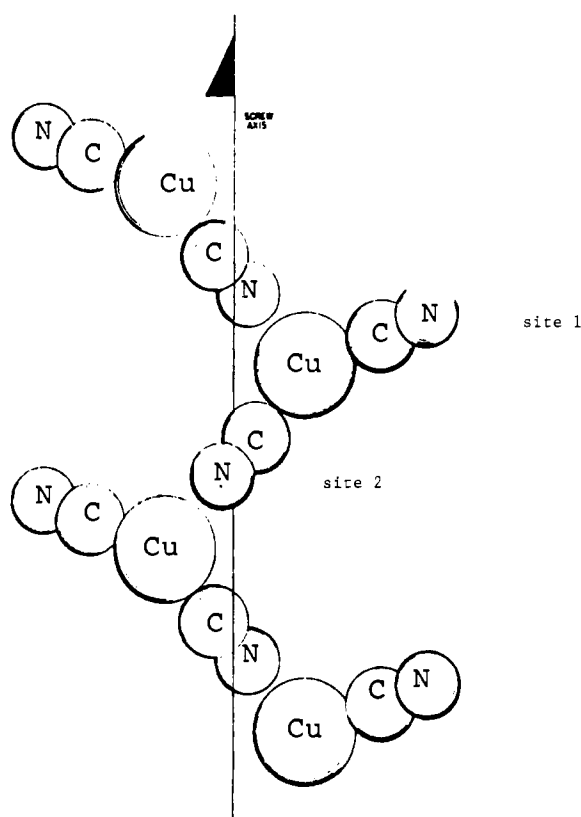(3) McKown, G. L.; Graybeal, J. D. *J. Chem. Phys.* **1966**, *44*, 610.

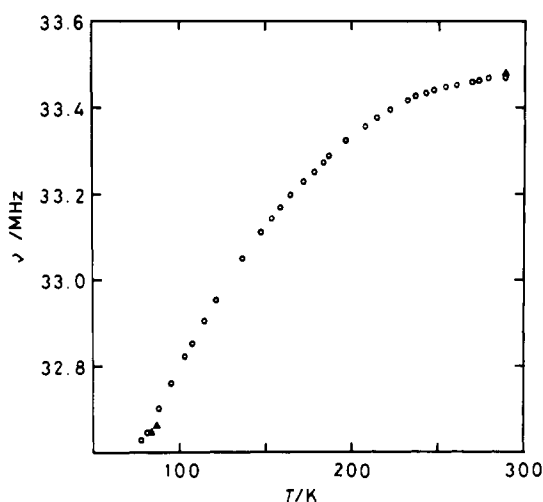**Figure 1.** Structure of the $Cu(CN)_2$ polymer chain.[1]

Figure 2. Temperature dependence of ^{63}Cu NQR frequency. Triangles are the data of Krüger and Meyer-Berkhout.[2]

results but also provide a further clue to the nature of ligand bonds of copper. The magnitudes of EFG's and their temperature coefficients will be successfully explained in terms of vibrational effect on the weak π back-bonding in the Cu-$(CN)_2^-$ anions.

Experimental Section

Crystalline $KCu(CN)_2$ was obtained by evaporation of an aqueous mixed solution of potassium cyanide and copper cyanide at room temperature according to the literature.[4]

The ^{14}N NQR signal was recorded with a modified Pound-Watkins type spectrometer with bidirectional square-wave frequency modulation. The ^{63}Cu NQR signal was observed with a Dean-type self-quenched superregenerative spectrometer.

Table I. ^{14}N NQR Frequencies, Quadrupole Coupling Constants, and Asymmetry Parameters for Inequivalent Sites

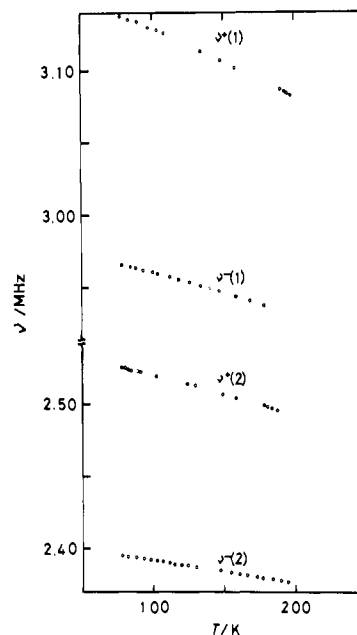|	ν^+/MHz	ν^-/MHz	e^2Qqh^{-1}/MHz	η
site 1	3.1382	2.9658	4.069	0.085
site 2	2.5253	2.3947	3.280	0.080

Figure 3. Temperature dependence of ^{14}N NQR frequencies.

The temperature dependence was determined by using a simple cryostat with liquid nitrogen as the refrigerant. Uniform sample temperature was achieved by placing the specimen inside a brass can having a large heat capacity. Temperature was measured with a chromel P–constantan thermocouple.

Results

Figure 2 shows the resonance frequency for a ^{63}Cu nucleus as a function of temperature. In this figure open triangles correspond to the data by Krüger and Meyer-Berkhout,[2] which are in good agreement with ours. The resonance frequency increases by 0.8 MHz with increase in temperature from 77 K to room temperature, passes through a maximum at about 300 K, and decreases on further heating.

Four ^{14}N resonance lines were observed, indicating that two kinds of inequivalent nitrogen sites exist, as predicted from the crystallographic data.[1] The resonance frequencies of these lines at 77 K are listed in Table I. In order to assign the four resonance frequencies, we used the Zeeman effect on a powdered specimen and observed the magnitude and the direction of the second-order shift of resonance lines as a function of the intensity of applied magnetic field; the results were analyzed by the method proposed by Pissanetzky.[5] As is seen from Table I, coupling constants, e^2Qq's, at the two different sites differ greatly from each other. We assigned the larger e^2Qq to the nitrogen atom at site 1 in Figure 1 since this nitrogen atom is free from the interionic covalent bonding as compared with the N atom at site 2, which serves to bridge between two Cu atoms. This assignment is consistent with our Townes–Dailey type model to be discussed later. Figure 3 shows ^{14}N NQR frequencies as a function of temperature. The principal components of the quadrupole coupling tensor obtained in the usual way are plotted in Figure 4, which shows

(4) Bassett, H.; Corbet, A. S. *J. Chem. Soc.* **1924**, *125*, 1660.

(5) Pissanetzky, S. *J. Magn. Reson.* **1979**, *34*, 515.

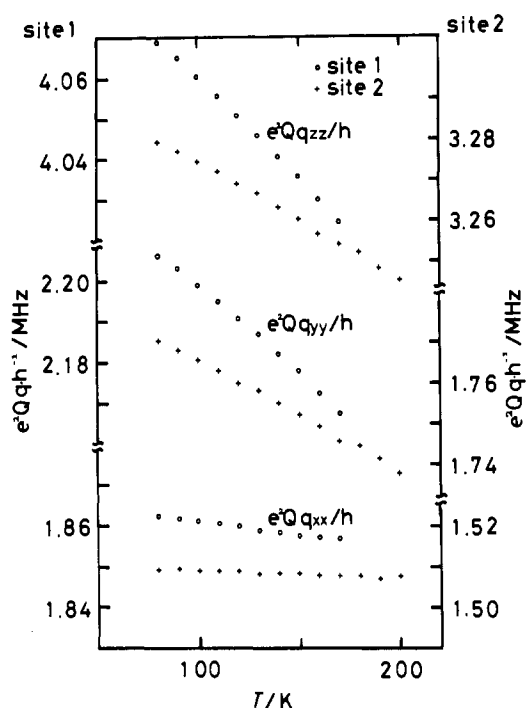(6) Graybeal, J. D.; McKown, G. L. *Inorg. Chem.* **1966**, *5*, 1909.

Figure 4. Temperature dependence of components of quadrupole coupling constants at ^{14}N nuclei.

the following characteristic features: (a) there is a large difference in e^2Qq's between sites 1 and 2; (b) the asymmetry parameters at sites 1 and 2 are about the same; (c) e^2Qq_{xx}/h are almost independent of temperature for both sites; (d) e^2Qq_{yy}/h and e^2Qq_{zz}/h depend strongly on temperature, with about the same temperature coefficients for both sites; (e) the temperature coefficients of the asymmetry parameters are nearly the same for both sites, being negative.

Discussion

I. Bond Model. The NQR parameters of ^{14}N determined in the previous section can be related to the nature of the chemical bond within and between Cu(CN)$_2^-$ complex anions. We will now look for a bond model that interprets consistently all of the features that were listed at the end of the last section.

Graybeal and McKown gave the asymmetry parameter of ^{63}Cu at room temperature a value of 0.78. They assumed that the sp^2-hybrid orbitals in Cu make σ bonds between the Cu and its three ligands, and that the 3d$_{x^2-y^2}$ and the 3d$_{xz}$ orbitals of Cu are involved in additional π bonds between the central Cu and the ligands. Their calculation of η of Cu with such a bond model led to a value of 0.61, in reasonable agreement with the experiment. A closer examination of their model, however, revealed that it must give rise to different asymmetry parameters at the two inequivalent ^{14}N sites, contrary to the present results, which indicated that the η's at ^{14}N sites 1 and 2 were comparable. It was also found that their model could not explain the large positive temperature coefficient of the ^{63}Cu NQR frequency. We will therefore attempt to construct a new bond model that would account for the features of NQR properties of ^{14}N as well as ^{63}Cu.

We take the coordinate axes fixed at each nuclear site as shown in Figure 5. In this figure, the z axis is the direction of the bond at the nitrogen sites, if slight nonlinearity of the C–N–Cu sequence is ignored. It is thus assumed that the principal axes of the EFG tensor at ^{14}N sites coincide with the coordinate axes x, y, and z in Figure 5. With regard to the Cu atom, the z principal axis is normal to the plane of Figure 5 and the x axis lies in the direction of the N–Cu bond.

As in the Graybeal-McKown treatment, we assume that the coordination σ bonds of Cu use three sp^2 orbitals of Cu that
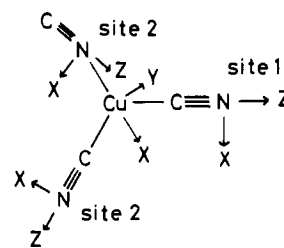

Figure 5. Principal axes at ^{63}Cu and ^{14}N nuclear sites.

overlap the sp orbitals from two C atoms and one N atom. We also introduce some additional d–π^* bonding between two d^2 hybrid orbitals of Cu, d$_{x^2-y^2}$ and d$_{xy}$, and the π_x^* orbitals of the two cyanides coordinating by carbon atoms.

II. Interpretation of the Nitrogen Data. a. Magnitudes of the Coupling Constant and the Asymmetry Parameter. The two inequivalent nitrogen atoms have chemical environments that are different from each other: one is bonded to a copper atom, but the other is not bonded to any other atom. However, the difference can be viewed primarily as a change that occurs at the lone-pair electrons of the nitrogen atom because the bond to the copper atom is a result of donation of the lone-pair electrons to a vacant sp^2 orbital of Cu. Thus, these two kinds of nitrogen atoms will be treated collectively.

The bond in a CN unit is a triple bond, with one σ and two π bonds. By application of the Townes–Dailey treatment to the N atom in a CN unit, expressions 1a–1c are obtained for

$$e^2Qq_{zz} = [(1 - \beta)l + \beta l' - (m + m')/2]e^2Qq_{zz}(2p_z) \times [1 - (3/2)(\langle\theta_x^2\rangle + \langle\theta_y^2\rangle)] \quad (1a)$$

$$e^2Qq_{yy} = [m - (m' + (1 - \beta)l + \beta l')/2]e^2Qq_{zz}(2p_z) \times [1 - 3\langle\theta_x^2\rangle] \quad (1b)$$

$$e^2Qq_{xx} = [m' - (m + (1 - \beta)l + \beta l')/2]e^2Qq_{zz}(2p_z) \times [1 - 3\langle\theta_y^2\rangle] \quad (1c)$$

the N coupling constants. Here, the vibrational effects have been included according to the Bayer theory in terms of the mean-square librational amplitudes, $\langle\theta_x^2\rangle$ and $\langle\theta_y^2\rangle$, about the x and y axes, respectively. In eq 1, β is the s character of the lone-pair orbital, l is the σ-bond population (sp orbital of N), l' is the lone-pair population (the other sp orbital of N), and m' and m are the π_x- and π_y-bond populations.

Now, because the nitrogen atom at site 2 denotes part of its lone-pair population to the copper atom, its l' is smaller than the l' of N at the site 1. This difference in l' leads to a smaller value of e^2Qq_{zz} (see eq 1a) at site 2, in agreement with the result give in Table I. Since the asymmetry parameters at the two sites are about the same in spite of the large difference in the values of e^2Qq_{zz}, there must be some difference in m and/or m' between sites 1 and 2 as a result of bonding to copper. This point will be discussed further in section IVa.

b. Temperature Dependence. We now consider the temperature dependence of the coupling constants of the nitrogen nuclei. When the bending mode of vibration of C–Cu–C groups is excited at higher temperature, the overlap between the d$_{x^2-y^2}$ and d$_{xy}$ orbitals of Cu and π_x^* orbitals of cyanides will decrease, some electrons being thus withdrawn from the π_x^* back into the d$_{x^2-y^2}$ and d$_{xy}$ orbitals. This causes m' (the p$_x$ atomic orbital population of N) to decrease while m remains unaffected because the p$_y$ atomic orbital does not participate in the bonding between cyanide and Cu.

If such changes in $\langle\theta^2\rangle$ and m' are small, eq 1 can be expanded with respect to these changes as in eq 2 by retaining

$$\Delta e^2 Q q_{zz} =$$
$$e^2 Q q_{zz}(2p_z)[(\Delta m'/2) - (3/2)Q_{zz}(\Delta\langle\theta_x^2\rangle + \Delta\langle\theta_y^2\rangle)] \quad (2a)$$

$$\Delta e^2 Q q_{yy} = -e^2 Q q_{zz}(2p_z)[-(\Delta m'/2) - 3Q_{yy}\Delta\langle\theta_x^2\rangle] \quad (2b)$$

$$\Delta e^2 Q q_{xx} = -e^2 Q q_{zz}(2p_z)[\Delta m' - 3Q_{xx}\Delta\langle\theta_y^2\rangle] \quad (2c)$$

$$Q_{zz} = (1 - \beta)l + \beta l' - (m + m_0')/2$$

$$-Q_{yy} = m - (m_0' + (1 - \beta)l + \beta l')/2$$

$$-Q_{xx} = m_0' - (m + (1 - \beta)l + \beta l')/2$$

$$m' = m_0' - m'(T)$$

the leading term only. Here Δ stands for the difference in a quantity at two different temperatures T_i and T_j; i.e., $\Delta F = F(T_i) - F(T_j)$ where $T_i > T_j$.

The fact that the x component of the EFG is almost independent of temperature (Figure 4) shows that $\Delta e^2 Q q_{xx}$ is extremely small. Therefore, from eq 2c one obtains

$$\Delta m' \simeq 3Q_{xx}\Delta\langle\theta_y^2\rangle \quad (3)$$

Also, since m is not appreciably different from m_0', one finds an approximate relation

$$Q_{zz} \simeq 2Q_{xx} \simeq 2Q_{yy} \quad (4)$$

Elimination of $\Delta m'$ from eq 2a and 2c by use of eq 3 leads to

$$\Delta e^2 Q q_{zz} \simeq -e^2 Q q_{zz}(2p_z)Q_{xx}[(3/2)\Delta\langle\theta_y^2\rangle + 3\Delta\langle\theta_x^2\rangle] \quad (5a)$$

$$\Delta e^2 Q q_{yy} \simeq e^2 Q q_{zz}(2p_z)Q_{xx}[(3/2)\Delta\langle\theta_y^2\rangle + 3\Delta\langle\theta_x^2\rangle] \quad (5b)$$

where eq 4 has been used. Thus, eq 5 indicates that the temperature gradients of the y and z components of the nitrogen EFG are the same to such an extent that the above approximations are valid. This is what is seen from Figure 4.

III. Interpretation of the Copper Data.
For a copper atom, Townes–Dailey theory gives eq 6, where N is the population

$$e^2 Q q_{zz} = [N_{d_{z^2}} + (N_{d_{xz}} + N_{d_{yz}})/2 - N_{d_{xy}} - N_{d_{x^2-y^2}}]e^2 Q q_{zz}(3d) + [N_{p_z} - (N_{p_x} + N_{p_y})/2]e^2 Q q_{zz}(4p) \quad (6a)$$

$$e^2 Q q_{yy} = [(N_{d_{yz}} + N_{d_{x^2-y^2}} + N_{d_{xy}})/2 - N_{d_{xz}} - (N_{d_{z^2}}/2)]e^2 Q q_{zz}(3d) + [N_{p_y} - (N_{p_x} + N_{p_z})/2]e^2 Q q_{zz}(4p) \quad (6b)$$

$$e^2 Q q_{xx} = [(N_{d_{xz}} + N_{d_{x^2-y^2}} + N_{d_{xy}})/2 - N_{d_{yz}} - (N_{d_{z^2}}/2)]e^2 Q q_{zz}(3d) + [N_{p_x} - (N_{p_y} + N_{p_z})/2]e^2 Q q_{zz}(4p) \quad (6c)$$

of an orbital. In the present model the copper atom forms σ bonds with three ligands using sp²-hybrid orbitals. These hybrid orbitals are written as

$$\Psi_1(N) = (1/3^{1/2})\chi_s + (2^{1/2}/3^{1/2})\chi_{p_x}$$

$$\Psi_2(C) = (1/3^{1/2})\chi_s - (1/6^{1/2})\chi_{p_x} + (1/2^{1/2})\chi_{p_y}$$

$$\Psi_3(C) = (1/3^{1/2})\chi_s - (1/6^{1/2})\chi_{p_x} - (1/2^{1/2})\chi_{p_y}$$

and therefore N_{p_x} and N_{p_y} are given by

$$N_{p_x} = 0.333x + 0.667y \qquad N_{p_y} = x$$

where x and y are the populations of Ψ_2 (Ψ_3) and Ψ_1, respectively. The copper atom forms d–π^* bonds with two ligands using d²-hybrid orbitals. These hybrid orbitals are written as

$$\Psi_4(\pi_1) = (3^{1/2}/2)\chi_{d_{x^2-y^2}} + (1/2)\chi_{d_{xy}}$$

$$\Psi_5(\pi_2) = (1/2)\chi_{d_{x^2-y^2}} - (3^{1/2}/2)\chi_{d_{xy}}$$

and therefore $N_{d_{x^2-y^2}}$ and $N_{d_{xy}}$ are given by

$$N_{d_{x^2-y^2}} = 0.75u + 0.25v \qquad N_{d_{xy}} = 0.25u + 0.75v$$

Table II. Orbital Populations of Nitrogen at the Two Sites

	site 1	site 2
m^a	1.15	1.16
m'^a	1.18	1.18
l'^a	2.00	1.82

a m, m', and l' are the populations of p_x, p_y, and σ (or lone-pair) orbitals, and the axes are taken as shown in Figure 5.

where u and v are populations of Ψ_4 and Ψ_5, respectively, which may be nearly equal because the Cu–C distances in sites 1 and 2 are nearly the same. Hence we can put

$$N_{d_{x^2-y^2}} = N_{d_{xy}} = u$$

Since d_{yz} and d_{z^2} orbitals are fully occupied and p_z is completely empty in our model, eq 4 is simplified as follows:

$$e^2 Q q_{zz} = [3 + (N_{d_{xz}}/2) - 2u]e^2 Q q_{zz}(3d) - (0.667x + 0.333y)e^2 Q q_{zz}(4p) \quad (7a)$$

$$e^2 Q q_{yy} = [u - N_{d_{xz}}]e^2 Q q_{zz}(3d) + (0.833x - 0.333y)e^2 Q q_{zz}(4p) \quad (7b)$$

$$e^2 Q q_{xx} = [(N_{d_{xz}}/2) + u - 3]e^2 Q q_{zz}(3d) - (0.167x - 0.667y)e^2 Q q_{zz}(4p) \quad (7c)$$

The first term is smaller than the second because $N_{d_{xz}}$ and u are close to 2. Hence the z component of the coupling constant is negative. Since $N_{d_{x^2-y^2}}$ increases as the vibrational amplitudes increase, we would expect an increase in the absolute value of $e^2 Q q_{zz}$ as well as the resonance frequency as the temperature is raised.

IV. Semiempirical Treatment. a. Nitrogen Sites.
Because we are looking at the Cu–N bond from either end, we shall now see how these data can be reconciled by making an order estimation of orbital populations through a simple calculation. At first we calculate the population of each orbital at the nitrogen sites on the basis of eq 1. The coupling constant and the asymmetry parameter are given by eq 8. The amount of

$$e^2 Q q_{zz} = [(1 - \beta)l + \beta l' - (m + m')/2]e^2 Q q_{zz}(2p_z) \quad (8a)$$

$$\eta = \frac{(3/2)(m' - m)}{(1 - \beta)l + \beta l' - (m + m')/2} \quad (8b)$$

s character of a lone-pair orbital was taken to be 0.5 as proposed by Pauling.[7] The value of $e^2 Q q_{zz}(2p_z)$ was taken as 8.4 MHz.[8] At site 1 we set $l' = 2.00$ and $l = 1.30$, which are considered to be normal values for a cyanide. From experimental values of $e^2 Q q_{zz}$ and η at site 1 we obtained 1.15 and 1.18 for m and m', respectively. At site 2 the nitrogen forms σ and π bonds with the copper. For the nitrogen at site 2 we used $l = 1.30$ and $m' = 1.18$, the same values for the site 1 nitrogen. Under these conditions l' and m were determined to be 1.82 and 1.16, respectively, with use of experimental values of $e^2 Q q_{zz}$ and η at site 2. If we assume that the value of m at site 2 is the same as that at site 1, we obtain 1.81 and 1.17 for l' and m', respectively. So, m' at site 2 is smaller than that at site 1 by 0.01. This may mean that a fraction of electrons in the p_x orbital at site 2 is donated to the copper orbital through the Cu–N π bond. This mechanism, however, cannot operate because there is no suitable orbital for the copper to accept the p_x electrons of the nitrogen. Therefore, it is probably more reasonable to assume that m' does not vary from site to site. Thus, it is concluded that 0.01 electron in

(7) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960.
(8) Schempp, E.; Bray, P. J. "Physical Chemistry"; Henderson, D., Ed.; Academic Press: New York, 1970; Vol. IV, p 572.

the d_{xz} orbital of the copper is donated to the site 2 nitrogen p_y orbital by 0.01. Table II shows the final results obtained from such calculations. The difference between m and m' reflects the fraction of electrons donated from the copper d^2-hybrid orbitals to the nitrogen p_x orbitals. Then if we further assume that the transferred electrons are shared equally by the carbon and the nitrogen, 0.06 (0.03 × 2) electron moves from the d^2-hybrid orbitals of the copper to the π_x^* orbitals, whereas 0.18 lone-pair electron of the nitrogen moves to the copper sp^2-hybrid orbital through the Cu–N σ bond. Furthermore, 0.01 electron of the d_{xz} orbital of the copper atom is donated to the nitrogen p_y orbital through the Cu–N π bond. From these orbital populations of nitrogen, we can estimate orbital populations of copper to be $u = 1.94$, $N_{d_{zz}} = 1.99$, and $y = 0.18$ using the parameters in Table II.

b. Copper Site. Consideration of the ^{14}N NQR data in the preceding subsection indicates that $u = 1.94$, and $N_{d_{zz}} = 1.99$ should be used in eq 6. Jørgensen's electronegativity data lead to a value 0.76 for x. Furthermore, $q_{zz}(3d)$ and $q_{zz}(4p)$ were calculated by using the Slater-type atomic orbital functions. With all these parameter values combined, the asymmetry

parameter η at the Cu site could be obtained as a function of y. Using 0.78 for η, which was determined by Graybeal and McKown, we obtain $y = 0.32$. This value is different from 0.18, which was determined in the preceding subsection. The discrepancy is small but reflects the inadequacy of certain assumptions such as the adoptation of the Slater-type functions, which are not very accurate at the nuclear position.

Conclusion

In view of the limitations of the present analysis, which are obvious from assumptions involved, we cannot carry the discussion too far. However, all the intriguing features of the experimental results have been accounted for satisfactorily. In particular, the remarkable positive temperature coefficient of the resonance frequency of Cu has been found to be due to weakening of d–π^* bonds between Cu and C atoms as a result of increasing vibrational amplitude.

Contribution from the General Chemistry Institute, Faculty of Pharmacy, University of Florence, Florence, Italy

Magnetic Resonance Spectra of a Heterodinuclear (Ni–Co) Metal Complex

L. BANCI, C. BENELLI, and D. GATTESCHI*

The single-crystal EPR spectra of the Ni(prp)$_2$enCo(hfa)$_2$ complex ((prp)$_2$en is the Schiff base formed by 2-hydroxypropiophenone and ethylenediamine; hfa is hexafluoroacetylacetonate) have been recorded at 4.2 K. Since the nickel(II) ion is in a square-planar environment and the cobalt(II) ion in an octahedral one, the EPR spectra are typical of high-spin cobalt(II) with $g_1 = 2.23$, $g_2 = 3.11$, $g_3 = 6.83$, $A_1 \simeq 150 \times 10^{-4}$ cm^{-1} $A_2 < 30 \times 10^{-4}$ cm^{-1}, and $A_3 \simeq 380 \times 10^{-4}$ cm^{-1}. Also the proton magnetic resonance spectra of acetone-d_6 solutions of the complex have been recorded at room temperature. The isotropic shifts of the aromatic protons are most unusual since all of them are upfield. A possible explanation of this behavior is offered. The spin-Hamiltonian parameters have been compared with those of similar adducts. The implications for the exchange mechanism with paramagnetic ions are considered.

Introduction

The copper(II) and nickel(II) complexes with the tetradentate Schiff bases formed by salicylaldehyde and aliphatic diamines are known to be able to act as bidentate ligands toward transition-metal complexes, yielding dinuclear species.[1–3]

In particular Drago et al.[4] studied the reactions of Co(SALen) and the Cu(SALen) (SALen is the Schiff base formed by salicylaldehyde and ethylenediamine) with metal hexafluoroacetylacetonates (M(hfa)$_2$) and found that starting either from Cu(SALen) and adding Co(hfa)$_2$ or from Co(SALen) and adding Cu(hfa)$_2$ the final product was the same, i.e., Cu(SALen)Co (hfa)$_2$. A kinetic study showed also the mechanism of the exchange of the two metal ions between the two coordination sites.[5]

A related series of complexes have been structurally characterized by Sinn et al.,[6] who used the M(prp)$_2$en complex as

the bidentate ligand instead of M(SALen), (prp)$_2$en being the Schiff base formed by ethylenediamine with 2-hydroxypropiophenone. They reported the crystal structure determination of M(prp)$_2$enM'(hfa)$_2$, where M = Cu or Ni and M' = Mn, Co, Ni or Cu, and found that the coordination environment remains largely constant throughout the series, with the exception of the Ni–Cu complex. A sketch of the dinuclear complexes is shown by **1**.

1
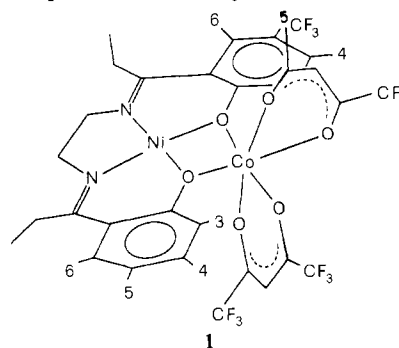
We are interested in the characterization of the electronic structures of heterodinuclear complexes,[7–9] with a particular

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