one metal center to the other is accompanied by transfer of Cl^-. Further studies on this point are in progress.

The rates of reduction of the alkylcobalamins are considerably higher than those of the corresponding cobaloximes;[10] k_2 values at 25° are Me 3.6 $\times$ 10^2, compared to 1.4 $\times$ 10^1, and Et 4.4, compared to 1.4 $\times$ 10^{-2}. This may reflect a greater strain of the Co—C bond in the cobalamins resulting from the upward-directed substituents on the corrin ring.[25] Similarly the release of alkyl radicals *via* the homolytic scission occurring during photolysis, $CoR \rightleftharpoons Co^{II} + R\cdot$, takes place more rapidly in cobalamins (Me, 5.9 $\times$ 10^{-2} sec^{-1}) than in cobaloximes (Me, 2.1 $\times$ 10^{-3} sec^{-1}).[26]

Formation of the alkylchromium(III) products by a two-step sequence involving first the homolysis of the CoR, followed by the rapid scavenging of $R\cdot$ by Cr^{2+} ($R\cdot + Cr^{2+} \rightarrow CrR^{2+}$),[27] is clearly ruled out by the form of the rate expression which shows a first-order dependence upon [Cr^{2+}].

The reactions of both the Me and Et derivatives occur

with quite negative values of $\Delta S^{\ddagger}$. This indicates a transition state with a highly ordered structure and has been noted previously in processes involving radical transfer.[28]

Experimental Section

Materials. Cyanocobalamin and hydroxocobalamin (Sigma Chemical) were used to synthesize aquo-, methyl-, and ethylcobalamin according to accepted literature procedures.[29] The cobalamins were purified on Bio-Rad Cellex CM cellulose. Cobalamins could be isolated for reuse from reaction solutions or other impure sources using Rohm and Haas XAD-4 macroreticular resin. Chromium(II) perchlorate solutions were prepared from $Cr(ClO_4)_3$ by reduction with amalgamated zinc.

Procedures. Fresh solutions of the alkyl cobalamins and of Cr^{2+} were made up for each series of experiments. Light was excluded from the former. The solutions were thoroughly freed of oxygen using Cr^{2+}-scrubbed nitrogen.

The slower reactions of the ethyl derivative were studied using a Cary 14 spectrophotometer; these reactions were carried out in a 5-cm quartz cell with a rubber serum cap. The more rapid reactions of the methyl derivative were followed using a Durrum stopped-flow instrument.

(25) (a) J. D. Brodie, *Proc. Nat. Acad. Sci. U. S.*, 62, 461 (1969); (b) P. G. Lenhert, *Proc. Roy. Soc., Ser. A*, 303, 45 (1968).

(26) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, 92, 2997 (1970).

(27) H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 320 (1972).

(28) (a) J. Halpern and P. F. Phelan, *J. Amer. Chem. Soc.*, 94, 1881 (1972); (b) P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *ibid.*, 91, 82 (1969).

(29) W. E. M. Lands, Ed., "Biochemical Preparations," Vol. 12, Wiley, New York, N. Y., 1968, pp 121–130.

Interdimer Exchange in Linear
Chain Copper Acetate–Pyrazine[1]

J. S. Valentine, A. J. Silverstein, and Z. G. Soos*

Contribution from the Departments of Chemistry, Douglass College, Rutgers University, New Brunswick, New Jersey 08903, and Princeton University, Princeton, New Jersey 08540. Received July 2, 1973

Abstract: Cu_2Ac_4pyr is shown to contain linear chains of binuclear Cu_2Ac_4 units with a singlet–triplet separation of $J = 325$ cm^{-1} and single-crystal epr parameters characteristic of binuclear copper complexes. The pyrazine bridged, interdimer Cu–Cu exchange of $J' \sim 1100$ G is deduced from the strong temperature-dependent epr line broadening. The resolved low-temperature hyperfine spectra rule out rapid triplet-excitation motion and, together with interdimer exchange, indicate a difference of at least 0.1 Å in the equilibrium Cu–Cu separation of the singlet and triplet states of Cu_2Ac_4.

The magnetic properties of small transition metal clusters have been intensively studied by both static susceptibility[2] and electron paramagnetic resonance[3] (epr) since Bleaney and Bower's beautiful study of the binuclear copper complex in copper acetate monohydrate,[4] $Cu_2Ac_4\cdot2H_2O$, which is a member of a large class[3,5] of binuclear copper alkanoates and carboxylates

with antiferromagnetic exchange interactions, J, of about 300 cm^{-1}. It has proved far more difficult[2] to measure exchange interactions, J', *between* clusters, since the usual case of $J' \ll J$ requires very low temperatures, where other approximations are suspect, to detect intercluster exchange. Furthermore, if J' is of the same order as electron dipolar interactions between clusters, then even nmr measurements, as in $Cu_2Ac_4\cdot 2H_2O$, may prove unable to distinguish between intercluster exchange and dipolar contributions.[6]

Intercluster interactions must nevertheless be established in order to identify magnetically one-dimensional polymer systems with more than one metal atom per unit cell. Only the simplest polymer, with one metal atom per unit cell and equally strong exchange with both neighbors, can be identified by measuring a single ex-

(2) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe, Ed., Cambridge University Press, Cambridge, England, 1968, Chapter 9; A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 5, 545 (1971).

(3) (a) G. F. Kokoszka and R. W. Duerst, *Coord. Chem. Rev.*, 5, 209 (1970); (b) G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, 5, 181 (1969).

(4) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, 214, 451 (1952).

(5) W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, 5, 47 (1969).

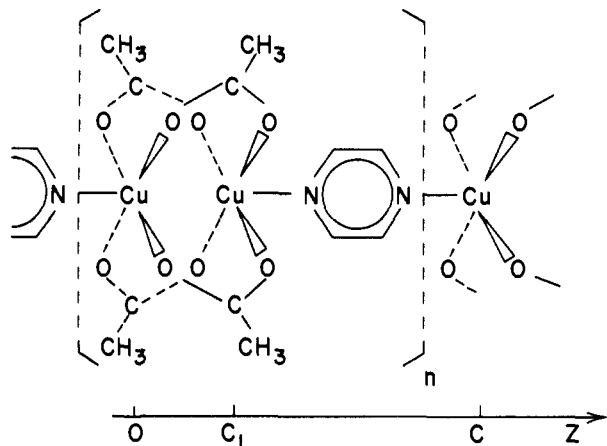(6) A. Kawamori, *J. Phys. Soc. Jap.*, 21, 1096 (1966); Y. Obata, *ibid.*, 22, 256 (1967).

Figure 1. Schematic representation of the pyrazine-bridged chain of Cu_2Ac_4 dimers in Cu_2Ac_4pyr.

change interaction.[7] There are vastly more polymeric Cu^{2+} systems with two or more ions per unit cell,[5,8] and thus with several potentially different exchange interactions along the polymer. While crystallographic data can suggest various exchange and superexchange pathways, it is evident that the *weakest* exchange along the polymer must be measured to establish a magnetically one-dimensional system. In the case of two ions per repeat unit, there are potentially two exchange interactions leading to a polymer of interacting dimers. Even more complex Cu^{2+} polymers, with for example four ions per repeat unit along the chain, have been suggested,[9] but without evidence for the magnitude of the weakest exchange.

We report here an epr study of a new linear chain material, Cu_2Ac_4pyr (pyr = pyrazine), which we synthesized as a prototype for a chain of interacting dimers. A variety of substitutions, including replacing the axial H_2O with pyridine, leave the copper acetate dimer in $Cu_2Ac_4 \cdot 2H_2O$ intact.[3] Thus a large intradimer exchange $J \sim 300$ cm^{-1} was anticipated for Cu_2-Ac_4pyr. On the other hand, Villa and Hatfield[10] have observed a 6 cm^{-1} exchange for Cu^{2+} ions linked by pyrazine in $Cu(NO_3)_2pyr$, where the Cu–pyrazine–Cu separation is 6.72 Å. Linking Cu_2Ac_4 units with the axially bidentate pyrazine molecule will in fact be shown to lead to the chain structure in Figure 1. An alternating exchange Hamiltonian is introduced (eq 1). Here

$$\mathfrak{K}_{ex} = J\sum_n s_{2n} \cdot s_{2n+1} + J'\sum_n s_{2n} \cdot s_{2n-1} \tag{1}$$

$s_n = \frac{1}{2}$ is the electronic spin of the $(3d)^9$ Cu^{2+} ions in the chain, J is the intradimer Cu_2Ac_4 exchange, and $J' \ll J$ is the pyrazine bridged interdimer exchange. In the limit $J' \rightarrow 0$, $\mathfrak{K}_{ex}$ corresponds to noninteracting dimers with a singlet ground state and a triplet excited state at J.

The general approach to measuring $J' \ll J$ is to focus

(7) R. B. Griffiths, *Phys. Rev. A*, **35**, 659 (1964); K. Takeda, S. Matsukawa, and T. Haseda, *J. Phys. Soc. Jap.*, **30**, 1330 (1971); for epr determinations of *J*, see M. Hennessy, C. D. McElwee, and P. M. Richards, *Phys. Rev. B*, **7**, 930 (1973); Z. G. Soos, T. Z. Huang, J. S. Valentine and R. C. Hughes, *Phys. Rev.*, B, **8**, 993 (1973).

(8) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(9) D. B. W. Yawney, J. A. Moreland, and R. J. Doedens, *J. Amer. Chem. Soc.*, **95**, 1164 (1973).

(10) J. F. Villa and W. E. Hatfield, *J. Amer. Chem. Soc.*, **93**, 4081 (1971).

on spin dynamics, or on the spin relaxation resulting from interdimer exchange, by studying the temperature dependence of the epr. The principal restriction on the smallness of J' is that it be larger than, for example, electron dipolar interactions between clusters and thus provide a major spin–lattice or spin–spin relaxation mechanism. Unless J' exceeds the dipolar terms, there is little reason for postulating an exchange Hamiltonian like eq 1 in the first place. The strong temperature-dependent broadening of the epr lines in Cu_2Ac_4pyr will be shown in the Interdimer Exchange section to represent an interdimer exchange $J' \sim 1100$ G, which is far larger than the 10–100 G dipolar line width.

Chains of interacting dimers of $s = \frac{1}{2}$ radicals have previously been encountered in organic free-radical salts[11] based on strong π acceptors like TCNQ or on strong π donors like TMPD. $\mathfrak{K}_{ex}$ in eq 1 has been used to interpret the mobile triplet excitons[11,12] in $TMPDClO_4$, which below a 186°K phase transition contains a dimerized stack of $TMPD^+$ radicals. The interdimer exchange J' in all organic free-radical solids studied so far has been sufficiently strong to exchange-narrow the hyperfine splitting. Indeed, the absence of hyperfine and narrow epr lines proved the existence of the triplet excitons characteristic of $\mathfrak{K}_{ex}$ for $J' \ll J$.

By contrast, the 77°K epr spectrum of Cu_2Ac_4pyr shows well-resolved hyperfine lines when the applied field H_0 is along the chain axis, the Cu–Cu axis, in Figure 1. The 1:2:3:4:3:2:1 hyperfine spectrum shown in Figure 2 is similar to the $Cu_2Ac_4 \cdot 2H_2O$ low-temperature spectra observed by Bleaney and Bowers[4] and corresponds to a triplet interacting with both $I = \frac{3}{2}$ copper nuclei of a dimer. The ~ 30 G width of the individual hyperfine components is an upper bound on the rate of motion of the triplet state, since exciton motion over Cu_2Ac_4 dimers with randomly oriented but fixed nuclear spins either broadens or collapses the hyperfine spectrum. Since J' controls the rate of exciton motion,[11] the unexpected observation of strong interdimer exchange *without* detectable exciton motion is evidence for exchange striction in Cu_2Ac_4pyr. As shown in the Discussion section, the assumption of slightly different Cu–Cu equilibrium separations in the singlet and triplet states of a Cu_2Ac_4 dimer greatly reduces, by the square of a Franck–Condon factor, the motion of a triplet excitation without reducing interdimer exchange.

Experimental Section

A preliminary 300°K single-crystal X-ray study showed that Cu_2Ac_4pyr is monoclinic, with space group $P2_1/m$, and unit cell parameters $a = 11.91 \pm 0.10$ Å, $b = 14.23 \pm 0.12$ Å, $c = 9.81 \pm 0.09$ Å, and $\beta = 85° 5' \pm 5'$. The density measured by flotation is 1.75 g/cm^3, which compares well with the calculated density of 1.77 g/cm^3 for $Z = 4$. The crystal c axis is the needle and, as

(11) P. L. Nordio, Z. G. Soos, and H. M. McConnell, *Annu. Rev. Phys. Chem.*, **17**, 237 (1966).

(12) D. D. Thomas, H. Keller, and H. M. McConnell, *J. Chem. Phys.*, **39**, 2321 (1963).
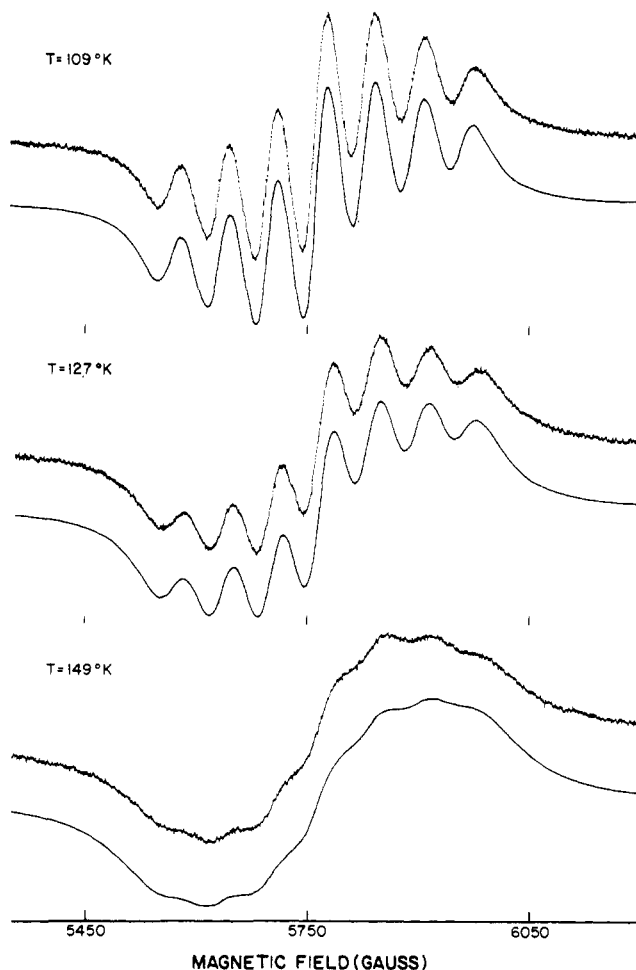
T = 109 °K

T = 127 °K

T = 149 °K

5450   5750   6050

MAGNETIC FIELD (GAUSS)

Figure 2. Experimental and simulated hyperfine spectra for Cu_2-Ac_4pyr with H_0 along the Cu–Cu axis (crystal c axis) as a function of temperature.

Figure 3. Relative integrated intensity of the high-field X-band epr signal, I, times the temperature, T, as a function of the triplet density, ρ, with $J = 325$ cm^{-1} in eq 2. Four different orientations of H_0 are shown: $\times$, along $\hat{z}$ axis; $\bigcirc$, along $\hat{y}$; $\square$, along $\hat{x}$; and I at 32° from $\hat{z}$.

shown by epr, is the common Cu–Cu axis of all Cu_2Ac_4 dimers. The polymeric Cu_2Ac_4pyr postulated in Figure 1, with the chains along the c axis, is consistent with the unit cell dimension $c = 9.81$ Å. The Cu–Cu distance is 2.64 Å in $Cu_2Ac_4 \cdot 2H_2O$ and in related dimers;[3] the Cu–N distance is 2.19 Å in $Cu_2Ac_4 \cdot 2pyr$;[13] the N–N distance in pyrazine is 2.74 Å.[14] As seen from Figure 1, $c = d_{Cu-Cu} + 2d_{Cu-N} + d_{N-N}$, which adds up to 9.76 Å, or within experimental error to $c = 9.81 \pm 0.09$ Å. Each polymer thus contains a single Cu_2Ac_4pyr unit per unit cell.

The X-band (9.1 GHz) epr measurements were obtained with a Varian E-12 spectrometer at 100 kHz modulation and a modified Varian V-4040 temperature control. The temperature was measured using a Cu–constantan thermocouple to an accuracy of ±5°. A small Cu_2Ac_4pyr crystal with well-developed faces was mounted with silicone grease at the end of a quartz rod, which could be rotated in the applied field, and the thermocouple was placed close to the crystal.

Q-Band (35 GHz) epr measurements, with $\hbar\omega_0$ larger than the zero-field splittings, at 300 and ~120 °K, showed the characteristic high-field triplet spectra.[3,12] The epr parameters deduced from X and Q bands were in close agreement. No evidence for differently oriented dimers was seen even at Q-band.

The relative X-band epr intensities shown in Figure 3 are unusually accurate due to the accidental coincidence of strongly increasing intensity and increasing line width as the temperature was raised. No adjustments of the gain or of the modulation ampli-

tude were thus required for a complete (77–400°K) temperature study. For H_0 not along the Cu–Cu axis ($\hat{z}$ in Figure 1), the relative epr intensity of the single, Lorentzian, high-field X-band line was obtained from the line width and amplitude variations. For H_0 along $\hat{z}$, the area of the resolved hyperfine in Figure 2 was obtained from the area of the simulated spectra, which were generated by taking the derivative of the Saunders Lorentzian line shape nmr program.[15] The exchange frequency (the rate of triplet motion) was zero in the best fit to the experimental spectra. Figure 2 thus corresponds simply to seven Lorentzian hyperfine lines, with relative intensities 1:2:3:4:3:2:1, with equal spacings of 65 G and the same, adjustable, temperature-dependent line width. The simulated spectra were computed on the Princeton University IBM 360/91 and the output was plotted on the Calcomp recorder.[15] The possibility that the collapse of the hyperfine with increasing temperature was due to triplet exciton motion was decisively ruled out by varying the exchange frequency for fixed line width. No agreement between experimental and simulated spectra was then found, primarily because the position of the outermost lines is very sensitive to exchange and the overall spectrum is thus much narrower when triplet motion over Cu_2Ac_4 dimers with randomly oriented nuclear spins is responsible for the broadening.

Magnetic Parameters of Cu_2Ac_4pyr

The difficulty in measuring interdimer exchange J' is that, for $J' \ll J$, the static susceptibility, g values, fine structure constants, and other observed magnetic parameters are almost exclusively those of an isolated dimer. The epr of Cu_2Ac_4pyr will first be discussed in the approximation $J' = 0$, to prove that the Cu_2Ac_4 dimers postulated in Figure 1 closely resemble the Cu_2Ac_4 dimers in $Cu_2Ac_4 \cdot 2H_2O$. The angular dependence of the epr spectra also establishes that all intradimer Cu–Cu axes are coparallel and along the crystal c axis, which will be taken as the z axis of the dimer spin Hamiltonian.

The exchange Hamiltonian $J\mathbf{s}_{2n} \cdot \mathbf{s}_{2n+1}$ for the nth dimer has, for $J > 0$, a singlet ground state and a triplet excited state at J. The thermal equilibrium density, ρ, of the triplet state is

$$\rho = (1 + \tfrac{1}{3}\exp(J/kT))^{-1} \qquad (2)$$

The spin paramagnetism for N dimers is

$$\chi_\alpha = \frac{S(S+1)g_\alpha^2\mu_B^2}{kT}N\rho \qquad (3)$$

(13) G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 5244 (1961).

(14) A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Crystallogr., Sect. B*, 26, 979 (1970). The pyrazine dimensions are slightly changed from crystalline pyrazine, presumably due to pyrazine–Cu bonding.
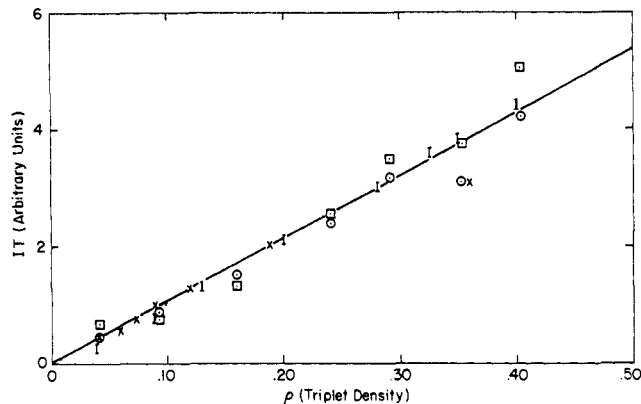
(15) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malurström, and T. Vänugard, Ed., Pergamon Press, Oxford, 1967, p 85. We thank J. Andose for the modified program using the Calcomp plotter.
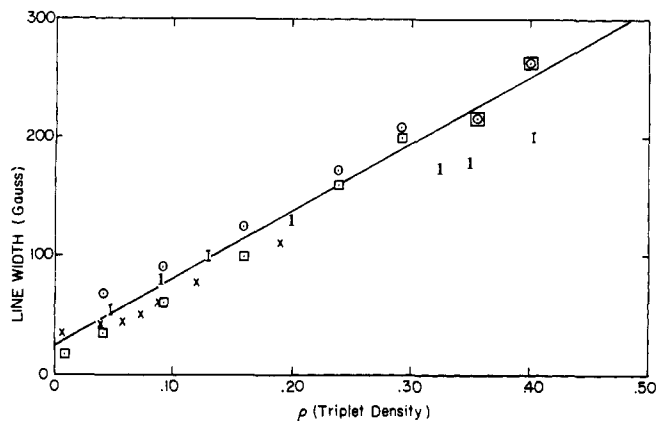
Figure 4. Variation of the half-height X-band line width as a function of the triplet density, ρ, for four orientations of H_0: ✕, along $\hat{z}$; ○, along $\hat{y}$; □, along $\hat{x}$; and I at $32°$ from $\hat{z}$.

where $S = 1$, μ_B is the Bohr magneton, k is the Boltzmann constant, and g_α is the g value of each dimer for a particular orientation of the applied external field, H_0. The coparallel Cu–Cu axes in Cu_2Ac_4pyr permit the simplification of using a single g_α in eq 3; by contrast there are several differently oriented dimers in $Cu_2Ac_4 \cdot 2H_2O$.[16] As shown in Figure 3, χT is directly proportional to ρ when we choose $J = 325 \pm 20$ cm^{-1} for any orientation of H_0. The error limits indicate that a 20 cm^{-1} change leads to a noticeably poorer linear fit required in eq 3. On account of the high degree of axial symmetry, the $\hat{x}$ and $\hat{y}$ orientations in Figure 3 are not identified with crystal axes and merely represent mutually orthogonal axes in the plane perpendicular to the $\hat{z}$ axis. The intradimer exchange in $Cu_2Ac_4 \cdot 2H_2O$ is 286 cm^{-1},[4,17] while that in $Cu_2Ac_4 \cdot 2pyr$, with similar Cu–N axial bonds, is 325 cm^{-1}.[18] The singlet–triplet splitting in Cu_2Ac_4pyr is thus in the 300 cm^{-1} range characteristic of such binuclear copper complexes.[3,18]

The triplet sublevels of a Cu_2Ac_4 dimer are further split by the fine-structure, Zeeman, and hyperfine interactions as indicated in the spin Hamiltonian for a triplet state, $S = 1$

$$\mathcal{H}_T = \mu_B H_0 \cdot g \cdot S + DS_z^2 + E(S_x^2 - S_y^2) + S \cdot A \cdot I \quad (4)$$

$\mathcal{H}_T$ in Cu_2Ac_4pyr is a small perturbation to the intradimer part of $\mathcal{H}_{ex}$. The first term represents the Zeeman interaction with an applied static magnetic field H_0 and leads to a Larmor frequency

$$\hbar\omega_0 = \mu_B H_0 g(\theta) = H_0\sqrt{g_{||}^2 \cos^2\theta + g_\perp^2 \sin^2\theta} \quad (5)$$

The azimuthal angle θ is taken relative to the common Cu–Cu axis. The nearly axial symmetry is indicated by using $g_x = g_y = g_\perp$. The D and E terms in (4) are the fine-structure interaction, which in binuclear complexes contains both spin–orbit[4] and electron dipolar interaction. Axial symmetry leads to $E = 0$. At Q-band, where $\hbar\omega_0$ is larger than D, the epr spectrum consists of two lines centered at $\mu_B H_0 g(\theta)$ and separated by $D(3\cos^2\theta - 1)$. The final term in (4) is the hyperfine interaction with the $I = {}^3/_2$ copper nuclei for either

(16) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.,* **6,** 451 (1952).

(17) A. K. Gregson, R. L. Martin, and S. Mitra, *Proc. Roy. Soc., Ser. A,* **230,** 473 (1971).

(18) E. Kokot and R. L. Martin, *Inorg. Chem.,* **3,** 1306 (1964).

^{63}Cu or ^{65}Cu and $I = I_1 + I_2$. The only significant component of $A = A_{||}\hat{z}\hat{z} + A_\perp(\hat{x}\hat{x} + \hat{y}\hat{y})$ is $A_{||} = 65$ G. The hyperfine interaction is resolved at liquid N_2 for H_0 along the Cu–Cu axis and the characteristic[3,4] $1:2:3:4:3:2:1$ splittings gives the value of $A_{||}$.

The epr parameters of Cu_2Ac_4pyr are collected in Table I and compared with those of the Cu_2Ac_4 unit

Table I. Magnetic Parameters of Cu_2Ac_4 in Cu_2Ac_4pyr and in $Cu_2Ac_4 \cdot 2H_2O^a$

	Cu_2Ac_4pyr	$Cu_2Ac_4 \cdot 2H_2O$
J^b	325 ± 20	286^c
D^b	0.33 ± 0.01	0.345
E^b	<0.01	0.007
$g_{||}$	2.37 ± 0.01	2.344
$g_\perp$	2.09 ± 0.01	2.073
$|g_x - g_y|$	<0.02	0.04
$A_{||}^b$	0.0074	0.008
$A_\perp^b$	<0.002	<0.001

^{a} Reference 3b. ^{b} In cm^{-1}. ^{c} Reference 17.

in $Cu_2Ac_4 \cdot 2H_2O$. The epr parameters in a variety of binuclear copper complexes[3b] show that the integrity of the Cu_2Ac_4 unit is usually maintained, as the data in Table I demonstrate for Cu_2Ac_4pyr.

Interdimer Exchange

The width of each hyperfine component for H_0 along the z axis increases, as seen from Figure 2, with increasing temperature. The X-band line width at other orientations of H_0, where even at $77°K$ a single Lorentzian absorption occurs for $A_\perp \sim 0$, also increases greatly with increasing T, as shown in Figure 4. The observed broadening is proportional to the triplet density, ρ, in the region $77-350°K$, broadens slightly faster than ρ at higher temperature, and is isotropic within experimental accuracy at X-band. The proportionality to ρ indicates interactions between adjacent triplets, while the isotropy of the broadening suggests an exchange interaction, for example, the J' term in (1). Dipolar interactions between adjacent triplets can be ruled out not only because they are expected to show angular dependence but because the nearest interdimer Cu–Cu distance of 6–7 Å leads to dipolar fields of less than 100 G. We therefore consider the theory of epr line widths to relate the line broadening and the interdimer exchange J'.

In the absence of spin–lattice relaxation or of interdimer exchange, Cu_2Ac_4pyr corresponds to an arbitrary fixed density, ρ, of paramagnetic triplet states and diamagnetic singlet states. Electron dipolar interactions among the magnetically dilute triplets are expected,[19] for $\rho \gtrsim 0.01$, to lead to a Gaussian epr line shape whose width is approximately given by the square root of the second moment $M_2(\rho)$[20]

$$M_2(\rho) = \rho M_d + M_N \quad (6)$$

Here M_d is the Van Vleck second moment[21]

$$M_d = {}^1/_4 s(s + 1)\frac{g^4\mu_B^4}{\hbar^2 N}\sum_{jk}' \frac{(3\cos^2\theta - 1)^2}{r_{jk}^6} \quad (7)$$

where, in the $T \to \infty$ limit, we sum over all $s = {}^1/_2$ cop-

(19) C. Kittel and E. Abrahams, *Phys. Rev.,* **90,** 238 (1953).

(20) Z. G. Soos, *J. Chem. Phys.,* **46,** 4284 (1967).

(21) J. H. Van Vleck, *Phys. Rev.,* **74,** 1168 (1948).

per sites $j \neq k$; θ_{jk} is the angle between the Cu–Cu vector $\mathbf{r}_{jk}$ and the applied field $\mathbf{H}_0$, which is assumed to be sufficiently large to allow truncating the dipolar interaction; the summation for the present discussion excludes copper ions in the same dimer, since their dipolar coupling is explicitly included in the D and E terms of the spin Hamiltonian (4) and is fully resolved in Cu_2Ac_4pyr. In eq 6 we have also included M_N, the second moment of the electron nuclear interaction, which can become important at very low temperature where $\rho \to 0$.

It is evident that $M_2^{1/2}(\rho)$, the width of the *Gaussian* epr line expected in the absence of spin–lattice relaxation, is inadequate to describe the *Lorentzian* absorption observed in Cu_2Ac_4py. The triplet excitations in Cu_2Ac_4 systems are thermal fluctuations, with finite lifetimes, and no dimer remains in a triplet state indefinitely. Even in $Cu_2Ac_4 \cdot 2H_2O$, where there is no obvious exchange pathway from one dimer to another, the proton nmr does not indicate a superposition of signals from ground and excited dimers.[6] Thus an interdimer exchange of 10–20 G, which, however, could be due simply to dipolar interactions, was postulated.[6]

A spin–lattice relaxation rate $W(\rho)$ modulates the dipolar interactions and leads, for $W(\rho) > M_2^{1/2}(\rho)$, to a Lorentzian epr line whose half-width at half-height Γ ($= (\sqrt{3}/2)\Delta H_{pp}$, the peak-to-peak derivative line width) is

$$\Gamma(\rho) = W(\rho) + \frac{M_2(\rho)}{W(\rho)} \qquad (8)$$

In the usual case of exchange or motional narrowing,[22] only the modulation of $M_2(\rho)$ is observed since the motion or exchange commutes with the spin Hamiltonian and thus is not a relaxation mechanism. Spin–lattice relaxation, which also limits the spin correlation functions $\langle S_i^z(t)S_i^z(0)\rangle$, also modulates the local dipolar fields and broadens the line as indicated in eq 8. The phenomenological $W(\rho)$ in (8) will be related to J' below. For the moment, we note that the 77°K Lorentzian line width observed in Cu_2Ac_4pyr shows that, even for $\rho \sim 0.01$, $W(0.01) > M_2(0.01)$. The spin–lattice relaxation for an isolated dimer, $W(0)$, must therefore be of order of 20–50 G. Furthermore, if we assume that adjacent triplets increase the spin relaxation rate by W_1, then the relaxation rate $W(\rho)$ for triplet density ρ will be

$$W(\rho) = W(0) + W_1 2\rho(1 - \rho) + 2W_1\rho^2 \qquad (9)$$
$$= W_0 + 2W_1\rho$$

The factors $2\rho(1 - \rho)$ and ρ^2 are, respectively, probabilities for noninteracting triplets to have one or two triplet neighbors. The slope of Γ in Figure 4 gives $W_1 \simeq 280$ G. The Lorentzian line in Cu_2Ac_4pyr thus indicates that the local dipolar fields are modulated, as would be expected from rapid spin–lattice relaxation. The temperature dependence of the epr then requires a spin–lattice relaxation $W(\rho)$ in (9) with $W_0 \sim 20$–50 G and $W_1 \simeq 280$ G.

The contribution $M_2(\rho)/W(\rho)$ to Γ in (8) turns out to be small for any ρ and to be at most weakly dependent on temperature. The nearest Cu–Cu distances for Cu

ions in different complexes is 6–7 Å, which leads to dipolar second moments of $\sim 10^4$ G^2. Cu_2Ac_4pyr is slightly less dense than $Cu_2Ac_4 \cdot 2H_2O$ and is thus expected to have at most the 50–100 G line width calculated in the latter between 77 and 300°K if dipolar fields dominate.[23] Indeed, the broadening of the epr line width with increasing temperature observed in $Cu_2Ac_4 \cdot 2H_2O$ is more than would be expected from $M^{1/2}(\rho)$ for at least one orientation of $\mathbf{H}_0$ and the lines are Lorentzian for $T \gtrsim 77°$K.[23] Both observations indicate that the local fields are fluctuating and that the line width is of the form of $\Gamma(\rho)$ in eq 8 rather than just $M^{1/2}(\rho)$. The nuclear second moment M_N is always small, of the order of 10^2 G^2. If $W_0 \sim 40$ G is used for the residual 77°K line width, it is evident that

$$\frac{M_2(\rho)}{W(\rho)} = \frac{M_n + \rho M_d}{W_0 + 2W_1\rho} \approx \frac{M_d}{2W_1} \qquad (10)$$

for $2W_1\rho > W_0$, or for $T \gtrsim 150°$K. Thus $M_2(\rho)/W(\rho)$ is weakly dependent on ρ for $T < 150°$K and is never more than about 40–50 G. The more complete analysis confirms the earlier conclusion that $2W_1 = d\Gamma/d\rho$ is just a specific spin–lattice relaxation mechanism for adjacent excitation. The angular variations of $M_2(\rho)$ only account for the low temperature line width anisotropy in Figure 4.

We now relate the phenomenologically introduced spin–lattice relation rate $W(\rho)$ to the interdimer exchange J' postulated for Cu_2Ac_4pyr in $\mathcal{3C}_{ex}$. It is convenient to introduce the dimer spin $S_n = s_{2n} + s_{2n+1}$ for the nth Cu_2Ac_4 unit. Each S_n can be 0 or 1 for a ground and excited triplet, respectively. Lynden-Bell and McConnell[24] have shown that, for a rigid lattice, the $J's_{2n} \cdot s_{2n-1}$ terms in $\mathcal{3C}_{ex}$ lead to: (a) triplet motion, with coefficient $J'/4$ for the integral $\langle ST|J's_{2n} \cdot s_{2n-1}|TS\rangle$ in which an excitation is moved to an adjacent *singlet* dimer; (b) an interaction $(J'/4)S_n \cdot S_{n+1}$ for adjacent triplets; (c) terms which create a triplet next to a triplet or which annihilate one of a pair of adjacent triplets; (d) terms which create and annihilate a pair of adjacent triplets. Processes c and d correspond to thermal fluctuations in which triplet excitations appear or disappear, with the overall equilibrium density ρ in the crystal fixed at any temperature according to eq 2. Process b can lead to exchange broadening whenever the three sublevels $|\alpha_1\rangle$, $|\alpha_2\rangle$, and $|\alpha_3\rangle$ of $\mathcal{3C}_T$ in eq 4 are not equally spaced and the fine structure can be resolved.[11] Such broadening, with subsequent line merging, has been observed in $TMPDClO_4$[12] and in several TCNQ salts.[25] The identification $W_1 \sim J'/4$ then leads to $J' \sim 1100$ G.

At Q-band, the Larmor frequency satisfies $\hbar\omega_0 > D$ and the eigenstates of $\mathcal{3C}_T$ are, in zeroth order, just the Zeeman levels $|1\rangle$, $|0\rangle$, and $|-1\rangle$ for $S = 1$. The fine-structure splittings follow $D(3 \cos^2 \theta - 1)$, with θ the angle between $\mathbf{H}_0$ and the Cu–Cu axis (crystal c axis). Exchange broadening can be suppressed at $\theta = 54°$, when the fine-structure splitting vanishes and the sublevels of $\mathcal{3C}_T$ are equally spaced. The $\theta = 54°$ line width at Q-band is, in fact, twice as narrow at 300°K than either the $\theta = 0$ or $\theta = 90°$ line. A detailed study near $\theta = 54°$ is complicated by the highly anisotropic

(22) R. Kubo and K. Tomita, *J. Phys. Soc. Jap.*, 9, 888 (1954); P. W. Anderson, *ibid.*, 9, 316 (1954); A. Abragam, "The Principles of Nuclear Magnetism," Clarendon, Oxford, England, 1961, Chapters IV and X.

(23) S. Matsumura and A. Kawamori, *J. Phys. Soc. Jap.*, 22, 1508 (1967).

(24) R. Lynden-Bell and H. M. McConnell, *J. Chem. Phys.*, 37, 794 (1962).

(25) M. T. Jones and D. B. Chesnut, *J. Chem. Phys.*, 38, 1311 (1963).

hyperfine interaction, which leads to different axes of quantization for the nuclear spins for different electronic subspaces.

It is worth emphasizing that, while W_1 is clearly of the order of J', the present data do not distinguish between spin–lattice relaxation due to adjacent triplets (process b) and spin–lattice relaxation arising from lifetime fluctuations (processes c and d) in which triplets are created and annihilated. The latter cannot be neglected, or the nmr could distinguish between isolated triplets and triplet pairs. The strong isotropic broadening shown in Figure 4 indicates, with the identification $W_1 = J'/4$, an interdimer exchange $J' \sim 1100$ G. A slightly smaller value of J' is indicated if processes c and d are comparable relaxation mechanisms. As shown below, however, the exciton creation and annihilation mechanisms, but not process b involving exchange between adjacent triplet excitations, are reduced if the Cu–Cu separation in Cu_2Ac_4 is different in the singlet and triplet states. Such an exchange striction would also inhibit excitation motion, and thus explain the resolved hyperfine for H_0 along $\hat{z}$.

Discussion

The epr data in Table I demonstrate the expected occurrence of the characteristic Cu_2Ac_4 unit in $Cu_2Ac_4\cdot$pyr. The strong temperature-dependent line broadening shown in Figure 1 indicates interdimer exchange interactions $J' \sim 0.1$ cm^{-1} which, on the basis of previously observed superexchange through pyrazine, is of the expected order of magnitude.[3,17] (Since the Cu–N distance in $Cu_2Ac_4\cdot2pyr$[13] is 0.21 Å longer than the Cu–N separation in $Cu(NO_3)_2pyr$[14], a weaker Cu–pyrazine–Cu superexchange was anticipated in $Cu_2Ac_4\cdot$pyr than the 6 cm^{-1} exchange[10] in $Cu(NO_3)_2pyr$.) The most interesting observation is the absence of detectable exciton motion in Cu_2Ac_4pyr in spite of an interdimer exchange $J' \sim 1100$ G.

It has long been conjectured[26,27] that the internuclear separation of exchange-coupled ions could depend on the total spin, increasing with increasing S. Such a hypothesis is supported by detailed epr studies[27] of $S = \frac{5}{2}$ Mn^{2+} ions which form oriented impurities of the type $Mn^{2+}-O-Mn^{2+}$ in MgO and CaO. The resulting dimer can have $S = 0, 1, 2, 3, 4,$ and 5, with the $S > 0$ paramagnetic states epr active. Similarly, a dimer of $S = \frac{1}{2}$ nuclei or molecular ions could have a slightly shorter internuclear separation in the $S = 0$ ground state than in the $S = 1$ excited state. Such an exchange-striction mechanism has been developed by Soos and McConnell[28] for exchange-coupled linear chains (1) with $J' \ll J$. The triplet state, accompanied by an elongation of the internuclear separation, is an example of a small polaron, and the hopping polaron motion is expected for such spin polarons.[28]

Exchange striction modifies the coefficients[28] of the interdimer processes (a–d) due to the $J'\mathbf{s}_{2n}\cdot\mathbf{s}_{2n-1}$ terms. The Franck–Condon factor

$$\gamma = \langle\varphi_S|\varphi_T\rangle < 1 \qquad (11)$$

now occurs in addition to purely electronic matrix elements. Here φ_S and φ_T are the nuclear (copper) wave functions for a Cu_2Ac_4 unit in the singlet or triplet electronic state, respectively. The complete matrix element $\langle S\varphi_S T\varphi_T|J'\mathbf{s}_{2n}\cdot\mathbf{s}_{2n-1}|T\varphi_T S\varphi_S\rangle$ for triplet motion becomes

$$t_m = \frac{J'}{4}\gamma^2 \qquad (12)$$

and is reduced by γ^2 from the rigid-lattice result of $\varphi_S = \varphi_T$ and $\gamma = 1$. The interaction between adjacent excitations, process b, is not reduced, since the excitation positions are not altered.[28] The matrix element for creation or annihilation of a single excitation is reduced by γ, while pair creation and annihilation is reduced by γ^2. It is evident that exchange striction permits a relatively strong interdimer exchange $J' \sim 1100$ G, as indicated by the temperature dependence of the epr line width, while reducing exciton motion to $t_m < 30$ G, as required from the low-temperature resolved hyperfine spectra. The upper bound of 30 G on excitation motion corresponds to $\gamma^2 \lesssim 0.10$.

The intradimer Cu–Cu stretching frequency is expected[29] to be about $\hbar\omega \sim 100$ cm^{-1}. At 77°K, we neglect the thermal population in excited vibrational states. Assuming harmonic oscillators with the same force constants, but displaced by b to longer Cu–Cu separation in the triplet state, we find the Franck–Condon factor

$$\gamma = \exp\left(-\frac{m(\hbar\omega)b^2}{4\hbar^2}\right) \qquad (13)$$

where m is the effective mass. We take $m = 2Cu = 130$ amu, which has been shown experimentally to be a reasonable approximation for transition metal clusters bridged by first-row ligands,[29] and $\hbar\omega \simeq 100$ cm^{-1}. The upper bound $\gamma^2 \lesssim 0.10$ then yields a minimum displacement $b \gtrsim 0.12$ Å.

A difference of more than 0.12 Å between the Cu–Cu separation in the singlet and triplet states of a Cu_2Ac_4 dimer should be observable by comparing X-ray data at 77°K, with about 1% triplets, and 300°K, with almost 40% triplets. Such a change in the equilibrium geometry would be characteristic of a Cu_2Ac_4 unit, regardless of interdimer interactions, and thus a property of many previously prepared binuclear copper complexes. The Cu_2Ac_4pyr crystal is, nevertheless, probably the most convenient for a variable-temperature X-ray study, since all the Cu–Cu are coparallel and along the unit cell c axis.

It remains to be shown that the extensive previous work[2–5,17,18] on binuclear copper complexes does not exclude the exchange striction deduced for Cu_2Ac_4pyr. Previous magnetic studies have focused[17] on the singlet–triplet gap, J, and on the parameters of the triplet state.[3] The latter do not involve the singlet state and, barring a very large internuclear change, would not be sensitive to the Cu–Cu separation. For example, the dipolar contribution to the zero-field splitting D is proportional to d_{Cu-Cu}^{-3}, but the relative dipolar and spin–orbit[4] contributions to D are not known accurately enough to detect a 0.1 Å change. Various contributions to J, which is expected to depend on the Cu–Cu separation, have been proposed.[17,18] A σ Cu–Cu bond is ruled

(26) C. Kittel, *Phys. Rev.*, **120**, 335 (1960).

(27) E. A. Harris, *Proc. Phys. Soc., London (Solid State Phys.)*, **5**, 338 (1972).

(28) Z. G. Soos and H. M. McConnell, *J. Chem. Phys.*, **43**, 3780 (1965).

(29) T. G. Spiro, *Progr. Inorg. Chem.*, **11**, 1 (1970). The same number was also assumed by R. L. Martin, *Inorg. Chem.*, **5**, 2065 (1966).

out by the g values, which indicate that the unpaired electrons are largely in $d_{x^2-y^2}$ orbitals. A weak δ bond is consistent with the g values, but may not be the most important[17] contribution to J in view of the substantially larger J in $[Cu_2(RCO)_4(NCS)_2]^{-2}$ for R = H than for R = CH_3, in spite of longer Cu–Cu separation for R = H.[30] Thus superexchange through the bridging ligands provides the largest contributions to J. Such contributions are not presently amenable even to semiquantitative analysis, and in practice J is a purely experimental quantity. Lines[31] has pointed out that exchange striction in a dimer of $S = {}^1/_2$ spins leads, through the distance dependence of J, to a slight temperature dependence of J. Gregson, Martin, and Mitra[17] are satisfied with a constant J for $Cu_2Ac_1 \cdot 2H_2O$ for the 77–300°K susceptibility, but Jotham, Kettle, and Marks[32] favor an additional excited singlet state in many binuclear copper complexes to provide greater

flexibility in fitting susceptibility data. A slight temperature dependence in J would also provide such additional flexibility and wider range susceptibility measurements may thus provide additional evidence for exchange striction. Previous magnetic studies, in which J was necessarily a phenomenological parameter, were therefore quite insensitive to exchange striction in binuclear copper complexes.[33]

(30) D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Commun.*, 629 (1969).

(31) M. E. Lines, *Solid State Commun.*, 11, 1615 (1972).

(32) R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, 428 (1972).

(33) NOTE ADDED IN PROOF. Dr. B. Morosin (private communication) has suggested that a centered $C2/m$ cell with $Z = 2$ is preferable for Cu_2Ac_4pyr and has undertaken both a 125 and 300°K structure determination.

The Manganous–Adenosine Triphosphate System.
A Reinvestigation of Its Proton Magnetic Resonance Spectra[1]

Victorio Wee,[2a] Isaac Feldman,*[2a] Philip Rose,[2b] and Stanley Gross[2b]

Contribution from the Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14642, and Eastman Kodak Research Laboratories, Rochester, New York 14650. Received June 8, 1973

Abstract: A reinvestigation of the Mn^{2+}-induced broadening of the H_8 and H_2 pmr signals of adenosine triphosphate has been carried out. Contrary to the literature, Mn^{2+} does *not* cause equal broadening of the H_8 signals of ATP and AMP. Rather, for an equimolar ATP and AMP mixture, 0.25 M each, containing 5.0×10^{-5} M Mn^{2+} in D_2O at pD 8 and 27°, the ATP H_8 signal was broadened 3.90 times as much as the AMP signal. When the Mn^{2+} concentration was 1.0×10^{-4} M, as in the literature, the ratio of these broadenings was less certain, but was between 3.1 and 6.6. In conjunction with our studies of the dependence of line broadening on temperature, pD, and concentration, the broadening ratio of 3.90 in the former solution is consistent with an equilibrium between >25% $MnATP^{2-}$ and <75% $Mn(ATP)_2^{6-}$, corresponding to a value of <29 for $K_{eq} = (1:2)/(1:1)(ATP^{4-})$. The results imply that *both* adenine H_8 protons in the 1:2 complex are about equally distant from the Mn^{2+} nucleus and couple with the metal magnetically. When the pD was lowered from 6.4 to 5.4 a drastic increase occurred in the Mn^{2+} broadening of both the H_8 and the H_2 signal of 0.25 M ATP but not of 0.02 or 0.1 M solutions. Consideration of the relative broadening values of the four adenine proton signals of an equimolar ATP–AMP mixture at pD 5.4 and at pD 8 suggested that the fundamental cause for the drastic pD effect in the pD 5.4–6.4 range might be a transition in the triphosphate chelation, from $\alpha\beta\gamma$ to $\beta\gamma$ resulting from phosphate protonation as the pD is lowered, with an accompanying change in the ligand exchange mechanism.

Because of the biochemical importance of metal ion–adenosine triphosphate complexes, their structures and stabilities have been extensively studied.[3] In 1968

Sternlicht, Jones, and Kustin[4] claimed to have cleared up apparent discrepancies between previous nuclear magnetic resonance results[5] and earlier ultraviolet spectroscopy[6] and temperature-jump studies.[7] These authors presented pmr evidence to support a suggestion of Brintzinger and Palmer[8] that the Mn(II)–ATP system

(1) (a) This paper is based on work performed partially under contract with the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project and has been assigned Report No. UR-3490-308. Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973. (b) Part of the Ph.D. Thesis of Victorio Wee, University of Rochester, Rochester, N. Y., 1973.

(2) (a) University of Rochester School of Medicine and Dentistry; (b) Eastman Kodak Research Laboratories.

(3) The literature up to 1966 was thoroughly reviewed by R. Phillips, *Chem. Rev.*, 66, 501 (1966). More recent papers are found among the following references.

(4) H. Sternlicht, D. E. Jones, and K. Kustin, *J. Amer. Chem. Soc.*, 90, 7110 (1968).

(5) H. Sternlicht, R. G. Shulman, and E. W. Anderson, *J. Chem. Phys.*, 43, 3133 (1965).

(6) P. W. Schneider, H. Brintzinger, and H. Erlenmeyer, *Helv. Chim. Acta*, 47, 992 (1964).

(7) G. G. Hammes and S. A. Levison, *Biochemistry*, 3, 1504 (1964).

(8) Cited as a personal communication in ref 4.