The series of complexes between *s*-trinitrobenzene and substituted anilines[15] occupy a position intermediate between the iodine–benzene and chloranil-benzene complexes. The intensity of the c-t. band is almost constant throughout the series, and what little variation there is, does not appear to be related to the variation in the equilibrium constant.

If we have a series of complexes in which the most stable configuration is one which allows the donor-excited states to contribute to the c-t. intensity, then we should also expect the intensity to increase as the complexes become more stable. Unfortunately there appear to be few examples in the literature which could be expected to satisfy these conditions (there is some evidence that the $I_2$–alcohol complexes may provide one example).[16] Most complexes which have been studied involve an aromatic molecule as a donor, and in these cases the direction of charge transfer in the most stable configuration is always roughly perpendicular to the plane of the aromatic molecule.

In the discussion so far we have considered the form of the interaction between the ground state and a typical c-t. state. However, it must be remembered that all c-t. states, and not only the one of lowest energy, can contribute to the stabilization of the ground state. In the complexes between iodine and a condensed aromatic hydrocarbon, we can expect that as the size of the hydrocarbon is increased, the overlap of the donating and accepting orbital will generally decrease, since the donor orbital is presumably spread over the whole molecule. The intensity of the c-t. band will therefore decrease and the stabilization of the ground state due to the lowest c-t. state probably will decrease also. However, as the hydrocarbon increases in size the number of c-t. states which can interact with the ground state is increased, and although their accompanying c-t. bands may be hidden beneath the absorption bands of the two components, they can all contribute to the stabilization of the complex. The net result of increasing the size of the aromatic molecule may therefore be to give more stable complexes which have weaker c-t. bands. This behavior is observed both for iodine and chloranil complexes (see Table II).

TABLE II

THE COMPLEXES OF IODINE AND CHLORANIL WITH SOME CONDENSED AROMATIC HYDROCARBONS

| | Complexes with iodine[17] | | | Complexes with chloranil[13] | | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | $\epsilon_{max}$ | $K_{eq}$ | $\lambda_{max}$ | $\epsilon_{max}$ | $K_{eq}$ |
| Benzene | 292 | 16400 | 0.15 | 340 | 2180 | 0.30 |
| Naphthalene | 360 | 2395 | 0.62 | 460 | 820 | 1.17 |
| Phenanthrene | 378 | 1492 | 1.06 | .. | .. | .. |
| Anthracene | 430 | 112 | 52.35 | 610 | 325 | 7.60 |

In conclusion therefore we can say that c-t. absorption can be observed even if no stable complex is formed but that the intensity of this absorption comes not from the ground state but from the donor-excited states. The relative behavior of the intensity of a c-t. band and the stability of the complex for a series of similar donors depends on the variation of the difference in energy between the most stable configuration and the configuration which gives the most intense c-t. band.

**Acknowledgment.**—I wish to thank Dr. R. S. Mulliken for the stimulating discussions and advice he has given me on this topic.

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[15] A. Bier, *Rec. trav. chim.*, **75**, 866 (1956).

[16] P. A. D. deMaine, *J. Chem. Phys.*, **26**, 1192 (1957).

[17] R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

# Proton Spin Relaxation in Aqueous Solutions of Paramagnetic Ions. III. Copper(II)–Diamine Complexes[1-3]

BY L. O. MORGAN, J. MURPHY AND P. F. COX[4]

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Proton spin relaxation times, $T_1$ and $T_2$, in copper(II) nitrate solutions are strongly dependent upon concentration of added ethylenediamine and 2,2′-bipyridine. Relaxation in ethylenediamine solutions is attributable to magnetic proton–electron dipole–dipole interaction and, at higher ethylenediamine concentrations, in part to isotropic proton–electron spin exchange in the complex species. In solutions having an excess of ethylenediamine beyond that required for formation of diaquobisethylenediaminecopper(II) ions, transverse relaxation ($T_2$) depends largely upon the rate of proton exchange between ligand molecules and solvent water molecules, permitting evaluation of the first-order proton exchange rate constants. The proton exchange rate $R$ obeys a bimolecular rate law: $R = k'[Cu(en)_2(H_2O)_2{}^{++}][en]$, in which $k' = 2.4 \times 10^7\ M^{-1}$ sec.$^{-1}$ at 27°. In copper(II)–2,2′-bipyridine solutions relaxation is by dipole–dipole interaction alone.

## Introduction

The influence of dissolved paramagnetic species on proton spin relaxation times in aqueous solutions has been discussed extensively in previous papers[3,5] and in references cited there. Of particular interest in connection with the work to be reported in this paper are the data on proton thermal ($T_1$) and phase memory, or transverse, ($T_2$) relaxation times in copper(II) salt solutions over a wide range of frequencies[3,6,7] and at a number of different temperatures.[7] The present consensus is

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[1] This work was supported by a grant from the Robert A. Welch Foundation, Houston, Texas.

[2] Presented in part at the 133rd National Meeting, American Chemical Society, San Francisco, California, April, 1958.

[3] Paper II: *J. Chem. Phys.*, **31**, 365 (1959).

[4] Magnolia Petroleum Company Fellow, 1958–1959.

[5] A. W. Nolle and L. O. Morgan, *J. Chem. Phys.*, **26**, 642 (1957).

[6] G. Laukien and J. Schlüter, *Z. physik*, **146**, 113 (1956).

[7] R. A. Bernheim, T. H. Brown, H. S. Gutowsky and D. E. Woessner, *J. Chem. Phys.*, **30**, 950 (1959).

that magnetic interaction between protons and paramagnetic ions in solution may be adequately described by consideration of electron–proton dipole–dipole interaction, explicitly formulated by Solomon,[8] and a scalar coupling $A\mathbf{I}\cdot\mathbf{S}$ between electron and proton spins (isotropic spin exchange) suggested by Bloembergen.[9] In a simplified form the combined relationships are

$$\frac{1}{T_1} = \frac{4}{30}\,\frac{S(S+1)g^2\beta^2\gamma_I{}^2p}{r^6}\left[3\tau_c + \frac{7\tau_c}{1+\omega_s{}^2\tau_c{}^2}\right] + \frac{2}{3}\,\frac{S(S+1)A^2p}{\hbar^2}\left[\frac{\tau_e}{1+\omega_s{}^2\tau_e{}^2}\right] \quad (1)$$

$$\frac{1}{T_2} = \frac{4}{60}\,\frac{S(S+1)g^2\beta^2\gamma_I{}^2p}{r^6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s{}^2\tau_c{}^2}\right] + \frac{1}{3}\,\frac{S(S+1)A^2p}{\hbar^2}\left[\tau_e + \frac{\tau_e}{1+\omega_s{}^2\tau_e{}^2}\right] \quad (2)$$

in which $\gamma_I$ is the proton gyromagnetic ratio; $p$, the probability that a proton occupy a position in the coördination spheres of the paramagnetic ions; $\tau_c$, the correlation time for dipolar interaction; $\tau_e$, the correlation time for isotropic spin exchange (electron spin relaxation time or proton residence time in the coördination sphere of the ion, whichever is shorter); and $\omega_S$, the electron precessional frequency. In each equation, the first term on the right-hand side represents dipolar interaction; the second, scalar coupling (isotropic spin exchange). In obtaining these equations from the more general ones, it was assumed that the proton precessional frequency $\omega_I$ is much less than $\omega_S$ and that at resonance frequencies in the range of interest in this work (> 1 Mc/sec.) $\omega_I{}^2\tau_c{}^2 << 1$. The probability factor $p$ is included in order to satisfy the requirements of the assumed ionic solution model, in which primary interaction occurs between protons in the first layer of molecules about the paramagnetic ion and the central atom. Rapid exchange of protons between the hydration sphere (in the case of simple hydrated ions) and the surrounding water molecules then leads to the observation of an average relaxation time for the entire proton population of the solution. The recent work of Connick and Poulson[10] on $O^{17}$ resonance in a number of aqueous solutions of paramagnetic ions indicates that lifetimes of water molecules in the coördination spheres of the ions are of the order of $10^{-5}$ sec. or less. The proton lifetimes must be much less than that and cannot be greater, so that the assumption of rapid exchange of protons is certainly valid for the hydrated ions in aqueous solutions. In calculations based on equations 1 and 2 the static magnetic susceptibilities $\mu_s$ can, in general, be substituted for the quantity $[S(S+1)g^2\beta^2]^{1/2}$ for ions of the first transition period elements.

In the specific case of aqueous copper(II) salt solutions, under a wide range of experimental conditions, it has been shown that isotropic spin exchange is not observable[5,7] and that consideration of dipolar interaction is sufficient to explain the behavior of the system. The appropriate $\tau_c$ appears to be the tumbling time for the entire hydrated ion and is approximately $2 \times 10^{-11}$ sec. at 27°.[3]

In a preliminary survey of the effect of addition of various complexing agents to copper(II) salt solutions, it was observed that extremely large $T_1/T_2$ ratios were obtained when ethylenediamine was present in excess of the amount required for formation of the bis complex. Such ratios are observed in manganese(II) solutions, for instance, and have been attributed to the contribution of isotropic spin exchange to $T_2$.[9] It is the purpose of this paper to present the results of a detailed investigation of proton relaxation in the copper(II)–ethylenediamine and copper(II)–2,2′-bipyridine systems and to propose an interpretation of the results in terms of the structural and kinetic features of the solutions.

## Experimental

**Materials.**—Stock solutions of ethylenediamine and 2,2′-bipyridine were prepared from technical grade reagents[11] by dilution with distilled water to the desired concentrations. Ethylenediamine was redistilled before use. Solutions were analyzed by titration with standard HCl solution. Copper(II) nitrate solutions were prepared from reagent grade salt and analyzed by electrodeposition. Experimental solutions were prepared by mixing the calculated volumes of stock solutions and, in the case of 2,2′-bipyridine solutions, heating gently until reaction was complete.

**Relaxation Time Measurements.**—$T_1$ and $T_2$ were determined by "spin-echo" methods as described in previous papers[3,5] and references cited there. For $T_2$ a 120-120° double-pulse method was used, with corrections for rectifier non-linearity. $T_1$ was obtained by a 90-90-90° triple-pulse recovery technique. Approximately 1-ml. samples of experimental solutions were sealed in *ca.* 1 cm. diameter Pyrex glass ampoules for measurement. All measurements were carried out at 27 ± 2°.

## Results and Discussion

Values of $T_1$ and $T_2$ for a number of 0.05 $M$ copper(II) solutions as functions of the en/Cu mole ratio are shown in Fig. 1. Those measurements were all made at a proton resonance frequency of 28 Mc./sec., where $\omega_S\tau_c > 1$, so that the observed dipolar relaxation times are reasonably well represented by the high frequency forms of equations 1 and 2. It is established in the following discussion that dependence of dipolar relaxation times on resonance frequency is very nearly the same for all solutions considered in these experiments.

In the interpretation of these data it must be remembered that of the several classes of protons present in the solutions those in water molecules are in great excess. Therefore, the proton relaxation times observed represent the water protons and others which undergo rapid exchange with the water protons. Ligand protons not undergoing rapid exchange, such as the C–H protons in ethylenediamine, are relaxed in times short compared to the observed times and were not detected in these experiments. At the higher concentrations of complexing agent some non-exchangeable protons were present in the excess reagent, but the total number was too small to affect appreciably the observed relaxation times.

It is now generally accepted that the copper(II) ion in aqueous solution is surrounded by six water

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[8] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[9] N. Bloembergen, *J. Chem. Phys.*, **27**, 572, 595 (1957).

[10] R. E. Connick and R. E. Poulson, *ibid.*, **30**, 759 (1959).

[11] Distillation Products Industries Division, Eastman Organic Chemicals, Rochester, N. Y.

molecules in a distorted octahedral array and that the hydrated ion thus formed moves to a large extent as a microcrystalline unit in the solution. Distortion of the octahedral microcrystal to tetragonal structure is said to occur as a result of stabilization through the Jahn–Teller effect,[12] so that two of the water molecules, *trans* to each other, are at a greater distance from the central atom than the other four. Formation of the ethylenediamine complexes occurs with substitution for the four planar water molecules until conversion to diaquobisethylenediaminecopper(II) is complete. In that ion the axial, or polar, water molecules are displaced outward from their positions in the hexaaquocopper(II) ion.[12] Subsequent reaction to form the tris complex requires the rearrangement of at least one of the planar ligands. From spectroscopic evidence, the trisethylenediaminecopper(II) ion is more nearly octahedral than the hexaaquocopper(II) ion, or any of the intermediate complexes. Stability constants for the three ethylenediaminecopper(II) complexes clearly support that sequence of structures: $\log K_1 = 10.72$, $\log K_2 = 9.31$, $\log K_3 = -0.90$[13] (measured at 25° in 1 $M$ $KNO_3$).

The first portions of the curves in Fig. 1 (en/Cu<2) reflect the replacement of water molecules in the coördination sphere by ethylenediamine molecules so that the value of $p$ in equations 1 and 2 decreases by a factor of 3. Taking account of the decrease of the magnetic moment of the central atom (from the static magnetic susceptibility, $\mu_s$) from 1.96 Bohr magnetons in hexaaquocopper(II) to 1.85$\beta$ in the bis complex[14] the predicted value of $T_1$ at en/Cu = 2 is 84 msec. If it is assumed that the Cu–$OH_2$ distances in the bis complex are approximately 6% greater than the average distance in hexaaquocopper(II) ion, the observed value of 120 msec. is obtained. From examination of the relaxation equations it is clear that the observed relaxation times are also dependent on the nuclear correlation time $\tau_c$ which may undergo change upon formation of the complex ion. The value $2 \times 10^{-11}$ sec. for hexaaquocopper(II) solutions[3] was arrived at in two ways: (1) from the low frequency limiting value of $T_1$, and (2) from the shape of the frequency dependence curve. Of these, the latter method is independent of the value of $p$ and permits comparison of data obtained for the several solutions of complex ions to determine whether or not a significant difference in $\tau_c$ occurs. $T_1$ values for four solution compositions at 28, 14, and 2.6 Mc./sec. are listed in Table I. Within experimental error these data are well fitted by a characteristic curve differing only in the absolute magnitudes of the relaxation times. Thus, it is reasonable to conclude that no very large change in $\tau_c$ occurs, and the tumbling times of the various ions in aqueous solution are not greatly different.

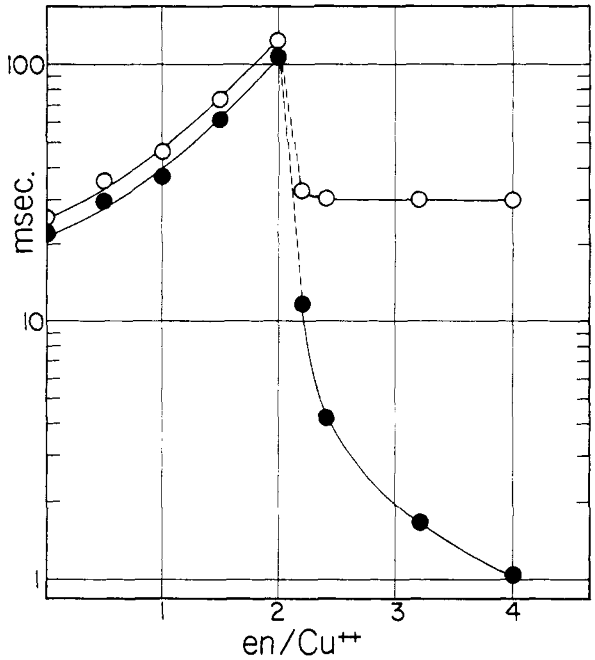

Fig. 1.—Effect of added ethylenediamine on the observed proton $T_1$, ○, and $T_2$, ●, in 0.050 $M$ copper(II) nitrate solutions at 27°; proton resonance frequency, 28 Mc./sec.

Implicit in the preceding interpretation is the assumption that proton exchange does not occur rapidly between ligand ethylenediamine molecules and water molecules in solution (slow compared to the observed relaxation times). At ethylenediamine concentrations required for en/Cu mole ratios greater than 2, reaction is no longer so nearly complete ($\log K_3 = -0.9$) and the concentration of free ethylenediamine in solution increases markedly as ethylenediamine is added. As a result, molecular exchange of ethylenediamine occurs more rapidly and leads to fast mixing of N–H and O–H protons. Thus, the value of $p$ increases to its original value and $T_1$ decreases to essentially the value observed for the *aquo* ions. Because of the previously noted decrease of $\mu_s$ from 1.96 to 1.85$\beta$ upon formation of the ethylenediamine complexes, the expected $T_1$ at high ethylenediamine concentrations is 28 msec. as compared to 29 msec. observed.

TABLE I

FREQUENCY DEPENDENCE OF $T_1$ IN 0.05 $M$ COPPER(II) SOLUTIONS

| Principal ionic species | 2.6 Mc./sec. | 14 Mc./sec. | 28 Mc./sec. |
|---|---|---|---|
| | $T_1$ (msec.) | | |
| $Cu(H_2O)_6^{++}$ | 12 | 18 | 26 |
| $Cu(en)(H_2O)_4^{++}$ | 22 | 34 | 43 |
| $Cu(en)_2(H_2O)_2^{++}$ | 54 | 82 | 120 |
| $Cu(en)_2(H_2O)_2^{++}$ + 0.02 $M$ en | 16 | 25 | 32 |

The decrease in $T_2$ at ethylenediamine concentrations in excess of that required for en/Cu = 2 is considerably greater than the corresponding decrease in $T_1$ and does not reach a constant value within the range of ethylenediamine concentrations used in these experiments. It is proposed that proton–electron spin exchange is the dominant contributor to transverse ($T_2$) relaxation of protons attached to nitrogen atoms within the coördination

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[12] L. E. Orgel, Proceedings 10th Solvay Congress, Brussels, 1956, p. 289.

[13] J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 307 (1948).

[14] C. D. Russell, G. R. Cooper and W. C. Vosburgh, THIS JOURNAL, **65**, 1301 (1943).

sphere of the diaquobisethylenediaminecopper(II) ion. If the appropriate correlation time for the spin exchange is the electron spin-lattice relaxation time, $\tau_s$ ($\tau_e = \tau_s$), and is of the order of $10^{-8}$ sec., then $\omega_s^2\tau_e^2 >> 1$ and $T_1$ is not affected (see equation 1). However, the extent to which isotropic spin exchange contributes to $T_2$ is determined by the value of $(A/h)^2p$, and may be quite great—sufficiently so that dipolar interaction becomes almost negligible by comparison. Thus, the transverse relaxation rate may be expected to be controlled primarily by the rate of chemical exchange of protons between bound amine groups and solvent water molecules over a rather wide range of ethylenediamine concentrations, the necessary conditions being

$$T_2(\mathrm{a}) > 1/k >> T_2(\mathrm{b})$$

in which $T_2(\mathrm{a})$ is the transverse relaxation time due to all mechanisms other than N–H proton exchange in the complex, $T_2(\mathrm{b})$ is the transverse relaxation time including spin exchange and assuming infinitely rapid exchange of protons between the complex and the solvent water, and $k$ is the first-order proton exchange rate constant. In the specified range

$$1/T_2(\text{obs.}) = 1/T_2(\mathrm{a}) + 1/T_2(\mathrm{c}) = 1/T_2(\mathrm{a}) + k$$

letting $T_2(\mathrm{C})$ = N–H proton exchange contribution to $T_2$(obs.).

Experimental results obtained at 28 Mc./sec. with a number of solutions of varying composition are given in Tables II and III. In the former, the data listed demonstrate the specific effect of ethylenediamine on the enhancement of relaxation rates in solutions comprising essentially diaquobisethylenediaminecopper(II) nitrate. Solutions were prepared by adding sufficient ethylenediamine to 0.05 $M$ copper(II) nitrate solutions to form the bis complex and then excess ethylenediamine, $NH_3$ or NaOH to obtain solutions of the specified $p$H. The results indicate clearly that effects noted for excess ethylenediamine cannot be attributed to basic hydrolysis alone but must depend specifically on the presence of ethylenediamine.[14a]

TABLE II

| Base | Total added, $M$ | $p$H | $T_1$ (msec.) | $T_2$ (msec.) |
|---|---|---|---|---|
| en | 0.02[a] | 11.1 | 30 | 4.1 |
| | .06[a] | 11.4 | 30 | 1.6 |
| | .10[a] | 11.6 | 30 | 1.0 |
| $NH_3$ | .04 | 10.7 | 106 | 33 |
| | .20 | 11.3 | 63 | 14 |
| | .40 | 11.4 | 51 | 8.4 |
| NaOH | .006 | 11.8 | 113 | 62 |
| | .01 | 12.0 | 90 | 50 |
| | .03 | 12.5 | 54 | 17 |

[a] In excess of that required for formation of the bis complex.

Values of $k$ are listed in column 7, Table III. $T_2(\mathrm{a})$ was evaluated in each case from $T_2$ (obs.) in solutions containing no ethylenediamine in excess of that required for formation of the bis complex.

TABLE III

PROTON EXCHANGE RATES (27°)

| $[Cu(en)_2(H_2O)_2^{++}]$, $M$ | $c_{en}$,[a] $M$ | $c_{HCl}$, $M$ | $p$H | [en][b] $M$ | $T_2$- (obs.) (msec.) | $k$ (sec.$^{-1}$) | $k'$ $M^{-1}$ sec.$^{-1}$ $\times 10^{-7}$ |
|---|---|---|---|---|---|---|---|
| 0.100 | 0.02 | .. | 11.1 | 0.018 | 3.1 | 310 | 1.9 |
| .100 | .06 | .. | 11.4 | .058 | 0.73 | 1350 | 2.6 |
| .100 | .10 | .. | 11.6 | .097 | 0.55 | 1800 | 2.1 |
| .075 | .02 | .. | 11.1 | .018 | 3.6 | 260 | 2.2 |
| .075 | .06 | .. | 11.4 | .058 | 1.0 | 990 | 2.5 |
| .075 | .10 | .. | 11.6 | .097 | 0.7 | 1420 | 2.2 |
| .050 | .02 | .. | 11.1 | .018 | 4.1 | 240 | 3.0 |
| .050 | .06 | .. | 11.4 | .058 | 1.6 | 620 | 2.4 |
| .050 | .10 | .. | 11.6 | .097 | 1.0 | 990 | 2.3 |
| .025 | .02 | .. | 11.1 | .018 | 7.0 | 140 | 3.5 |
| .025 | .06 | .. | 11.4 | .058 | 3.4 | 290 | 2.2 |
| .025 | .10 | .. | 11.6 | .097 | 1.8 | 550 | 2.6 |
| .050 | .053 | 0.00 | 11.1 | .049 | 2.3 | 430 | 1.9 |
| .050 | .053 | .02 | 10.2 | .033 | 3.4 | 290 | 1.9 |
| .050 | .053 | .05 | 8.8 | .0033 | 20 | 41 | 2.7 |
| | | | | | | Av. | 2.4 |

[a] Amount of ethylenediamine added in excess of that required for the bis complex. [b] Using $pK_1 = 7.40$, $pK_2 = 10.10$, from data listed in "Stability Constants, Part 1, Organic Ligands," The Chemical Society, London, 1957.

$$T_2(\mathrm{a}) = T_2\ (\text{obs. for en/Cu} = 2)$$

On the plausible assumption that the proton exchange rate

$$R = k(2)[H_2O]$$

conforms to a bimolecular rate law

$$R = k'[Cu(en)_2(H_2O)_2^{++}][en]$$

with rapid exchange occurring between N–H protons in free ethylenediamine and O–H protons in water, $k'$ was calculated for each solution composition and the results are listed in column 8, Table III. Agreement there is considered to be within the experimental error in $T_2(\mathrm{c})$.

The mean residence time for a proton in the coördination sphere of the diaquobisethylenediaminecopper(II) ion is given by

$$\tau_r = 8[Cu(en)_2(H_2O)_2^{++}]/R$$

For solutions containing 0.10 $M$ ethylenediamine excess, $\tau_r = 3 \times 10^{-6}$ sec. This value is somewhat larger than that assumed for $\tau_s$, so that the original assumption that the latter represents the effective $\tau_e$ is probably valid.

The value of $\tau_s$ for copper(II) acetylacetonate in dioxane solution has been estimated by McGarvey[15] to be about $2 \times 10^{-8}$ sec., an order of magnitude greater than that observed in ionic Tutton salts by Bagguley and Griffiths.[16] This increase was attributed to the stronger bonds between copper and its neighbors in the complex. Certainly a similar situation exists in the ethylenediamine complexes,[17] so that $\tau_s$ of the order of $10^{-8}$ sec. is entirely reasonable.

Recognizing that there are 8 N–H protons in the diaquobisethylenediaminecopper(II) ion and

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(14a) In accordance with a suggestion from Professor R. G. Pearson approximate values of the base hydrolysis constant $k_{OH} = k(2)[H_2O]/(8)[Cu(en)_2(H_2O)_2^{++}][OH^-]$ were calculated from the NaOH data of Table II. The individual values for the three concentrations listed were $3 \times 10^5$, $3 \times 10^5$, and $4 \times 10^5$ $M^{-1}$sec.$^{-1}$.

(15) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).

(16) D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Phys. Soc.* (*London*), **A65**, 594 (1952).

(17) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

assuming that all are active in the exchange process, an approximate limit may be set on the coupling frequency $A/h$. The shortest $T_2$ observed in 0.05 $M$ copper(II)–ethylenediamine solutions was 1.0 msec. At other concentrations the shortest times were equivalent to that value. Taking 1 msec. as the upper limit for the value of $T_2$ with very rapid exchange of protons between ligand $NH_2$ groups and solvent water and using equation 2 in the high frequency limit, the minimum value of $(A/h)^2\tau_e$ is $3 \times 10^4$ c.²/sec. Letting $\tau_e = 10^{-8}$ sec., the minimum value of $A/h$ is $1.7 \times 10^6$ c./sec. which is compatible with the concept of relatively strong Cu–N bonding in the ethylenediamine complexes.

The structure of 2,2′-bipyridine is similar to that of ethylenediamine except that there are no protons attached directly to N. If the isotropic spin exchange contribution to proton spin relaxation in solutions of copper(II)–ethylenediamine complexes is correctly attributed to exchange with ligand N–H protons, the effect should be totally absent in solutions of the copper(II)-2,2′-bipyridine complexes. Plots of $T_1$ and $T_2$ *vs.* bipy/Cu mole ratio are shown in Fig. 2. The behavior of both relaxation times is similar to that observed in the corresponding ethylenediamine systems at low concentrations of complexing agent, but deviate markedly in the higher concentration range. The continued rise in $T_1$ and $T_2$ reflects the fact that further complex formation simply results in the reduction of the number of water molecules in the coördination sphere. It is interesting to note that at bipy/Cu = 2 the observed $T_1$ (94 msec.) is much closer to the predicted value (84 msec.) than in the ethylenediamine case, suggesting that there is very little Cu–$OH_2$ bond lengthening in the diaquo-bis-2,2′-bipyridinecopper(II) ion relative to the hexaaquocopper(II) ion. If, as has been suggested from spectroscopic evidence,[18] the 2,2′-bipyridine complex is primarily in the *cis* rather than the *trans* form, little or no bond lengthening is to be expected. Over the entire range of 2,2′-bipyridine concentrations the $T_1/T_2$ ratio is very close to that expected for dipole–dipole interaction above the critical frequency region $(\omega_s^2\tau_c^2 > 1)$.

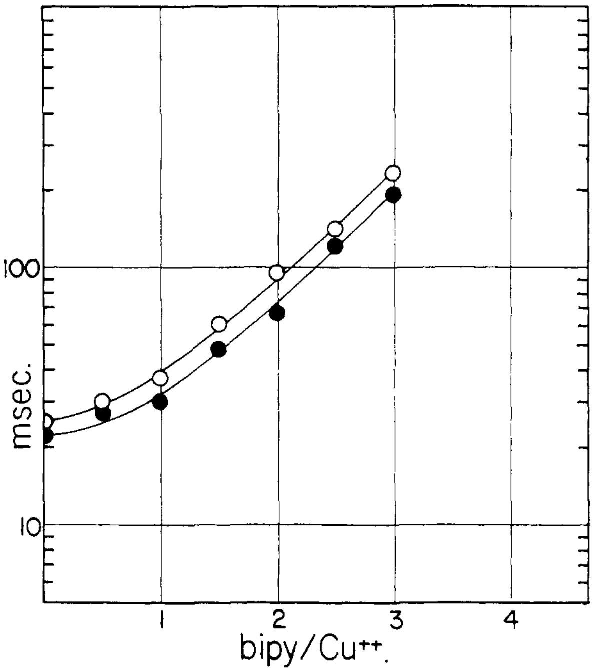

Fig. 2.—Effect of added 2,2′-bipyridine on the observed proton $T_1$, ○, and $T_2$, ●, in 0.050 $M$ copper(II) nitrate solutions at 27°; proton resonance frequency, 28 Mc./sec.

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AUSTIN, TEXAS

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[18] C. K. Jorgensen, Proceedings 10th Solvay Congress, Brussels, 1956, p. 355.