cies could result in the indicated dimeric cation. Because the systems reported in this paper were studied at 25°, it is not surprising that the reaction products were different from those obtained by Watt and Cude, who refluxed more concentrated and more acidic solutions for several hours at 100°.

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Bis(2-ethylhexyl)phosphoric Acid Exchange in Dilute Solutions of Copper(II) Complexes by Nuclear Magnetic Resonance Spectroscopy

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The temperature dependence for the exchange of bis(2-ethylhexyl)phosphoric acid with the copper(II) complex of this acid has been studied in trichloroethylene using nmr line-broadening techniques. The chemical-exchange rate constant is 8.8 × 10^6 sec^{-1} at 298°K (assuming two sites for relaxation of the acid hydrogen). The scalar coupling constant is 1.8 × 10^6 Hz. The spin–lattice relaxation time for the unpaired electron of the copper(II) complex is 4.9 × 10^{-7} sec.

Introduction

The ligand exchange of copper(II) complex ion systems has been studied by nuclear magnetic resonance (nmr) spectroscopy,[2–13] electron spin resonance (esr) spectroscopy,[8–10,13] ultrasonic relaxation,[14] polarography,[15,16] and isotopic dilution,[17–19] employing various ligands (H_2O,[2,3,6,8,9,13,14,19] NH_3,[5,7,17,18] F^-,[12] CH_3OH,[4] ethylenediamine,[2,7,9,10] alkyl-substituted ethylenediamines,[11] 2,2-dipyridine,[13] ethylenediaminetetraacetic acid,[15,16] and glycines[7]). In most cases only approximate values of limits for the rate constant could be given. The more reliable rate constants have been obtained from nmr and esr line widths. Most of the copper systems using nmr and esr were carried out in a temperature region where the line widths were dependent upon several relaxation mechanisms. In this study nmr techniques have been used to observe the chemical exchange of bis(2-ethylhexyl)phosphoric acid, HD2EHP, with the copper(II) complex ion of this acid without interference from other relaxation mechanisms.

When a ligand is coordinated to a paramagnetic metal complex ion, the spin–spin relaxation time, T_2, of hydrogen atoms near the metal center is decreased by the magnetic interaction between the hydrogen nuclei and the unpaired electrons. This decrease in T_2 measurably broadens the hydrogen line widths of the uncomplexed ligand. The line width at half its maximum amplitude, $\Delta\nu$, in hertz is related to T_2 by $1/T_2 = \pi\Delta\nu$. Two processes of relaxation contribute to T_2. The process which is independent of the presence of the paramagnetic ion will be designated $T_{2\mathrm{L}}$, and the process which is dependent on the presence of the paramagnetic ion will be designated $T_{2\mathrm{P}}$. If $T_{2\mathrm{L}}$ and $T_{2\mathrm{P}}$ are independent of each other, then for dilute solutions $1/T_2 = (1T_{2\mathrm{L}}) + (1/T_{2\mathrm{P}})$ and $T_{2\mathrm{P}}$ can be determined. For the limiting case of a dilute, single paramagnetic species causing only a small shift in the resonance frequency, it can be shown[6] that $T_{2\mathrm{P}}P_\mathrm{M} = T_{2\mathrm{M}} + \tau_\mathrm{M}$, where $T_{2\mathrm{M}}$ is the spin–spin relaxation time of the ligand hydrogens in the coordination sphere of the paramagnetic complex ion and P_M is a probability factor relating τ_M, the chemical-exchange lifetime of the ligand hydrogens in the metal coordination sphere, to τ_L, the chemical exchange lifetime of the uncomplexed ligand hydrogens. P_M is approximately equal to $m[\mathrm{M}]/l[\mathrm{L}]$, where l is the number of hydrogens in an uncomplexed ligand contributing to the observed resonance line, m is the number of these hydrogens subject to relaxation in a paramagnetic coordination sphere, [M] is the molar concentration of the paramagnetic ion, and [L] is the molar concentration of the uncomplexed ligand. Normally m/l is set equal to n, and this notation will be followed.

Because $T_{2\mathrm{M}}$ and τ_M differ in their temperature dependencies, there may be temperature regions where one will dominate. For the copper–D2EHP system, a temperature region was found where the ligand-exchange rate dominated the other relaxation mechanisms.

Experimental Section

A Varian A-60 spectrometer was used to record the magnetic resonance of the acid hydrogen ($\delta \sim 12$ ppm) of $(\mathrm{HD2EHP})_2$. Operating parameters such as radiofrequency field strength, filter band width, and sweep time were optimized so as not to

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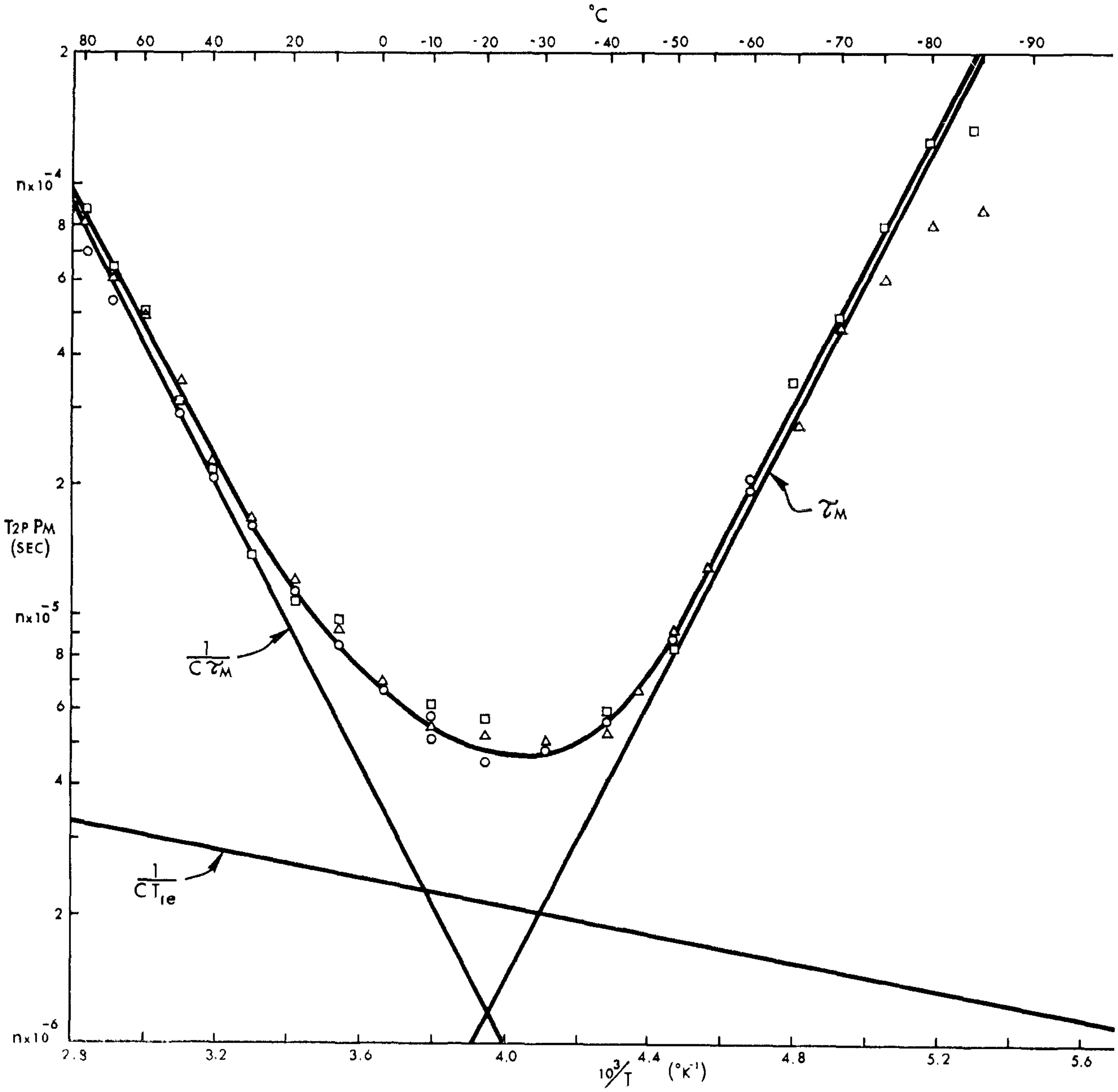

Figure 1.—Temperature dependence of $T_{2P}P_M$ for 0.5 M $(HD2EHP)_2$ with 1.0×10^{-4} M (○), 5.0×10^{-4} M (△), and 1.0×10^{-3} M (□) $Cu(D2EHP)_2$.

influence the resulting spectra. Temperature control was accomplished using a Varian Associates V-6031 variable-temperature probe and a V-6040 controller. Measurements were made from +80 to −80°.

Analytical reagent grade 1,1,2-trichloroethylene, $CHCl{=}CCl_2$, was used as the solvent because of the favorable position of its single resonance and because of the favorable temperature region between the melting and boiling points. The crystalline $Cu(D2EHP)_2$ used was prepared in this laboratory and was found to have a ratio of 1:2 for Cu to D2EHP. *Anal.* Calcd for $Cu(D2EHP)_2$: Cu, 9.10; C, 54.4; H, 9.64; P, 8.78; O, 18.14. Found: Cu, 9.23; C, 55.67; H, 8.85; P, 8.81; O, 17.70. The $(HD2EHP)_2$ was purified to approximately 98% by Victor Chemical Co.

In order to optimize line-width measurements throughout the temperature range of +80 to −80°, solutions of 1.0×10^{-4}, 5.0×10^{-4}, and 1.0×10^{-3} M $Cu(D2EHP)_2$ were used. In each solution, the concentration of the uncomplexed ligand as a dimer,[20] $(HD2EHP)_2$, was 0.500 M. TMS was added for an internal standard and for tuning the spectrometer. A solution of 0.500 M $(HD2EHP)_2$ in $CHCl{=}CCl_2$ was analyzed in the temperature range of interest in order to determine T_{2L}.

Results and Discussion

Figure 1 shows the temperature dependence of the T_{2P} process. The product of $T_{2P}P_M$ has been plotted in order to normalize the data obtained from the different solutions which varied in their concentration of $Cu(D2EHP)_2$.

The value of n is determined by m and l. From solvent extraction dependencies[21] in excess HD2EHP, it has been shown that two HD2EHP molecules are complexed to each $Cu(D2EHP)_2$. It is reasonable that acid hydrogen relaxation in the copper complex occurs at the site of these two HD2EHP molecules. Hence m equals 2. On each uncomplexed $(HD2EHP)_2$ dimer there are

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TABLE I

COMPARISON OF OBSERVED A/h AND T_{1e} WITH THE VALUES OF OTHER COMPLEXES

Complex	A/h(proton), Hz	T_{1e}, sec	Ref
Cu–HD2EHP system	1.8×10^6	4.9×10^{-7}	This study
$Cu(H_2O)_6^{2+}$	$(0.6–1.9) \times 10^5$		23
	1.5×10^5		24
		9.3×10^{-10}	8, 9
$Cu(NH_3)_6^{2+}$	-2.6×10^6		25
$K_2(Zn,Cu)(SO_4)_2 \cdot 6H_2O$		1.7×10^{-9}	8
$Cu(en)(H_2O)_4^{2+}$		2.3×10^{-9}	9
$Cu(en)_2(H_2O)_2^{2+}$	6.1×10^6	2.7×10^{-9}	9, 10
$Cu(en)_x^{2+}$	2.7×10^7	$(3–4) \times 10^{-8}$	10
$Cu(dipy)(H_2O)_4^{2+}$		1.6×10^{-9}	13
$Cu(dipy)_2(H_2O)_2^{2+}$		1.3×10^{-9}	13
$Cu(dipy)_3^{2+}$		1.0×10^{-9}	13

two acid hydrogens that can be relaxed by exchange into the copper complex. Hence l equals 2 and n equals 1.

Two prominent regions are observed in Figure 1: the 80 to 20° region and the −40 to −80° region. The 80 to 20° region is T_{2M} controlled since (1) $\Delta\omega_M$ is estimated to be very small from the chemical shift and also because an unreasonably high value of the scalar coupling constant would be required to explain a $\Delta\omega_M$-controlled region and (2) the negative slope would not correspond to a τ_M process. The −40 to −80° region is τ_M controlled since τ_M decreases with increasing temperature.

Of primary interest is the region from −40 to −80° which may be analyzed to determine the chemical kinetics of the exchange. In this region relaxation by the T_{2M} process is fast compared to the chemical exchange and τ_M is controlling the rate at which the ligand hydrogens may relax by the T_{2M} process. The reaction as carried out is pseudo first order, and $1/\tau_M$ can be equated to the pseudo-first-order rate constant. At 298°K, $1/\tau_M$ equals 8.8×10^6 sec^{-1}. From a fit of the Arrhenius equation to the temperature dependence of τ_M, the Arrhenius factor equals 3.4×10^{12} sec^{-1} and the energy of activation equals 7.6 kcal/mol.

Above −20° the chemical exchange is rapid compared to the T_{2M} process and the rate of relaxation becomes dependent on T_{2M}. Under the limiting conditions where dipole–dipole interaction can be neglected in comparison with contact hyperfine interaction and where the electron spin resonance frequency and the contact hyperfine correlation time, τ_e, are large

$$T_{2M} = [{}^1/_3S(S + 1)A^2/\hbar]^{-1}\tau_e^{-1}$$

where S is the copper spin quantum number and $A/\hbar$ is the scalar coupling constant.[22] Assuming that τ_e is determined by the interplay of only τ_M and T_{1e}, the spin–lattice relaxation time, then $1/\tau_e = (1/T_{1e}) + (1/\tau_M)$. In the 40 to 80° temperature region, $1/\tau_M > 1/T_{1e}$ and T_{2M} will be controlled by the interruption due to the chemical exchange. In Figure 1, $C = [{}^1/_3S(S + 1) \cdot A^2/\hbar]^{-1}$. The temperature dependence of T_{2P} in this region has the negative slope of the −40 to −80° region. This substantiates that the dominant relaxation process has been correctly assigned for each temperature region. From the relationship of T_{2M} as a function of τ_M only, the value of the scalar coupling constant can be determined. The absolute value of A/h is given in Table I and is compared with values[8–10,13,23–25] reported for other copper complex systems.

In the transition region between +40 and −40°, where T_{1e} is approximately equal to τ_M, the $1/\tau_M$ contribution can be subtracted from T_{2M} to give the $1/T_{1e}$ dependency. The value of T_{1e} at 298°K is given in Table I. Compared to the other reported values, T_{1e} is long. Experimentally, a shorter value of T_{1e} cannot be justified since τ_M very quickly dominates T_{2M} as the temperature increases. This means that τ_M must be smaller than T_{1e} and that T_{1e} could not be as short as 10^{-9} sec. If the principal electronic relaxation process is spin–rotational interaction[26] a very long correlation time could result from the massive ligands. The temperature dependence of T_{1e} in Figure 1 correlates with this interaction.

Below −70°, it is possible that the T_{2P} curve may be bending over because of a dipolar coupling mechanism that enhances the T_{2M} process[27] as the temperature is decreased. Evidence for the existence of this dipolar coupling cannot be strongly supported owing to nearly equal values of T_2 and T_{2L} and to a lack of accurate temperature control in this region.

Rates of ligand exchange for several copper complex systems are given in Table II. Owing to questionable interpretation of what is causing relaxation during the measurement, some of the rates listed may not be accurate since the temperature range was not always wide enough to characterize the chemical-exchange relaxation independent of other mechanisms.

The $(HD2EHP)_2$ α-hydrogen line is a triplet in the uncomplexed state. In the presence of copper it collapses to a singlet. Although the line was narrow under the conditions of this study, it appeared to follow the width of the acid hydrogen line at low temperatures. Assuming that the acid-hydrogen and the α-hydrogen line widths are varying in the same manner with temperature and concentration, then exchange of the entire HD2EHP molecule with the copper complex must be occurring. A proton-exchange mechanism might appear reasonable for exchange with the acid hydrogen,

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TABLE II

COMPARISON OF RATE CONSTANTS WITH THE VALUES OF OTHER SYSTEMS

System	k_1 or k_2	Temp, °K	E_a, kcal/mol	Ref
$Cu(D_2EHP)_2$ with HD2EHP	8.8×10^6 sec^{-1}	298	7.6	This study
$Cu(H_2O)_6^{2+}$ with H_2O	$>6 \times 10^5$ sec^{-1}			3
$Cu(NH_3)_4^{2+}$ with NH_3	$\sim 7 \times 10^6$ sec^{-1}	305		5
$Cu(NH_3)_4^{2+}$ with NH_3 in aqueous soln	$\geq 1.9 \times 10^7$ M^{-1} sec^{-1}	300	>4	7
$Cu(glyOH)_2^{2+}$ with ethylene glycol	$>1.1 \times 10^5$ sec^{-1}	300		7
$Cu(en)_2(H_2O)_2^{2+}$ with en in aqueous soln	3.0×10^6 M^{-1} sec^{-1}	300	4.8	2
	$k_{OH} = 2.6 \times 10^6$ M^{-1} sec^{-1}	300	7	7
	$k_{CH_2} = 1.8 \times 10^6$ M^{-1} sec^{-1}	300	7	7
	3.6×10^6 M^{-1} sec^{-1}	300		10
$Cu(en)_x^{2+}$ with en in concentrated en aqueous soln	2.6×10^8 sec^{-1}	300		10
$[Cu(gly)_2]$ with glycine in aqueous soln	$k_{OH} = 8.2 \times 10^6$ M^{-1} sec^{-1}	300	6	7
	$k_{CH_2} = 2.6 \times 10^6$ M^{-1} sec^{-1}	300	6	7
$[Cu(sar)_2]$ with sarcosine in aqueous soln	$k_{OH} = 6 \times 10^5$ M^{-1} sec^{-1}	300	7	7
$[Cu(N,N\text{-}(CH_3)_2gly)_2]$ with N,N-dimethylglycine in aqueous soln	$k_{CH_2} = 1.3 \times 10^4$ M^{-1} sec^{-1}	300	9.5	7

since protons are available (HD2EHP solutions are acidic) and since broadening and shifts of the acid hydrogen resonance are abserved in the absence of copper complex. However, a proton-exchange mechanism appears unreasonable for the α-hydrogen resonance since in the absence of the copper complex the α-hydrogen resonance contains all of its fine structure with no indication of shifts or broadening. Furthermore, the rate of proton exchange with the α hydrogen is expected to be not only different from the rate of proton exchange with the acid hydrogen but also even slower than nmr time limits.

In nonpolar organic solvents it is well known that HD2EHP is dimerized through hydrogen bonding[20] and that HD2EHP may exist in metal complexes as dimerized, bidentate ligands.[28,29] Since two extra HD2EHP molecules are complexed to each $Cu(D2EHP)_2$ in solutions containing excess HD2EHP,[21] it is reasonable to assume that two D2EHP–HD2EHP$^-$ bidentate ligands exist around the copper in a square-planar configuration. HD2EHP exchange occurs by attack on these bidentate ligands.

Since Cu(II) ions often have two additional, more distant neighbors forming a tetragonally distorted octahedron and since our crystal field interpretation of the visible spectra indicates that $Cu(D2EHP)_2$ in the crystalline state exists in a square-planar configuration which becomes a distorted octahedron upon solvation in excess HD2EHP, attack may initially occur at the weak axial position. Relaxation might occur in the axial position but Lewis, Alei, and Morgan[9] have shown for H_2O exchange on copper(II)–ethylenediamine that the unpaired electron exists in the equatorial orbitals and that nuclear–electron coupling at the axial position is negligible. If this is also true for the Cu–D2EHP system, then this mechanism should include a rearrangement to the equatorial position.

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