J. Am. Chem. Soc. **1986**, *108*, 3298–3303

NMR Proton Relaxation in Bimetallic Complexes of Zinc(II), Nickel(II), and Copper(II)

Charlotte Owens, Russell S. Drago,* Ivano Bertini, Claudio Luchinat, and Lucia Banci

Contribution from the Department of Chemistry, University of Florida. Gainesville, Florida 32611, and The Department of Chemistry, University of Florence, Florence, Italy.

Received August 30, 1985

Abstract: The metal complexes of 2,5-di(2-pyridyl)-3,4-diazahexa-2,4-diene (PMK) with formula $MM'(PMK)_3^{4+}$ (M and M′ being Zn^{2+}, Cu^{2+}, Ni^{2+}) have been investigated through magnetic susceptibility, EPR, and ^1H NMR. Magnetic coupling has been detected for $Ni_2(PMK)_3^{4+}$ through magnetic susceptibility measurements and its extent estimated, whereas in the case of $Cu(PMK)_3^{4+}$ magnetic coupling has only been barely detected through EPR spectroscopy. The ^1H NMR spectra have been investigated for all the complexes. For $MZn(PMK)_3^{4+}$, a σ spin delocalization is proposed for the moiety directly bound to the paramagnetic center whereas π spin polarization is found to be dominant in the moiety attached to zinc. When both ions are paramagnetic, the isotropic shifts are additive. Longitudinal nuclear relaxation rates T_1^{-1} are found to be dominated by the rotational correlation rates. When both ions are paramagnetic, nuclear T_1^{-1} are additive only for the case of $Cu_2(PMK)_3^{4+}$ for which very weak magnetic coupling is proposed. For $Ni_2(PMK)_3^{4+}$ and $CuNi(PMK)_3^{4+}$, some theoretical considerations allow us to account for the essential features of nuclear relaxation.

The synergistic interactions evident in molecules containing two or more metals have spurred considerable interest in obtaining fundamental information concerning the various ways in which this synergism can occur. The potential application of these concepts in catalysis and in understanding biological systems has provided additional impetus to investigations in this area. Recently, it has been shown that some very interesting changes in the electronic properties of metals in polymetallic metalloenzymes can occur. The substitution of zinc(II) in bovine erythrocyte superoxide dismutase by cobalt(II) leads to an observation of contact shifted resonances of the portion of the enzyme bound to copper.[1] The rapidly relaxing electron spin of cobalt(II) has shortened the electronic relaxation time of copper(II), making the detection of the NMR possible. In the ferredoxin systems,[2] the partially reduced iron(II),(III) ferrodoxin is found to result in the observation of NMR lines for the ligands bound to high-spin iron(III), a system that normally gives broad resonances for coordinated ligands. The potential use of partial metal substitution to permit NMR investigation of the ligand environment around metals with long electron spin lifetimes has many important applications and the process should be understood in detail.

This article reports the results of a detailed study of the proton NMR spectrum of bimetallic complexes containing weakly interacting metal ions. We chose as a system the bimetallic complexes of [2,5-di(2-pyridyl)-3,4-diazahexa-2,4-diene], $MM'(PMK)_3^{4+}$. Earlier studies[3] have shown the metals to be weakly interacting and to possess the necessary solubility for carrying out these measurements. The structure[4] has been determined for the dicobalt complex, and the ligand rigidity simplifies the problem of rotational correlation time estimates.

Experimental Section

A. Synthesis. The ligand is prepared by the reported procedure[3] and the complexes[3-5] made by dissolving stoichiometric amounts of metal nitrates together in a minimum of water and adding the ligand to the magnetically stirred solution. The water-insoluble ligand dissolves as the soluble complex forms; after a few minutes, a few drops of acetone are added to dissolve any remaining unreacted ligand. After a half hour of stirring, acetone is added to the solution until the complexes precipitate, then the solid product is filtered and put in a desiccator. The predominantly copper complexes are too soluble in water to precipitate even with a large amount of acetone, so they are prepared in methanol, with the ligand and metal nitrates dissolved separately. The ligand solution is then added slowly to the metal ions. The product forms and precipitates immediately. The green copper complex forms and is filtered after a half hour and then washed with acetone. The methanol filtrate is quite dark. This is consistent with the decomposition behavior seen by O'Connor and co-workers;[5] indeed, refluxing of a dark methanol solution, formed from a 1:1 ratio of ligand to copper ion, leads to the formation of the blue-green $Cu(PMK)(NO_3)_2$. Reactions were carried out on a scale to make about one-half millimole of product.

The mixed-metal complexes, which cannot be made purely, are made by the aqueous solution procedure described above from the metal nitrates in the desired ratio. The resulting samples are a mixture of the two homo-binuclear complexes with the mixed-metal complex. The nickel complexes are difficult to obtain pure and often contain impurity peaks in the NMR. The best sample, obtained when a larger amount of water than usual is used in the preparation, is used for NMR and magnetic studies.

B. NMR. The ^1H NMR spectra and ^1H T_1 values are measured on an NIT 360 Fourier transform instrument, capable of a total frequency range of over 200 ppm. In the creation of the spectrum, no base line smoothing is done, lest very broad peaks be "created" or obliterated. Apparently, because of the broad ranges used and the weakness of some of the very quickly relaxing signals, a very broad (~100 ppm) *roll* in the base line is visible. This might be due[6] to the timing of the gate (the dead time between the pulse and the start of acquisition) being significant compared to the very short pulses used. For some data, the gate time was altered so that the sum of the times is appropriate, but this had no effect.

The T_1 values are obtained with use of an inversion recovery method of a 5-pulse sequence. This sequence has the great advantage[7] of making the same field felt over a broad frequency range, so that the T_1 values could be obtained from one sequence on the entire spectra of all the complexes reported. The pulse lengths are determined by finding the length of the 360° pulse (slight dispersion) of the HDO peak and the center frequency is set near the center of the spectrum but not on a peak. Samples are deoxygenated.

The T_1 values are calculated by fitting a 3-parameter equation in exponential form to the data obtained. Test τ values for the inversion recovery experiment[7] are chosen to range from much less than the T_1 of the fastest relaxing peak to much longer than the T_1 of the slowest relaxing peak of interest, and the T_1 spectra were run at delay times between the pulses chosen run in a jumbled order, in an effort to reduce systematic time-dependent errors. T_2 values are estimated from the peak half-widths.

---

* University of Florida.

(1) Bertini, I.; Lanini, G.; Luchinat, C.; Messori, L.; Monnanni, R.; Scozzafava, A. *J. Am. Chem. Soc.* **1985**, *107*, 4391.

(2) (a) Dunham, W. R.; Palmer, G.; Sands, R. H.; Bearden, A. J. *Biochim. Biophys. Acta* **1971**, *253*, 373. (b) Bertini, I.; Lanini, G.; Luchinat, C. *Inorg. Chem.* **1984**, *23*, 2723.

(3) Dei, A.; Gatteschi, D.; Piergentili, E. *Inorg. Chem.* **1979**, *18*, 89. Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1982**, *21*, 1284.

(4) Boyd, P. D. W.; Gerlock, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1974**, 1097.

(5) O'Connor, C. J.; Romananch, R. J.; Robertson, M.; Eduok, E.; Fronczek, F. R. *Inorg. Chem.* **1983**, *22*, 449.

(6) Hoult, D. I.; Chen, C. N.; Eden, H.; Eden, M. *J. Magn. Reson.* **1983**, *51*, 110.

(7) Levitt, M. H. *J. Magn. Reson.* **1982**, *50*, 95.

0002-7863/86/1508-3298$01.50/0

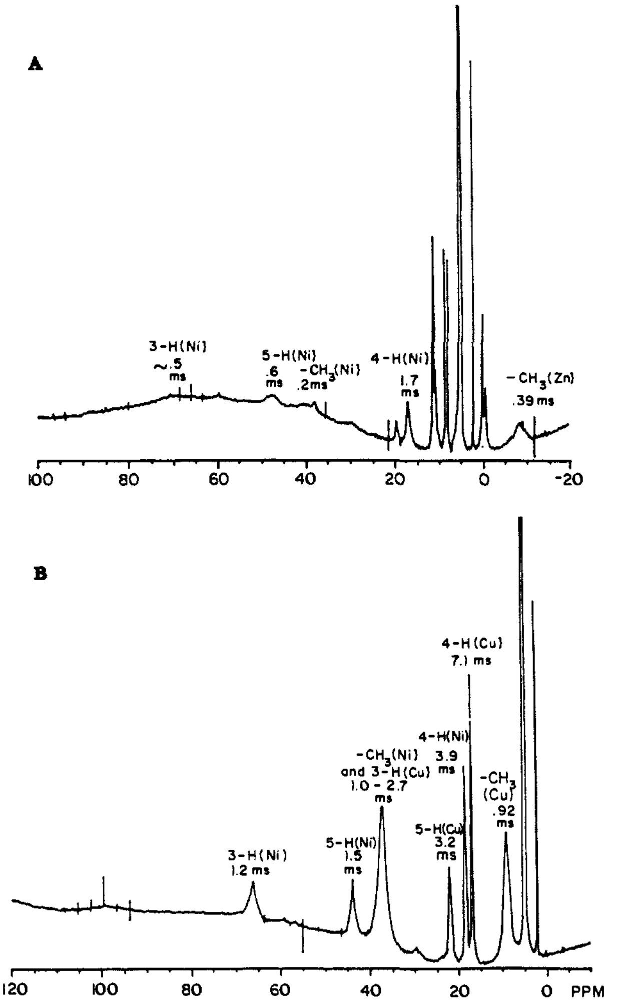

Figure 1. Proton NMR spectra showing the peak assignments: (A) $ZnNi(PMK)_3NO_3$, (B) $CuNi(PMK)_3(NO_3)_3$.

C. EPR Spectra. Several X-band EPR instruments and cavities were used. Because of the width of the signals, the instrument base line was often a problem; few cavities have a flat base line over large field ranges at powers of 15 mW and high modulation amplitude. The room temperature spectra were obtained in an aqueous cell on a Varian E-9 X-band EPR; the solutions were roughly 2 × 10^{-3} M in the species of interest. Because of decomposition, especially $Cu_2(PMK)_3(NO_3)_4$, the samples were dissolved immediately before the spectra were run.

The frozen samples were dissolved in a mixture of approximately a 3:2 volume ratio of glycerol and water and then frozen and subjected to about 3 freeze–pump thaw cycles. For 130 K, the samples were run on a Bruker X-band instrument with automatic temperature control.

A sample of DPPH in salt (g = 2.0037) was used to calibrate the center of the field, and the linearity of the field was checked by finding DPPH at different field values for the center of the spectrum, while keeping constant the sweep range.

D. Magnetic Susceptibiltiy. Bulk magnetization data from 5 to 200 K were measured on a SQUID magnetometer, which provides those data directly; a calibration curve of the sample holder was used for the base line.

Results

Table I contains a summary of the results from the NMR studies of the bimetallic system. The isotropic shifts relative to $Zn_2(PMK)_3^{4+}$ are reported along with the proton T_1 values, T_2 values, and the ratio of T_1/T_2. Representative spectra are shown in Figure 1. Spectra of the complexes were run in varying mixtures (10^{-2} to 10^{-3} M) of $M_2(PMK)_3^{4+}$ plus $ZnM(PMK)_3^{4+}$ or $MM'(PMK)_3^{4+}$. The T_1's for the complexes were found to be insensitive to these changes in environment.

Room temperature EPR spectra could only be obtained on samples of $ZnCu(PMK)_3^{4+}$ and $Cu_2(PMK)_3^{4+}$. Samples of the mixed-metal complexes cannot be made pure. Even those made from a 1 to 9 ratio of copper nitrate to nickel nitrate contained features of $Cu_2(PMK)_3^{4+}$ in the EPR spectra.

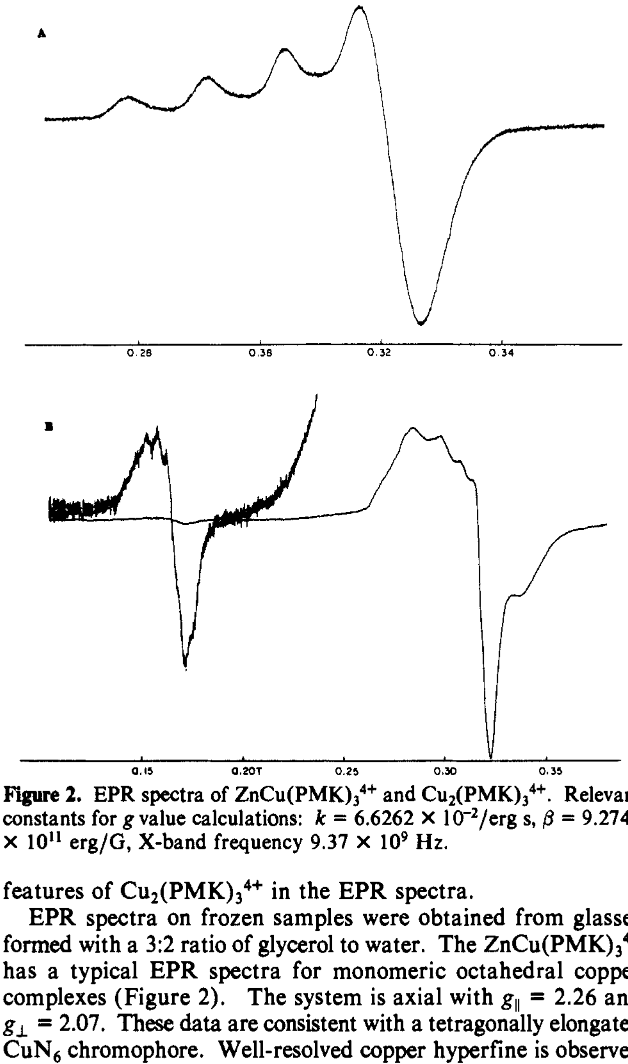

Figure 2. EPR spectra of $ZnCu(PMK)_3^{4+}$ and $Cu_2(PMK)_3^{4+}$. Relevant constants for g value calculations: $k = 6.6262 \times 10^{-2}$/erg s, $\beta = 9.2741 \times 10^{11}$ erg/G, X-band frequency 9.37×10^9 Hz.

EPR spectra on frozen samples were obtained from glasses formed with a 3:2 ratio of glycerol to water. The $ZnCu(PMK)_3^{4+}$ has a typical EPR spectra for monomeric octahedral copper complexes (Figure 2). The system is axial with $g_{\parallel} = 2.26$ and $g_{\perp} = 2.07$. These data are consistent with a tetragonally elongated CuN_6 chromophore. Well-resolved copper hyperfine is observed in the parallel region. The A value of 137 × 10^{-4} cm^{-1} agrees well with one measured from the powder EPR spectrum of a doped sample [0.01 $CuZn(PMK)_3(NO_3)_4$].

The spectrum of $Cu_2(PMK)_3^{4+}$ at 130 K is characteristic of two copper(II) ions (Figure 2) undergoing spin–spin interactions. The most striking feature is the half-field, $\Delta m_s = 2$, transition centered at 0.165 T. The broad features between 0.270 and 0.337 T can be interpreted on the basis of weakly coupled dimeric copper(II) complexes. As suggested to us,[8] the relative intensities of the half-field and allowed transitions are consistent with the 0.38-nm distance found between the two metal centers of $Co_2(PMK)_3^{4+}$ by X-ray diffraction. The EPR spectrum of $NiCu(PMK)_3^{4+}$ cannot be detected at room temperature but exhibits a broad featureless peak at liquid-nitrogen temperature.

Variable-temperature magnetic data from liquid-helium temperatures were collected on a SQUID magnetometer. Because the heterobimetallic complexes cannot be made purely, only the homobimetallic complexes were examined. The bis-zinc complex, diamagnetic, as expected, has negative values of χ at all temperatures, ranging from -6.0×10^{-1} m^3 mol^{-1} at 150 K and above down to -2.1×10^{-1} m^3 mol^{-1} at 5 K. For the other complexes, a χ_d of -3.0×10^{-1} m^3 mol^{-1} per mol % Zn^{2+} is used as the diamagnetic correction. The bis-copper complex exhibits Curie–Weiss behavior, having a linear plot of $1/\chi$ vs. T with a correlation coefficient of 0.99999 and $\theta = -1.352$, as defined by $1/\chi = mT + \theta$. Over the range from 5.67 to 296 K, the effective magnetic moment varied from 1.8 to 1.9 μ_B.

Much more dramatic is the behavior of the bis-nickel complex (Figure 3), which exhibits antiferromagnetic behavior. From room

---

[8] Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

Table I. NMR Results on $M_2(PMK)_3^{4+}$ Complexes[a]

Zn_2	3-H(Zn)	4-H(Zn)	5-H(Zn)	6-H(Zn)	$-CH_3$(Zn)					
HDO_{Rt}(4.80p)	d, 8.32p	tr, 8.48	tr, 7.99	d, 8.67	2.05					
^{1}H T_1's (s)	1.34[c]	1.17	1.15	1.07	1.05					
T_2 (ms)	106									
ZnCu	3-H(Cu)	4-H(Cu)	5-H(Cu)	6-H(Cu)	$-CH_3$(Cu)	3-(Zn)	4-H(Zn)	5-H(Zn)	6-H(Zn)	$-CH_3$(Zn)
isotropic shifts (ppm)	39.68	5.68	23.43	not seen	17.26	−4.19	1.31	−3.67	0.87	−3.55
^{1}H T_1's (ms)		4.26 ± 0.05	1.90 ± 0.2		0.83 ± 0.02	8.50 ± 0.7	23.1 ± 0.5	15.6 ± 1.5	8.26 ± 0.2	1.41 ± 0.02
T_2 (ms)	0.18 ± 0.015	2.05 ± 0.15	0.30 ± 0.01		0.33 ± 0.01	3.7 ± 0.15	9.1 ± 0.85	6.9 ± 0.3	4.7 ± 0.3	0.95 ± 0.025
calcd τ_c (s)		1.3×10^{-10}	1.5×10^{-10}			1.0×10^{-10}	1.8×10^{-10}	3.0×10^{-10}	1.7×10^{-10}	
ZnNi	3-H(Ni)	4-H(Ni)	5-H(Ni)		$-CH_3$(Ni)	3-H(Zn)	4-H(Zn)	5-H(Zn)	6-H(Zn)	$-CH_3$(Zn)
isotropic shifts (ppm)	62.98	8.54	40.29		39.23	−9.15	2.76	−8.07	2.11	−10.51
$^1HT_1$'s (ms)	0.5 ± 0.1	1.7 ± 0.01	0.614 ± 0.04		0.17 ± 0.01	2.7 ± 0.1	8.5 ± 0.6	7.2 ± 0.5	3.2 ± 0.1	0.39
T_2 (ms)	0.19 ± 0.01	1.2 ± 0.04	0.31 ± 0.03		0.25 ± 0.015	1.9 ± 0.2	5.3 ± 0.8	3.5 ± 0.3	2.0 ± 0.3	0.35 ± 0.03
T_1/T_2	~2.5	1.4	2.0		0.7	1.4	1.6	2.0	1.6	1.1
calcd τ_c (s)	1.5×10^{-10}	1.2×10^{-10}	1.8×10^{-10}			1.3×10^{-10}	1.8×10^{-10}	2.0×10^{-10}	1.6×10^{-10}	
Ni_2	3-H(Ni)	4-H(Ni)	5-H(Ni)	6-H(Ni)	$-CH_3$(Ni)					
isotropic shifts (ppm)	51.54	11.11	30.07		27.84					
T_1 (ms)	0.91 ± 0.04	2.49 ± 0.03	1.11 ± 0.03		0.41 ± 0.01					
T_2 (ms)	0.42 ± 0.015	1.73 ± 0.04	0.71 ± 0.04		0.30 ± 0.01					
T_1/T_2	2.2	1.4	1.6		1.4					
calcd τ										
uncoupled (s)	1.3×10^{-10}	1.5×10^{-10}	1.9×19^{-10}							
Cu_2	3-H(Cu)	4-H(Cu)	5-H(Cu)	6-H(Cu)	$-CH_3$(Cu)					
isotropic shifts (ppm)	35.38	7.05	19.41		14.71					
T_1 (ms)	1.38 ± 0.08	3.53 ± 0.14	1.82 ± 0.08		0.78 ± 0.02					
T_2 (ms)	0.31 ± 0.04	1.72 ± 0.1	0.78 ± 0.06		0.56 ± 0.02					
T_1/T_2	4.4	2.1	2.3		1.4					
calcd τ										
uncoupled (s)	1.2×10^{-10}	1.4×10^{-10}	1.4×10^{-10}							
coupled (s)	3.3×10^{-10}	4.9×10^{-10}	5.5×10^{-10}							
NiCu	3-H(Ni)	4-H(Ni)	5-H(Ni)	6-H(Ni)	$-CH_3$(Ni)	3-H(Cu)	4-H(Cu)	5-H(Cu)	6-H(Cu)	$-CH_3$(Cu)
isotropic shifts (ppm)	57.73	9.70	35.41		34.77	28.50	8.29	13.83		6.67
T_1 (ms)	1.18 ± 0.06	3.93 ± 0.04	1.54 ± 0.08		1–2.7[b]	1–2.7[b]	7.13 ± 0.07	3.19		0.92 ± 0.06
T_2 (ms)	0.545 ± 0.015	2.49 ± 0.08	0.85 ± 0.035				3.62 ± 0.2	1.27 ± 0.08		0.68 ± 0.015
T_1/T_2	2.2	1.6	1.8				2.0	2.5		1.4
calcd τ										
uncoupoled (s)	5.3×10^{-11}	4.7×10^{-11}	6.2×10^{-11}				5.2×10^{-11}	6.8×10^{-11}		
coupled (s)	7.1×10^{-11}	6.2×10^{-11}	8.2×10^{-11}				1.1×10^{-10}	1.6×10^{-10}		

[a] All shifts are with respect to $Zn_2(PMK)_3$ (except those of Zn_2PMK itself, which are set with respect to HDO at 4.82 ppm). Positive shifts are downfield. The symbols d and tr refer to doublet and triplet, respectively. [b] Direct overlap. $^1HT_1$'s = $\{([1/T_1(\text{exptl})] - [1/T_1(Zn_2PMK)]\}^{-1}$ and are in ms, except $Zn_2(PMK)_3$ values. $T_2 = 1/\pi$ (fwhm in Hz). T_1's and T_2's are in units of time per radian. [c] One peak of doublets.

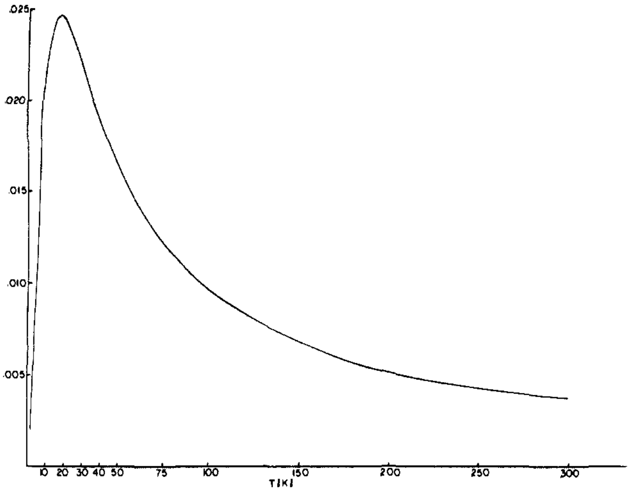

Figure 3. Temperature-dependent magnetic susceptibility, $\chi_p = \chi$ (per mol of Ni^{2+}) $- \chi_d$, where $\chi_d = -2.4 \times 10^{-4}$.

temperature downward, the magnetization rises to a maximum at 17.5 K and then falls rapidly with decreasing temperature. At 298 K, μ_{eff} is 2.9 μ_B. The curve can be reproduced by assuming an antiferromagnetic coupling between two $S = 1$ centers. This provides an estimate of an isotropic J value of 11.8 cm^{-1}.

Discussion

Structural Considerations. The X-ray crystal structure of the tris(μ-[2,5-di(2-pyridyl)-3,4-diazahexa-2,4-diene])dicobalt(II), $Co_2(PMK)_3^{4+}$, has been reported[4] as the $ZnCl_4^{2-}$ and $Zn(H_2O)Cl_3^-$ salts with water of hydration: The complex can be visualized as a triple helix of ligands around a pole of two metal ions. Because the crystal was grown slowly from an evaporating aqueous solution containing a fourfold excess of potassium chloride and zinc chloride, metal ion exchange was certainly possible, so the crystal could have also contained the cobalt–zinc and dizinc complexes. We shall assume this structure for all of the $M_2(PMK)_3^{4+}$ complexes.

The ligands which provide N_6 sites for the metal ions are reported to be too strained for the sites to be octahedral or trigonal antiprismatic. In a true trigonal antiprism, a site's triangle of pyridine nitrogen atoms would be 60° away from an eclipsed position with the triangle of bridging nitrogen atoms; in the determined structure, the triangles are 42.5° away from the eclipsed position, hence 17.5° from the true antiprism. The ligands are twisted around the N–N bond, but not nearly as much as if only one PMK ligand were in the complexes: The planes formed by the cobalt ions and one of the ligand's two bridging nitrogen atoms have an average dihedral angle of 44° in this structure, while in a structure of $Cu_2(PMK)Cl_4$, in which only one ligand chelates to the two ions,[5] the dihedral angle is 70.8°. The methyl groups are very important to the rigidity of the cation's structure, in that the complexes are more stable to hydrolysis than their analogues made from pyridine aldehyde azine, which begin to hydrolyze rapidly.

The average distances[9] from the metal, $M(2)$, to the protons for the three ligands in the complex are contained in brackets in Figure 4. The numbering scheme used to label the protons are indicated in parentheses. The distances indicated from the metal to the methyl groups are the metal–carbon distances.

The 3:2 stoichiometry of the complexes studied is supported by elemental analysis, and the composition in solution is supported by the NMR spectra, which show five (or fewer) peaks for the pure homobimetallic complexes, indicating the protons on both ends of the ligand are in similar environments. The NMR spectra of the mixed-metal complexes also provide ample support that each ligand is bound to metal ions; when two types of metal ions are in solution more than the five peaks of the pure complexes are seen, and they can be assigned well by adding the contributions to the shift from M–Zn to produce M–M or from M–Zn and Zn–M′ to produce M–M′. This additivity gives strong support for the binuclear nature of the complexes, but also for the similarity of stoichiometry and structure for all the complexes. In order for the effect of the metal ions on the shifts to be additive, the metal ion must be transferring similar amounts of unpaired electron density into similar orbitals and also causing similar dipolar effects.

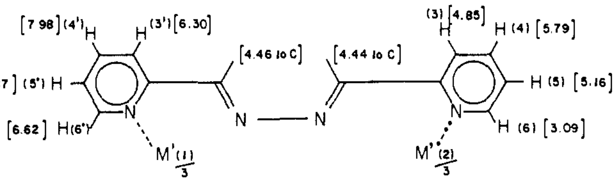

Figure 4. Average distances from the ring protons and methyl carbon to the metal, M(2). The metal M(1) in the general formula M(1)M(2)$(PMK)_3^{4+}$ will be that with the smallest value of S. The 3 and 3′ protons, for example, will be distinguished in the text by indicating the closest metal.

Interpretation of the T_1 Values in $ZnM(PMK)_3(NO_3)_4$ (where M = Zn, Cu, Ni). Figure 1 illustrates a sample NMR spectra of the ZnNi complex studied along with the peak assignment and the measured T_1 values. The peak assignments in these complexes can be made on the basis of the shifts and the relaxation times. As expected for protons in a paramagnetic environment, the peaks are shifted relative to the diamagnetic $Zn_2(PMK)_3^{4+}$ analogue and the T_1's are much shorter (~1 s for $Zn_2(PMK)_2^{4+}$ and milliseconds for the paramagnetic complexes). A decrease in the magnitude of the isotropic shift as one moves away from the metal indicates σ delocalization in the half of the molecule bound to the paramagnetic center, while alternation of the isotropic shift indicates spin polarization of spin density into the π system in the half of the ligand system bound to zinc. Shifts assigned in this way for a $ZnM(PMK)_3^{4+}$ complex (where M is a paramagnetic ion) can be added (e.g., 3H + 3H′, etc.) to produce the shift in the homobimetallic complex $M_2(PMK)_3^{4+}$, and good agreement with experiment results. The 4-H and 6-H protons around zinc are shifted downfield while the 3-H and 5-H protons are shifted upfield. Within each of the two sets of peaks one relaxes much faster than the other. On the basis of their shorter distances to the Cu(II) or Ni(II) ion, the faster relaxing peaks are assigned to the 3-H and 6-H proton. All of the assignments in the paramagnetic complexes are confirmed from the T_1 values by assuming a τ_s dependence (see later). It should be noted that the high magnetic field, by increasing the separation of the signals but not the line width, permits the recording of ^1H NMR spectra of a copper(II) complex as well as of a dicopper(II) complex. These are the best NMR spectra of the few copper(II) systems reported.

The principal contribution to proton T_1 relaxation in these systems is dipolar in nature.[10] Some contact contribution[11] can be operative in determining T_2 in copper(II) systems.[12] Indeed the T_2 values parallel the T_1 values except for copper-containing systems and for those signals experiencing large isotropic shifts. Also, the slightly shorter values of T_2 generally observed are possibly due to the fact that at 360 MHz even the dipolar contributions to T_1 and T_2 start to differ for correlation times of the order of 10^{-10} s (see below).

The dipolar contribution to longitudinal relaxation is given by the Solomon equation[10]

$$T_{1M}^{-1} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_N^2 g_e^2 \mu_B^2 S(S+1)}{r^6}\left(\frac{7\tau_c}{1+\omega_s^2\tau_c^2}+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right) \tag{1}$$

where μ_0 is the permeability of vacuum and $\mu_0/4\pi = 10^{-7}$ H m^{-1}.

---

(9) These distances are calculated from the reported crystal structure.

(10) Solomon, I. *Phys. Rev.* **1955**, *99*, 599.

(11) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 572.

(12) Espersen, W. G.; Martin, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 40.

For the proton, the constants $(2/15)(\mu_0/4\pi)^2\gamma_N{}^2g_e{}^2\mu_B{}^2$ have the value 3.29×10^{-44} m^6 s^{-2}. S is the spin quantum number, r is the distance from the metal center to the proton, and ω_S and ω_I are the transition frequencies for the electron and nucleus, respectively. This equation serves as the basis for interpreting T_1 values in paramagnetic systems where dipolar relaxation is the dominant effect.

The correlation time τ_c in eq 1 and 2 is the reciprocal of rate constant τ_c^{-1} for a first-order process. This overall rate τ_c^{-1} is the sum of rates for a number of different processes

$$\tau_c^{-1} = \tau_S^{-1} + \tau_r^{-1} + \tau_M^{-1} \qquad (2)$$

where τ_S^{-1} is the electron spin relaxation rate, τ_r^{-1} the rotational correlation rate, and τ_M^{-1} a ligand exchange rate with bulk solvent. In this system, τ_M is of no consequence and τ_r can be estimated from the Stokes–Einstein equation[13]

$$\tau_r = \frac{4\pi\eta a^3}{3kT} \qquad (3)$$

where η is the solvent viscosity and a the radius of the molecule. Using an average 5-H to 5-H′ distance of 1.28 nm from the crystal structure and a twist angle of 17°, one calculates the length of the molecule as 1.22 nm. Substituting a radius of 0.61 nm into eq 3 leads to a τ_r value of 2.2×10^{-10} s or a value of τ_r^{-1} of 4.5×10^9 s^{-1}.

Substituting the T_1^{-1} values for $ZnCu(PMK)_3{}^{4+}$ into eq 1, along with the distances in Figure 1, and values of $\omega_I = 2.26 \times 10^9$ rad s^{-1} and $\omega_S = 1.49 \times 10^{12}$ rad s^{-1}, the τ_c values reported in Table I are obtained. The excellent agreement between the various values of τ_c calculated by using the different proton T_1 values in the molecule is strong support for our assignment of the peaks in the spectrum. Considering that we used spherical approximation for a cylindrical molecule with anisotropic rotational correlation times in calculating τ_r by eq 3, the excellent agreement between this calculated value of $\tau_r = 2.2 \times 10^{-10}$ s (which is probably the upper limit because we have chosen the longest molecular axis) and the average value of $\tau_c = 1.7 \times 10^{-10}$ s for $ZnCu(PMK)_3{}^{4+}$ indicates that T_1 is being dominated by the rotational correlation time. This is a reasonable conclusion, for typical τ_S values for copper(II) are around 3×10^{-9} s. Thus, τ_S^{-1} is small compared to τ_r^{-1} in eq 3 and the τ_c value in eq 1 is essentially τ_r.

A similar analysis of $ZnNi(PMK)_3{}^{4+}$ produces the τ_c values reported in Table I when the different proton T_1 values are substituted into eq 1. An average value of $\tau_c = 1.6 \times 10^{-10}$ s results and again we conclude that the T_1 values in this system are dominated by τ_r with τ_S making a negligible contribution. This long lower limit for τ_S is due to the large magnetic field. NMR measurements[14-16] at variable magnetic field indicate that τ_S increases with magnetic field above 50–100 MHz. The absence of a detectable EPR for this complex is attributed to a zero-field splitting that is large compared to microwave energies.

Interpretation of the T_1 Values in $Cu_2(PMK)_3(NO_3)_4$ and $Ni_2(PMK)_3(NO_3)_4$. This series of complexes introduces the additional complication of metal–metal coupling into the calculation of T_1. If one assumes that the metals are uncoupled, the T_1^{-1} value at any one proton (e.g. 5-H in Cu-Cu) should be given by the sum of the two T_1 values for that proton position in the Zn–M–$(PMK)_3{}^{4+}$ complex (e.g., 5′-H(Cu–Zn) + 5-H(Cu–Zn)). This corresponds to calculating τ_c from

$$T_1^{-1} = K_{Cu}\left(\frac{1}{r^3} + \frac{1}{r'^6}\right)f(\tau_c) \qquad (4)$$

Table II. x_1 and x_2 Coefficients Calculated for $M_1 - M_2$ Exchange—Coupled Pairs According to Equation A3

	X_2 / X_1	5/2	2	3/2	1	1/2
S_1	1/2	17/18 19/54	23/25 9/25	7/8 3/8	7/9 11/27	1/2 1/2
	1	$\frac{1049}{1225}$ $\frac{13}{35}$	$\frac{43}{54}$ $\frac{7}{18}$	$\frac{467}{675}$ $\frac{19}{45}$	1/2 1/2	
	3/2	$\frac{107}{144}$ $\frac{173}{432}$	$\frac{113}{175}$ $\frac{379}{875}$	1/2 1/2		
	2	$\frac{102031}{165375}$ $\frac{6257}{14175}$	1/2 1/2			
	5/2	1/2 1/2				

where $f(\tau_c)$ is the term in parentheses in eq 1 and K_{Cu} is the product of the constants before this term when $S = {}^1/_2$. These values are reported as the uncoupled values in Table I. As far as nuclear relaxation is concerned, the uncoupled analysis should pertain if $|J| < \hbar\tau_c^{-1}$. Under these conditions, the coupling will make perturbations that are too small to make significant contribution to T_1^{-1}. On the other hand, if $|J| > \hbar\tau_c^{-1}$ then the Solomon eq 1 needs to be modified to take into account the fact that the electronic situation is now better described by the coupled representation with an $S = 0$ and 1 multiplets. It has been shown that for two $S = {}^1/_2$ ions in the strong coupling limit (but as long as $|J| \ll kT$) the effect on nuclear $T_{1M}{}^{-1}$ from each metal ion is just one-half of that predicted in the absence of coupling.[17] Therefore, K_{Cu} in eq 4 should be multiplied by ${}^1/_2$ to account for the effect of strong magnetic coupling on the nuclear spin system. Since this phenomenon is analogous to that producing changes of the measured hyperfine coupling constant in the ESR spectra of coupled systems, which are easily predicted,[18-20] the appropriate coefficients to be used in front of the Solomon equation can be calculated for any M–M′ pair as shown in Appendix I. These coefficients are shown in Table II. If coupling between the two metals exists to the extent that $|J| \gg \hbar\tau_s^{-1}$, the electronic relaxation rate of the pair may be increased by up to a factor of 2. This qualitative expectation depends on the fact that each unpaired electron can exchange energy either directly with the lattice or with the other metal electron, which then exchanges energy with the lattice. As long as $\tau_s^{-1} \ll \tau_r^{-1}$, as is likely in the present copper(II)-containing systems, a factor of 2 increase in τ_s^{-1} is of no consequence on the effective τ_c^{-1} of the system.

The τ_c values calculated using the uncoupled model (eq 4) and the coupled model (see Appendix I) for homodimer systems are

$$\frac{1}{2}K_M\left(\frac{1}{r_1{}^6} + \frac{1}{r_2{}^6}\right)f(\tau_c) \qquad (5)$$

given in Table I. An average value of 1.3×10^{-10} s results for the uncoupled calculation in excellent agreement with the τ value for $ZnCu(PMK)_3{}^{4+}$, suggesting that this system is also dominated

---

(13) Dwek, R. A. *Nuclear Magnetic Resonance in Biochemistry*; Clarendon: Oxford, 1975.

(14) Friedman, H. L.; Hertz, H. G.; Holtz, M.; Hirata, F. *J. Chem. Phys.* **1980**, *73*, 6031.

(15) Banci, L.; Bertini, I.; Luchinat, C. *Inorg. Chim. Acta* **1985**, *100*, 173.

(16) Benetis, N.; Kowalewski, J.; Nordenskiöld, L.; Wennezstrōm, H.; Westlund, P.-O. *Mol. Phys.* **1983**, *43*, 329.

(17) Bertini, I.; Lanini, G.; Luchinat, C.; Mancini, M.; Spino, G. *J. Magn. Reson.* **1985**, *63*, 56.

(18) Chao, C. C. *J. Magn. Reson.* **1973**, *10*, 1.

(19) Banci, L.; Beucini, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 393.

(20) Gatteschi, D. In *The Coordination Chemistry of Metalloenzymes*; Bertini, I., Drago, R. S., Luchinat, C., Eds.; D. Reidel Publishing Co.: Dordrecht, 1983; p 215.

by the rotational correlation time. The results from the coupled calculation produce a longer τ value (average 4.6×10^{-10} s), and since it is physically unreasonable to have a longer correlation time than that for $ZnCu(PMK)_3^{4+}$, we conclude that there is little or no coupling between the copper ions of the complex. From the relation $|J| < \hbar\tau_c^{-1}$ and taking $\tau_c = 1.6 \times 10^{-10}$ s, an upper limit for $|J|$ of about 0.03 cm^{-1} can be estimated. This conclusion is consistent with the temperature dependence of the magnetic susceptibility, which shows Curie–Weiss behavior all the way down to 5 K and with the EPR spectrum which is indicative of weak coupling.

In $Ni_2(PMK)_3^{4+}$, the τ_c calculated from the sum of the two metal contributions (eq 4 with K_{Ni}) results in values that are considerably shorter than the correlation time for molecular tumbling. This result is inconsistent with a treatment that assumes noninteracting metal centers, because either the τ_S values are being substantially decreased to make significant contributions to τ_c or the $S(S + 1)$ term in eq 1 should be modified for the coupling. Calculating τ_c values for the coupled system with eq 5 produces the result shown in Table I. The average value of τ_c of 1.6×10^{-10} s is consistent with the value obtained for $ZnNi(PMK)_3^{4+}$ which was attributed to dominance by τ_r. If τ_S is decreased by the metal–metal interaction, such a decrease is expected not to be detected because of the dominance of τ_c^{-1} by τ_r^{-1}. Consistent with this nonadditivity of the T_1^{-1}'s is the result from the magnetic susceptibility investigation of $Ni_2(PMK)_3^{4+}$. A weak antiferromagnetic exchange interaction with a J of 12 cm^{-1} was observed.

Interpretation of T_1 Values in $CuNi(PMK)_3(NO_3)_4$. The final complex to be discussed involves the mixed metal $CuNi(PMK)_3^{4+}$ complex. When the uncoupled model is employed, the result again indicates a reduced τ_c value relative to τ_r so additivity of the T_1^{-1}'s is not appropriate. Indeed, we do note a pronounced perturbation of the T_1^{-1} and T_2^{-1} values with respect to $ZnNi(PMK)_3^{4+}$ and $ZnCu(PMK)_3^{4+}$. This is evidence of magnetic coupling between the two metal ions. Again, since $\tau_s^{-1} < \tau_c^{-1}$ for both isolated metal ions, the perturbation observed on the nuclear relaxation properties should be due to $|J|$ being larger than τ_c^{-1}. Under such circumstances the following equation should be used

$$T_1^{-1} = \left[K_{Cu}'\left(\frac{1}{r^6}\right) + K_{Ni}'\left(\frac{1}{r'^6}\right)\right]f(\tau_c) \qquad (6)$$

where K_{Cu}' and K_{Ni}' are the original K_M values multiplied by the appropriate coefficients, X, calculated for the pair $S = {}^1/_2$ and ${}^3/_2$ (Appendix I and Table II). Calculating τ_c values with this expression produces the results shown in Table I. The τ_c values for the protons in the nickel(II) environment are reduced just below τ_r, and those around copper(II) continue to be dominated by τ_r. The substantial agreement of the latter values with those obtained for the CuZn and NiZn systems indicates that inclusion of the appropriate weighing coefficients in the Solomon equation for both metal ions is sufficient for satisfactorily accounting for the nuclear relaxing properties of the coupled pair. The slightly shorter τ_c values obtained for the protons in the nickel(II) environment are probably a consequence of the zero-field splitting in the isolated nickel(II) ion, which is not taken into account in the expression for the C_1 and C_2 coefficients[18-20] given in Appendix I. It has been shown that zero-field splitting in one of the two metals in a coupled pair may sensibly alter such coefficients.[21]

Conclusions

We have shown here that for pairs of metals both having electronic relaxation times longer than the rotational correlation time the effect of the magnetic coupling (when $|J| > \hbar\tau_c^{-1}$) is that of reducing the contribution of each metal ion to nuclear relaxation according to coefficients obtainable from simple considerations. This occurs virtually without altering the correlation time for the electron nucleus interaction. Changes in the correlation times can be expected when, at variance with the present systems, one of the two metal ions has a short electronic relaxation time that dominates τ_c. Cases of this type are under investigation.

Acknowledgment. Support of this research by the National Science Foundation through Grant NSF 84 08149 is greatly appreciated. Most of the experimental work reported was carried out at the University of Illinois and details are contained in the Ph.D. Dissertation of C. Owens, University of Illinois, 1987. Discussion of these results with R. L. Belford and discussion with D. Gatteschi on the possible use of formulas for the EPR-detectable part of the hyperfine interaction in coupled systems is gratefully acknowledged.

Appendix I

In a coupled system consisting of metal ions with associated S_1 and S_2 electronic spins, the hyperfine coupling constants with each metal nucleus are obtained by multiplying the corresponding values in the isolated ions by coefficients, C_1 and C_2, given by[15-17]

$$C_{1i} = |S_i(S_i + 1) + S_1(S_1 + 1) - S_2(S_2 + 1)|(2S_i(S_i + 1)) \qquad (A1)$$

$$C_{2i} = |S_i(S_i + 1) + S_2(S_2 + 1) - S_1(S_1 + 1)|(2S_i(S_i + 1)) \qquad (A2)$$

where S_i is the total spin value for each multiplet, i, in the coupled system. Since nuclear relaxation depends on the square of the electron nucleus interaction energy, $S_1(S_1 + 1)$ in the Solomon equation for the interaction of a nucleus with metal 1 should be substituted by a function of the C_{1i}^2. Such function can be evaluated for each multiplet, i, in the coupled system by weighing the relative $S_i(S_i + 1)$ term by C_{1i}^2 times the fraction of spin states belonging to that multiplet, $(2S_i + 1)/\sum_1(2S_i + 1)$. A summation is then performed over all the multiplets, assumed to be equally populated ($|J| \ll kT$). Such quantity, further divided by the original $S_1(S_1 + 1)$ value, is the appropriate coefficient, X_1, that should multiply the Solomon equation relative to metal 1

$$X_1 = \frac{1}{S_1(S_1 + 1)}\left(C_{1i}^2 S_i(S_i + 1)\frac{2S_i + 1}{\sum_{I}(2S_i + 1)}\right) \qquad (A3)$$

where C_{1i} is the coefficient for each i multiplet, as defined above, and the summation is over all such multiplets. A similar equation will give the corresponding correlation coefficient, X_2, for metal 2. In such a way the values listed in Table II are obtained.

Registry No. $Zn_2(PMK)_3^{4+}$, 68200-91-9; $ZnCu(PMK)_3^{4+}$, 68200-97-5; $ZnNi(PMK)_3^{4+}$, 68200-94-2; $Ni_2(PMK)_3^{4+}$, 47892-62-6; $Cu_2(PMK)_3^{4+}$, 68200-89-5; $NiCu(PMK)_3^{4+}$, 68200-98-6.

---

(21) Bencini, A.; Gatteschi, D. *Mol. Phys.* **1985**, *54*, 969.