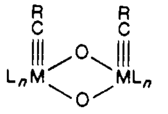
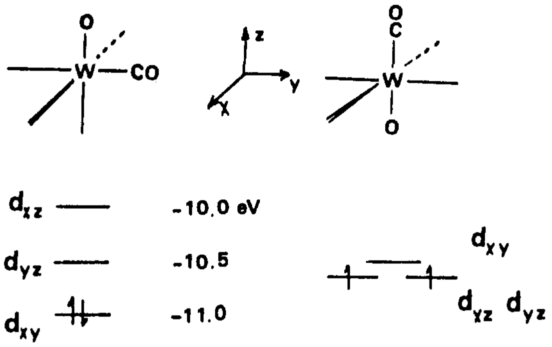
Scheme II



Scheme III



limits the utility of conventional oxidation state descriptions in any case. Nonetheless it is accurate to depict the proposed d^0 *cis*-(oxo–carbyne) (O^{2-},CR^{3-}) complexes as electron rich at oxygen. One attractive reaction path available to such a monomer is dimer formation as shown in Scheme II. This removes the π-bonding requirement of the oxo ligand and cancels the dπ-orbital conflict responsible for excessive electron density on the terminal oxygen in the monomer.

Oxo–Carbonyl Complexes. A d^2 octahedral oxocarbonyl derivative, $W(O)(CO)(PPh_2Me)_2Cl_2$, has recently been reported by Rheingold, Mayer, and co-workers.[23] Given that the conflict characterizing identical π ligands trans to one another (either π-acidic or π-basic) can be eliminated by replacing one with a π-innocent ligand, what is the effect of a strong π-donor trans to a strong π-acceptor?

The isolated dπ orbital energies (Scheme III) for cis and trans d^2 $[M(O)(CO)H_4]^{2-}$ model compounds answer this question and also reveal why the cis isomer is favored. Clearly π-acid and π-base ligands prefer to avoid sharing dπ orbitals. In terms of three-center dπ–ligand π interactions, the shared dπ orbital is pushed up by π-donation and down by π-acceptance. The two effects nearly cancel one another in the M(O)(CO) case, and this cancellation leads to a net nonbonding result.

The trans O=M—CO arrangement produces three nearly degenerate dπ orbitals. The d_{xy} orbital is π-innocent and conflicting oxygen 2p donation and CO π^* acceptance leave d_{xz} and d_{yz} near their original energies. The *cis*-M(O)(CO) moiety allows for two constructive 2-center 2-electron π bonds: stabilization of the lone filled dπ level by CO π^*_x and destabilization of the vacant d_{xz} by O p_x. The remaining dπ orbital is shared by O^{2-} and CO and is nearly nonbonding. It is vacant in the d^2 tungsten monomer which has been isolated. A d^4 configuration would bind the CO more tightly but the confrontation of the oxide p_y with a filled d_{yz} would weaken the M=O bond and create a nucleophilic terminal oxygen analogous to the $M(CO)(CR)L_4$ d^0 monomer discussed above.

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Nuclear Magnetic Resonance Proton Relaxation in Bimetallic Complexes Containing Cobalt(II)

Ivano Bertini,*[†] Charlotte Owens, Claudio Luchinat, and Russell S. Drago*[‡]

Contribution from the Departments of Chemistry, University of Florida, Gainesville, Florida 32611, and University of Florence, Florence, Italy. *Received May 27, 1986*

Abstract: The ^1H NMR spectra of $CoM(PMK)_3{}^{4+}$, where M is Zn^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+}, and PMK = 2,5-bis(2-pyridyl)-3,4-diazahexa-2,4-diene, have been analyzed with the aim of understanding nuclear and electron relaxation rates. Very short electron relaxation rates have been found for $CoZn(PMK)_3{}^{4+}$ and $Co_2(PMK)_3{}^{4+}$. The cobalt(II) has a significant influence on the electronic relaxation times of copper and nickel in the $CoCu(PMK)_3{}^{4+}$ and $CoNi(PMK)_3{}^{4+}$ complexes, thereby dramatically sharpening their ^1H NMR peaks as compared to those of the $ZnCu(PMK)_3{}^{4+}$ and $ZnNi(PMK)_3{}^{4+}$ complexes. Modifications of the Solomon equations are proposed to interpret the relaxation rates in magnetically coupled equations. We find that a magnetic coupling constant slightly larger than the maximum dipolar coupling between Cu(II) and Co(II) is capable of making the signals of protons on ligands bound to Cu(II) essentially as sharp as those bound to the high-spin, six-coordinate, cobalt(II). Supporting magnetic and variable-temperature T_1 data are included.

The understanding of nuclear relaxation induced by paramagnetic metal ions can, in principle, provide information on the structure of (Figure 1), under investigation and on the time-dependent phenomena concerning the resonating nucleus.[1-4] A theoretical description of the coupling between the nucleus and the unpaired electron has been proposed under a variety of conditions.[5-16] The contributions to nuclear relaxation have been identified and their magnitudes predicted on the basis of appropriate spin Hamiltonians.[12-16] Such treatments pertain, however, to isolated paramagnetic metal ions or to two magnetically coupled $S = {}^1/_2$ ions.[17a] No theory and almost no experimental data are described for other heterobimetallic systems where both metal ions are paramagnetic and magnetically coupled.

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[‡] University of Florida.

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Table I. Proton Isotropic Shifts (ppm) and T_{1M}^{-1} Values (s^{-1}, Estimated Errors in Parentheses)

		3-H	4-H	5-H	6-H	$-CH_3$
$CoZn(PMK)_3^{4+}$						
shifts	(Co)	66.81	2.74	42.31	141.47	44.99
	(Zn)	-9.88	2.41	-10	-0.69[b]	8.08
T_{1M}^{-1}	(Co)	36.1 (0.9)	11.5 (0.3)	29.2 (0.7)	670 (220)	71.9 (1.6)
	(Zn)	6.9 (0.3)	1.41 (0.02)	1.78 (0.06)	3.97 (0.06)[b]	37.3 (0.6)
$NiZn(PMK)_3^{4+}$ [c]						
shifts	(Ni)	62.98	8.54	40.29		39.23
	(Zn)	-9.15	2.76	-8.07	2.11	-10.51
T_{1M}^{-1}	(Ni)	2000 (500)	590 (5)	1630 (110)		5900 (350)
	(Zn)	370 (15)	120 (10)	140 (10)	310 (15)	2600
$CuZn(PMK)_3^{4+}$ [c]						
shifts	(Cu)	39.68	5.68	23.43		17.26
	(Zn)	-4.19	1.31	-3.67	0.87	-3.55
T_{1M}^{-1}	(Cu)		235 (3)	526 (60)		1200 (40)
	(Zn)	118 (10)	43.3 (1)	64 (6)	121 (2)	709 (10)
$Co_2(PMK)_3^{4+}$						
shifts		56.46	5.08	31.99	141.21	51.88
T_{1M}^{-1}		48.5 (0.5)	17.0 (0.1)	35.8 (0.3)	588 (35)	114 (2)
$CoNi(PMK)_3^{4+}$						
shifts	(Co)	56.54	4.74	34.47	149.55	33.75
	(Ni)	50.75	11.05	28.91	148.8[a]	44.65
T_{1M}^{-1}	(Co)	52.1 (1.4)	18.6 (0.2)	38.0 (0.6)	645 (17)	180 (0.4)
	(Ni)	112 (3)	35.2 (0.5)	88.5 (1.6)	909 (83)[a]	225 (7)
$CoCu(PMK)_3^{4+}$						
shifts	(Co)	62.43	3.78	38.61	143.84	41.35
	(Cu)	27.60	8.06	12.21	87.38	24.65
T_{1M}^{-1}	(Co)	40.8 (1.8)	13.5 (0.4)	30.3 (1.2)	529 (28)	94.3 (3.6)
	(Cu)	37.7 (1.8)	8.33 (0.14)	24.2 (0.4)	307 (10)	75.8 (2.3)

[a] Broad and overlapping with the other 6-H signal. [b] Direct overlap with 5-H (Zn_2). [c] Reference 23.

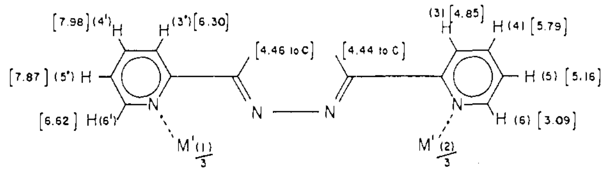

Figure 1. Numbering system and distances in the $[MM'(PMK)_3]^{4+}$ complexes.

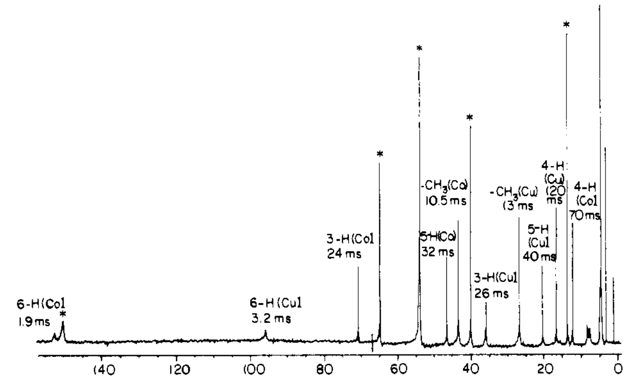

Figure 2. The proton NMR spectrum of $CuCo(PMK)_3^{4+}$. Peaks of $Co_2(PMK)_3^{4+}$ are indicated with an asterisk.

We have investigated through ^1H NMR at 360 MHz, deuterium oxide solutions of bimetallic systems of the type $MM'(PMK)_3^{4+}$ (Figure 1) where M and M' = Co, Ni, or Cu. Earlier reports of the ^1H NMR at 80 MHz suggested that this is an ideal system for investigating nuclear relaxation behavior.[18,19] In this paper we report a detailed ^1H NMR analysis of the cobalt(II)-containing systems. High-spin cobalt(II) is characterized by very short electronic relaxation times, and in this work we demonstrate that cobalt(II) can cause relaxation rate enhancements of the electrons of a nearby metal-like copper(II) or nickel(II). The surprisingly sharp resonances obtained for ligands bound to copper(II) in the CuCo heterobimetallomer are shown in Figure 2. Further studies of bimetallic systems containing copper and cobalt are quite meaningful in understanding the structure of copper–zinc superoxide dismutase (Cu_2Zn_2SOD). When zinc(II) has been replaced by cobalt(II) in SOD, well-shaped isotropically shifted signals are observed with short nuclear T_1 values.[20] Experimental data on the complexes reported here provide further information for the understanding of the relevant problem of the influence of quickly relaxing electron spin systems on slowly relaxing magnetically coupled metal ions. The results have implications for future application of this technique to biological systems.

Experimental Section

A. Synthesis. The ligand[17b] and complexes[18,19,21,23] are prepared by the reported procedures. The mixed-metal complexes, which cannot be made purely, are also made by the reported aqueous solution procedure.[23]

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The resulting samples are a mixture of the two homobinuclear complexes with the mixed-metal complex.

B. NMR. The ^1H NMR spectra and ^1H T_1 values in deuterium oxide are measured on an NIT 360 Fourier transform instrument, capable of a total frequency range of over 200 ppm. The procedures followed have been reported previously. The T_1 values are obtained by using an inversion recovery method of a five-pulse sequence[24a] as described previously.[23] 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 three-parameter equation in exponential form to the data obtained.

C. Magnetism. Bulk magnetization data from 5.5 to 300 K of $Co_2(PMK)_3(NO_3)_4 \cdot 3H_2O$ were measured at 10 KG on a VTS-50 SQUID.[23]

Results

NMR. The proton NMR signals of $ZnCo(PMK)_3^{4+}$, $Co_2(PMK)_3^{4+}$, $CoNi(PMK)_3^{4+}$, and $CoCu(PMK)_3^{4+}$ complexes are well-resolved peaks, shifted significantly from the diamagnetic $Zn_2(PMK)_3^{4+}$ complex; most peaks are shifted downfield. All the peaks are strikingly sharper than those of the Co(II) and Ni(II) complexes reported earlier.[23] Listed in Table I are the shifts, from which the Zn_2 shifts have been subtracted, and T_1^{-1} values, from which the T_1^{-1}'s of the Zn_2 protons have been subtracted.

In the $ZnNi(PMK)_3^{4+}$ and $ZnCu(PMK)_3^{4+}$ complexes the peaks can be assigned on the basis of unpaired electron density delocalized into the σ system of the pyridine ring ligated to the Ni(II) or Cu(II) and spin polarization of the π system of the distant ring. When only a pair of peaks can be assigned to a pair of protons, the exact assignment can be made by assuming the more distant proton relaxes more slowly. This is true for dipolar relaxation but can also be true for hyperfine exchange relaxation, if the coupling constant is larger for the closer proton. If the complex is assumed to have a comparable geometry to $Co_2(PMK)_3^{4+}$, distances can be calculated from available X-ray data.[21] The shifts of these complexes, added appropriately, fit the observed shifts of the $Cu_2(PMK)_3^{4+}$, $Ni_2(PMK)_3^{4+}$, and $CuNi(PMK)_3^{4+}$ complexes. Even though Co(II) has an unpaired t_{2g} electron, the peaks of $Co_2(PMK)_3^{4+}$ are shifted remarkably similarly to the $Ni_2(PMK)_3^{4+}$ complex, except for the methyl signal, and the peaks can be assigned accordingly. The additivity of shifts holds for all the above complexes, so all peaks can be assigned. Considering the solvent and field strength differences, our results are in reasonable agreement with data reported on these complexes[18] and the assignments are consistent with those of analogous moieties.[25]

Compared to those of the ZnNi and ZnCu complexes, the spectra of the ZnCo, Co_2, CoCu, and CoNi complexes have much sharper peaks, indicating their protons are much less effectively relaxed by the paramagnetic ions, and have much longer T_{1M} values; the measured T_{1M}^{-1} values in Table I reflect this. As a result, the T_{1M}^{-1} values of the CoNi and CoCu complexes cannot be fit by adding the T_{1M}^{-1} values of CoZn and ZnNi or CoZn and ZnCu complexes, contrary to a previous report.[19] The protons of the ZnCo, Co_2, CoCu, and CoNi complexes still relax more quickly than those of the Zn_2 complex.

Variable-temperature T_1 measurements have been made on deuterium oxide solutions of the CoCu and Co_2 complexes from 5 to 55 °C. These T_1 values, uncorrected for the diamagnetic contribution, have been plotted as ln $(1/T_1)$ vs. $1/T$ (K),[42] for insight into activation energies of the processes controlling the proton relaxation. For the Co_2 complexes, the slopes of plots for the various protons are very similar: 1.06×10^3 K; if the slope is the activation energy divided by R, this corresponds to an activation energy of 8.8 kJ/mol. The slopes are determined by linear regression.

In general, the T_1's have been harder to measure for the CoCu complex, especially because of decomposition at higher temperatures. For protons nearer Co(II), the plots are similar to those for the Co_2 complex, but with more variation. Of the three plots with T_1's measured at 55 °C, the slopes are 977 K for 3-H, 1.04×10^3 K for 5-H, and 687 K for 4-H. Around Cu(II), however, the slopes vary widely: 50.4 K for 3-H (Cu), 393 K for 4-H (Cu), 275 K for 5-H (Cu), and 887 K for 6-H (Cu).

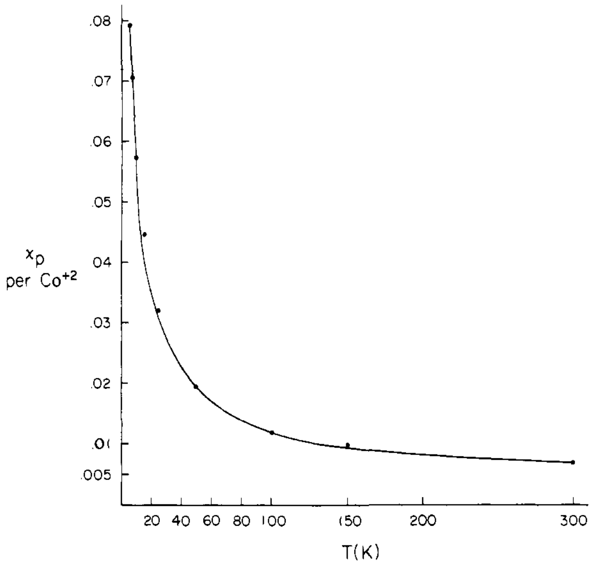

Figure 3. Paramagnetic susceptibility per mole Co(II) of $Co_2(PMK)_3(NO_3)_4 \cdot 3H_2O$ vs. temperature (K).

Magnetism. The paramagnetic susceptibility per mole Co(II) of $Co_2(PMK)_3(NO_3)_4 \cdot 3H_2O$ is plotted in Figure 3. It rises steadily from 300 to 5.5 K and does not go through a maximum value. The μ_{eff} falls from 4.0 μ_B at 300 K to 3.1 μ_B at 100 K.

Discussion

Analysis of the T_1^{-1} Data. Analysis of the nuclear relaxation data on the ZnCo system should first consider the metal-centered, dipolar contribution to nuclear relaxation as given by the Solomon equation:[5]

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

Here $T_{1M}(i)^{-1}$ is the paramagnetic contribution to the longitudinal relaxation rate of the ith proton at distance r_i from the cobalt(II) ion, ω_s and ω_I are the electron and proton Larmor frequencies, τ_c is the correlation time for the electron–nucleus interaction, ($\tau_c^{-1} = \tau_s^{-1} + \tau_R^{-1}$), and the other symbols have their usual meaning. In this case, $\omega_I = 2.26 \times 10^9$ rad/s and $\omega_s = 1.49 \times 10^{12}$ rad/s.

For the CoZn system, when average r_i values estimated from X-ray data (Figure 1) and experimental T_{1M} values (Table I) are used in the Solomon equation, the average value of ($3\tau_c + 7\tau_c/[1 + \omega_s^2\tau_c^2]$) resulted in a τ_c value of 0.60 ps. In contrast, the τ_c's of the CuZn and NiZn systems were consistent at ~160 ps and were determined by the rotational correlation time, as the electron spin lifetimes were longer than the rotational time. Correlation times are defined under Redfield's density matrix approach.[3,24b,c] Clearly, in the ZnCo system, τ_c is not determined by rotation and the system is in the short-time regime where the Redfield limit does not hold, a problematical theoretical area. In this paper, we assume that a nonrotational mechanism exists with a correlation time shorter than the electron relaxation time so that τ_s could fall within the "Redfield" limit and correlation times could be defined; work on this assumption has been reported elsewhere.[12,13,15] Under this assumption, the τ_c is mainly that of the undescribed phenomenon doing the averaging and τ_s is longer than τ_c. However, as this unknown phenomenon does not affect the ZnCu and ZnNi systems, it is directly a function of the Co ion in the ZnCo system and may, for the sake of discussion, be called τ_s.

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An estimate of the hyperfine exchange relaxation can be made which is probably an overestimate. If the isotropic shifts are only contact in origin, the Fermi contact coupling constant $A/\hbar$ can be evaluated from the following[28]

$$\frac{A}{\hbar} = \left(\frac{\Delta\nu}{\nu_0}\right)^{\text{con}} \frac{3\gamma_1 kT}{g_e\mu_B S(S+1)} \tag{2}$$

and the contact contribution to T_1 can be estimated through the Bloembergen equation[6], where τ_s is the electron spin lifetime.

$$T_{1M(FC)}(i)^{-1} = \frac{2}{3}\left(\frac{A}{\hbar}\right)_i^2 S(S+1)\frac{\tau_s}{1+\omega_s^2\tau_s^2} \tag{3}$$

This mechanism has its maximum contribution to longitudinal (T_1) relaxation when τ_s^{-1} equals ω_s, the Larmor frequency of the paramagnetic ion, and cannot be the major relaxation mechanism for these complexes. The maximum calculated T_1^{-1} values as a percentage of the experimental T_1^{-1} values are 10% or less, except for 20% for the 3-H (Co) proton. Therefore, the paramagnetic Co(II) ion relaxes its ligands' protons much more by dipolar than by exchange coupling.

The $Co_2(PMK)_3^{4+}$ complex has nuclear relaxation rates similar to those of the CoZn analogue (Table I). If it is assumed that any magnetic coupling between metal ions is less than $\hbar\tau_c^{-1}$, then nuclear relaxation is expected to be additive, i.e.

$$T_{1M}(i)^{-1} = K\left(\frac{1}{r_{1i}^6} + \frac{1}{r_{2i}^6}\right)f(\tau_c) \tag{4}$$

where r_{1i} and r_{2i} are the distances of the ith proton from Co(1) and Co(2), respectively; K is the product $(2/15)(\mu_0/4\pi)^2\gamma_1^2 g_e^2\mu_B^2 S(S+1)$ in eq 1 and $f(\tau_c)$ is the pair of terms containing τ_c in eq 1. When $T_1(i)^{-1}$ values are calculated by using 0.6 ps, the average τ_c value of the CoZn complex, the calculated $T_{1M}(i)^{-1}$ values range from 78% to 112% of the experimental values for the Co_2 complex. Also, the additivity of the experimental T_{1M}^{-1} data from $CoZn(PMK)_3^{4+}$ produces values in reasonable agreement with the experimental T_{1M}^{-1}'s of the Co_2 complex. Because τ_c^{-1} is so large, the magnetic coupling between ions needs to be at least 9 cm^{-1} for the coupled case to apply. The energy of dipolar coupling, in a strong external field which aligns both Co(II) electronic moments along the laboratory-fixed z axis, can be expressed as $\mu_2\mu_1(1 - 3\cos^2\theta)/r_3$; θ is the angle between the orientation of the moments and the molecular axis r connecting the ions.[39] With $\mu_2 = \mu_1 = g\mu_B S = 2.002\mu_B(^3/_2)$ and a Co–Co distance of approximately 3.8×10^{-8} cm, the maximum dipolar interaction is 0.07 cm^{-1}. Also, the pseudodipolar interaction can be neglected when the isotropic exchange $|J|$ (as in $H_{ex} = J\bar{S}_1\cdot\bar{S}_2$) is roughly 30 cm^{-1} or less.[40] Therefore, the only reasonable mechanism of interaction which can be 9 cm^{-1} is the isotropic exchange, J.

If J is larger than $\hbar\tau_c^{-1}$, then the electron relaxation rate is expected to increase, since the electron of each metal ion can relax by coupling with the electrons of the other metal ion.[17a] This should be true if (i) the energy separation of all the coupled levels is less than kT, (ii) the electronic relaxation times are the same for the coupled levels, and (iii) there is no zero field splitting in the coupled S' levels which would lead to different τ_s values for the transitions between different M_s levels.[8] Furthermore, under these conditions each metal ion would contribute half to the nuclear relaxation of a given proton.[23,38] When K of eq 4 is multiplied by the appropriate coefficient,[23] $^1/_2$, and the average τ_c of the CoZn complex is also halved, the calculated T_{1M}^{-1} values are only 25–35% of the experimental values. Therefore, for $Co_2(PMK)_3^{4+}$ the experimental data are better fit by the uncoupled mechanism.

If two ions are antiferromagnetically coupled, the magnetic susceptibility should reach a maximum value and then fall dramatically as the temperature falls. If J between the Co(II) ions were 9 cm^{-1}, such a maximum should be easily seen above 5.5 K. In fact, no such mechanism is seen in the magnetic susceptibility data for $Co_2(PMK)_3(NO_3)_4{\cdot}3H_2O$, thereby supporting the better fit of the T_{1M}^{-1} data by the "uncoupled" case. The magnetic susceptibility data do not fit the Curie–Weiss law, but this need not be due to Co–Co interaction. Monomeric six-coordinate Co(II) complexes with similar ligands can show a range of even more unusual magnetic behavior.[41] These monomeric Co(II) complexes are thought to undergo "spin-crossover" from the $^4T_1(^4F)$ to the $^2E(^2G)$ state with falling temperature. The μ_{eff}'s from our data are lower than those reported earlier.[18] One explanation might be some oxidation to diamagnetic Co(III), but even if this did occur, it would not affect the basic shape of the susceptibility curve with respect to temperature, so the absence of a maximum should still be meaningful.

If the CoNi and CoCu complexes are uncoupled, the relaxation rates of the protons of the ZnNi and CoZn complexes should equal those in the CoNi complex and those of the ZnCu and CoZn complexes should equal those in the CoCu complex. This means the protons in the CoNi and CoCo complexes should relax as fast as in the ZnNi and ZnCu complexes, and their peaks should be at least as broad. Clearly, this is not true, as can be seen in Table I. The remarkable sharpness of the CoNi and CoCu proton peaks relative to ZnNi and ZnCu peaks indicates the relaxation by Ni(II) and Cu(II) has been severely interrupted. For the CoNi and CoCu complexes to appear totally uncoupled, $|J|$ must be less than $\hbar\tau_{c(CoZn)}^{-1}$, but also less than $\hbar\tau_{c(NiZn)}^{-1}$, about 0.03 cm^{-1}. As the proton T_{1M}^{-1}'s of the CoNi and CoCu complexes are clearly much less than those of the NiZn and CuZn complexes, $|J|$ is greater than 0.03 cm^{-1}.

When the coupling is greater than $\hbar\tau_c^{-1}$ of the more slowly relaxing ion, the faster relaxing metal ion can interact with the metal ion which typically undergoes slow electronic relaxation and cause the more slowly relaxing ion to relax more quickly, possibly as quickly as the faster one. In the strongly coupled case, $|J|$ is greater than $\hbar\tau_{c(CoZn)}^{-1}$, and the bimetallic system can be treated[3,11,16] as having a single electronic relaxation rate, which is at least as fast as $\tau_{c(CoZn)}^{-1}$.

$$\tau_c(J)^{-1} = \tau_{c(1)}^{-1} + \tau_{c(2)}^{-1} \tag{5}$$

Also, when eq 4 is modified for a heterobimetallic system

$$T_{1M}(i)^{-1} = K'\frac{1}{r_{1i}^6}f(\tau_{c1}) + K''\frac{1}{r_{2i}^6}f(\tau_{c2}) \tag{6}$$

the K values must be multiplied by the appropriate coefficients.[23] When this is done and the ions have the same electronic relaxation rate, the contribution of Co(II) to the proton T_1^{-1} values should be a factor of 35/3 greater than Cu(II) in the CoCu complex and a factor of 467/152 greater than Ni(II) in the CoNi complex; this means the protons around the Co(II) ion should be relaxed much more quickly than those around Ni(II) or Cu(II). This is clearly not seen in these complexes: in the CoNi complex, the protons nearer Ni(II) are relaxed more quickly than those near

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Table II. Estimated τ_s Values (ps) for Ni(II) and Cu(II) in Co and $CoCu(PMK)_3^{4+}$

		3-H	4-H	5-H	6-H	av τ_s (τ_s of ZnM in parentheses)
$CoNi(PMK)_3$	(Co)	20.4	33	51.5	*a*	23.2 ± 4.70
	(Ni)	16.7	15.4	16.1	9.1	(>160[23])
$CoCu(PMK)_3$	(Co)	20.8	32.3	40.9	*a*	20.5 ± 3.90
	(Cu)	14.9	9.64	15.4	9.4	(~3000[23])

[a] T_{1M}^{-1} for this proton in $CoZn(PMK)_3$ is slightly larger than those in the CoNi and CoCu derivatives, possibly due to the large error in the former (see Table I).

Co(II). In the CoCu complex, the protons near Cu(II) relax at 60% or greater of the rate of those nearer Co(II), while the coupled treatment predicts they, except for the 6-H (Cu) proton, would relax only about twice as fast as the protons nearer Zn(II) in the CoZn complex. Therefore, the strongly coupled treatment and its expectation of one effective electronic rate do not apply, and $|J|$ is less than $\hbar\tau_{c(CoZn)}^{-1}$, about 9 cm^{-1}.

When $\hbar\tau_{c(NiZn)}^{-1} < |J| < \hbar\tau_{c(CoZn)}^{-1}$, the following relationship, based on the work of Bertini and co-workers,[17a] is proposed for the intermediate coupling case of the CoNi complex:

$$\tau_{c(\text{Ni in CoNi})}^{-1} = \tau_{c(\text{Ni in NiZn})}^{-1} + \left(\frac{J}{\hbar}\right)^2 \tau_{c(\text{Ni in NiZn})} \qquad (7)$$

In $NiZn(PMK)_3^{4+}$, the correlation time for the electron–nucleus interaction has been found to be about 160 ps, essentially determined by the rotational correlation time of the molecule,[23] so the Ni(II) electronic lifetime is even longer. In order to estimate $\tau_{c(\text{Ni in CoNi})}^{-1}$, the contribution of Ni(II) to nuclear relaxation in the CoNi complex, we shall assume that the Co(II) electronic relaxation rate remains the same as in $CoZn(PMK)_3^{4+}$. This is reasonable if the coupled system does not provide additional relaxation mechanisms due to the presence of new, excited energy levels; otherwise, Co(II) would give a smaller contribution to T_1^{-1} values. With the K values being multiplied by the appropriate coupling coefficients,[23] eq 6 is modified to

$$T_{1(\text{Ni})}(i)^{-1} = T_{1(\text{CoNi})}(i)^{-1} - K_{\text{Co}}\left(\frac{1}{r_{2i}^6}\right) f[\tau_{c(\text{CoZn})}] \qquad (8)$$

where $T_{1(\text{CoNi})}(i)^{-1}$ are the experimental values. The effective τ_c of the Ni(II) contribution in the CoNi complex can then be calculated:

$$T_{1(\text{Ni})}(i)^{-1} = K_{\text{Ni}}\left(\frac{1}{r_{1i}^6}\right) f[\tau_{c(\text{Ni in CoNi})}] \qquad (9)$$

The resulting $\tau_{c(\text{Ni in NiCo})}$ values, listed in Table II, average 23 ps, much longer than the average τ_c of the CoZn complex (0.6 ps), yet much shorter than the rotational correlation time (160 ps) and the electronic lifetime of Ni(II) in the NiZn complex. If $\tau_{c(\text{Ni in CoNi})}$ is 23 ps and $\tau_{c(\text{Ni in NiZn})}$ is 160 ps, then from eq 6, $|J|$ is 0.08 cm^{-1}, slightly higher than the maximum energy possible from the ion–ion dipolar coupling.

The extension of this analysis for the CoNi complex to the CoCu complex provides an averaged estimate of the effective $\tau_{c(\text{Cu in CoCu})}$ of 20 ps, again longer than τ_c of the CoZn complex, but much shorter than the electronic lifetime of Cu(II) in the CuZn complex. If $\tau_{c(\text{Cu in CoCu})}$ is set to 20 ps, and $\tau_{c(\text{Cu in CuZn})}$ to 160 ps, then from eq 6, $|J|$ is 0.09 cm^{-1}.

The variable-temperature T_1 data for the CoCu and Co_2 complexes also undermine the idea of strong coupling and the presence of only one effective electronic relaxation rate in the CoCu complex. In a strongly coupled system with one effective electronic relaxation rate, whatever controls that rate should show the same temperature dependence for all the protons in the complex. Clearly, this is not so in the CoCu complex: while the temperature dependence of the T_1^{-1}'s of the protons around Co(II) maintains some similarity to that of the Co_2 system, the slopes of the ln $(1/T_1)$ vs. $1/T$ (K) plots for the protons near Cu(II) vary widely. Further implications of these slopes are unclear at this time, but what is clear is that the same process that dominates the proton relaxation around Co(II) does not control the proton relaxation around Cu(II), at least to the same extent.

One should also take into consideration, however, that all the present discussion neglects the effect of zero field splitting both in the starting cobalt(II) and nickel(II) ions and on the levels arising from magnetic coupling. The presence of zero field splitting introduces the possibility of having angular coefficients which depend on the angles between the zero field splitting tensor axes and the vector connecting the metal to the resonating nucleus. Furthermore, zero field splitting may alter the values of the coefficients to obtain K' and K'' in the Solomon equation.[35] However, the effects of zero field splitting are probably of the same order of magnitude as the effects of magnetic coupling on the coefficients in the Solomon equation. Therefore, their possible inclusion would not drastically change the overall picture.

The treatment of the above data in the frame of the Solomon equation, in the absence of a further refinement of the theory, is capable of accounting for the observed patterns to such a degree as to permit prediction of the nuclear relaxation behavior in analogous systems.

General Conclusions

It is intuitively accepted that in heterobimetallic pairs in which one of the two metal ions has electronic relaxation times that are intrinsically much shorter than those of the partner, exchange coupling would sizeably shorten the relaxation time of the latter ion.[36,37] EPR experiments qualitatively confirm this expectation; however, attempts aimed at a deeper understanding of such behavior are still lacking. The present analysis accounts for the essential features of the physical phenomenon and gives an idea of the size of the effect as related to the values of the exchange coupling constant and of the electronic relaxation time of the fast relaxing ion. Of particular interest is the manifestation of this phenomenon in copper–cobalt pairs, owing to its possible applications to systems of biological relevance, where the interaction of cobalt(II) with the native copper(II) ion can open up the system to NMR investigations.

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