Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta T6G 2E1 Canada

Solvent Proton Line Broadening Study of Schiff Base Complexes of Cobalt(II) and Copper(II)

L. L. RUSNAK and R. B. JORDAN*

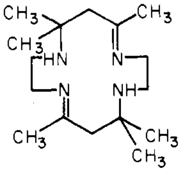
Received April 4, 1975

AIC50249J

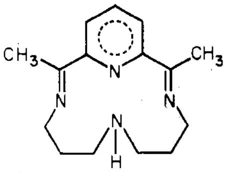
The ^{1}H NMR line broadening and shift effects have been investigated for 5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradeca-4,11-dienecobalt(II) (Co(*trans*-[14]diene)$^{2+}$) in water, methanol, and *N,N*-dimethylformamide (DMF), 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenecobalt(II) (CoCR^{2+}) in DMF, and CuCR^{2+} in water and DMF. None of the systems show chemical exchange effects on the ^{1}H NMR line width and shifts, and the observations are quantitatively accounted for by the sum of inner-sphere dipolar and scalar and outer-sphere dipolar relaxation mechanisms. Observable shifts were found only for Co(*trans*-[14] diene)$^{2+}$ in acetonitrile and CuCR^{2+} in DMF. The temperature dependence of the shift in the latter system is unusual and may be accounted for by a five–six-coordinate equilibrium.

Introduction

In connection with studies of solvent exchange rates from metalloporphyrins and Schiff base model complexes several cobalt(II) and copper(II) Schiff base systems have been studied. The low-spin cobalt(II) complex of I (referred to as Co(*trans*-[14]diene)$^{2+}$) has been studied in water, methanol, and acetonitrile. The low-spin cobalt(II) complex of II was studied in *N,N*-dimethylformamide (DMF), while that of copper(II) was studied in DMF and water.



I



II

In all cases no solvent exchange rate controlled line broadening was observed in the accessible temperature region. Therefore the discussion centers mainly on whether exchange is too fast or too slow to observe. Once this is decided either upper or lower limits for the exchange rates can be given. The line broadening results also provide data on activation energies and correlation times which may be useful in future studies in the same solvents.

Experimental Section

Materials. The Co(*trans*-[14]diene)(ClO$_4$)$_2$[1] and its tetrafluoroborate salts, CoCR(ClO$_4$)$_2$[2] and CuCR(BF$_4$)$_2$,[3] were prepared by minor modifications of published procedures. The details are available elsewhere.[4] The compounds were characterized by C, H, N, and Co analysis,[5] where applicable, and by comparison of infrared[1,2] and electronic[6] spectra to published results. All cobalt(II) complexes were prepared and handled under a nitrogen atmosphere, or in vacuo.

Solvents were triply distilled under vacuum and dried over Linde 3A molecular sieve before each distillation.

Sample Preparation. Solvent was distilled under vacuum onto a weighed amount of the appropriate salt, and the weight of the solvent was determined. Internal standard was distilled into the sample and the NMR tube sealed. The internal standard was cyclopentane in methanol and DMF, tetramethylsilane in acetonitrile, and *tert*-butyl alcohol or acetone in water.

In general solution concentrations were close to saturation, in order to maximize the observed broadening, and were in the range of 0.05 to 0.5 *m* depending on the system. At least two, and generally three, different metal ion concentrations were studied and the line broadening always increased linearly with the concentration.

Magnetic susceptibilities were measured by the NMR method[7] using precision coaxial tubes (Wilmad Glass Co.).

Instrumentation. The ^{1}H NMR spectra were recorded on Varian Associates A56/60 and HA-100 spectrometers equipped with standard temperature controllers. Temperatures were determined from peak separations in methanol and ethylene glycol standards at 60 MHz and with a copper–constantan thermocouple at 100 MHz.

The EPR spectra were obtained on a Varian A-4502 spectrometer at X band frequency. Samples were sealed in flattened quartz tubes.

Results

The results will be discussed in terms of the relaxation rate effect due to the paramagnetic ion given by

$$(T_{2P})^{-1} = \pi(\Delta\nu_M - \Delta\nu_{Sol}) \tag{1}$$

where $\Delta\nu_M$ is the full-width at half-height of the solvent resonance in the presence of the paramagnetic ion, and $\Delta\nu_{Sol}$ is the analogous width in the pure solvent. The values of $(T_{2P})^{-1}$ are normalized by the ratio of solvent molecules in the first coordination sphere of the metal to those in the bulk solvent, given by

$$P_M = n(m)/((S)_0 - n(m)) \tag{2}$$

where *m* is the molality of the metal ion, *n* is the number of solvent molecules in the first coordination sphere of the metal ion, and $(S)_0$ is the molality of the pure solvent.

If solvent molecule exchange is too slow, then the relaxation effects being observed are due to the interaction of unpaired electrons on the metal complex and protons on solvent molecules in second and higher coordination spheres of the complex. This outer-sphere effect has been given by Luz and Meiboom[8] as

$$\left(\frac{1}{T_{2P}}\right)_0 = \frac{4\pi}{45}(\rho N(m) \times 10^{-3})\frac{(S)(S+1)(\gamma_I g\beta)^2}{d_0^3} f_D(\tau_D) \tag{3}$$

where ρ is the solvent density, N is Avogardro's number, d_0 is the average distance of closest approach of the nucleus in the second coordination sphere and the metal ion center, and $f_D(\tau_D)$ is a function of the correlation time for the nuclear–electron interaction defined later. Other symbols have their usual meaning. Since it is common practice to divide experimental $(T_{2P})^{-1}$ values by P_M, it is convenient to define

$$\left(\frac{1}{P_M T_{2P}}\right)_0 = \frac{1}{T_{2O}} = \frac{4.14 \times 10^{13}(S)(S+1)\rho(S)_0}{nd_0^3} f_D(\tau_D) \tag{4}$$

where numerical constants and γ_I for the proton have also been inserted into eq 3, and the units of d_0 are ångströms.

If solvent molecule exchange is too fast to control $(T_{2P})^{-1}$, then the proton relaxation will be controlled by the rate of relaxation in the first coordination sphere $(T_{2M})^{-1}$. Outer-sphere effects are still present of course, so that

$$\frac{1}{T_{2P}P_M} = \frac{1}{T_{2M}} + \frac{1}{T_{2O}} \tag{5}$$

The value of $(T_{2M})^{-1}$ is given by[9,10]

$$\frac{1}{T_{2M}} = \frac{1}{\langle r_i^{6}\rangle}\,\frac{(\gamma_I g\beta)^2(S)(S+1)}{15}\,f_D(\tau_D) + \frac{1}{3}\left(\frac{A}{\hbar}\right)^2 (S)(S+1) f_e(\tau_e) \tag{6}$$

where the first term gives the electron–nuclear dipolar interaction and the second term gives the scalar interaction, and $\langle 1/r_i^6\rangle$ is the average magnitude of the reciprocal of the sixth power of the vector connecting the interacting spins, and $(A/\hbar)$ is the scalar coupling constant. The functions $f_D(\tau_D)$ and $f_e(\tau_e)$ depend on the dipolar (τ_D) and electronic (τ_e) correlation times. If ω_I and ω_e are the precessional frequencies of the proton and electron respectively $\omega_I << \omega_e$, and normally $\omega_I^2\tau_e^2 << 1$, $\omega_I^2\tau_D^2 << 1$, then[11]

$$f_D(\tau_D) = 7\tau_{D1} + \frac{13\tau_{D2}}{1 + \omega_e^2\tau_{D2}^2} \tag{7}$$

$$f_e(\tau_e) = \tau_{e1} + \frac{\tau_{e2}}{1 + \omega_e^2\tau_{e2}^2} \tag{8}$$

where

$$\frac{1}{\tau_{D1}} = \frac{1}{\tau_{e1}} + \frac{1}{\tau_r} = \left(\frac{1}{T_{1e}} + \frac{1}{\tau_M}\right) + \frac{1}{\tau_r} \tag{9}$$

$$\frac{1}{\tau_{D2}} = \frac{1}{\tau_{e2}} + \frac{1}{\tau_r} = \left(\frac{1}{T_{2e}} + \frac{1}{\tau_M}\right) + \frac{1}{\tau_r} \tag{10}$$

and τ_r is the rotational correlation time of the paramagnetic complex, T_{1e} and T_{2e} are the longitudinal and transverse electron spin relaxation times respectively, and τ_M is the lifetime of a solvent molecule in the first coordination sphere of the metal ion.

In order to describe the temperature dependence of T_{2M}^{-1} and T_{2O}^{-1} an exponential function is normally used. This assumes, in effect, that $\omega_e^2\tau^2$ terms in eq 7 and 8 are smaller than one, and that τ_{D1}, τ_{D2}, τ_{e1}, and τ_{e2} have the same temperature dependence. The latter assumption is based on the idea that these correlation times will directly or indirectly follow the Debye–Stokes–Einstein relationship

$$\tau_C = \frac{4\pi r^3}{3kT}\eta \tag{11}$$

at least in that the temperature dependence of τ_C will be given by eq 11.[12] In general the temperature dependence of the solvent viscosity can be described by

$$f_T(\eta) = \eta_\infty \exp(E/T) \tag{12a}$$

or for water[13]

$$f_T(\eta) = \eta_\infty \exp(E/T^3) \tag{12b}$$

If $(T_{2P}P_M)^{-1} \propto \tau_C$, then the temperature dependence should be given by

$$(T_{2P}P_M)^{-1} = Cf_T(\eta)/T \tag{13}$$

where C is a proportionality constant. Equation 13 was used here to determine if deviations from simple exponential behavior were due to chemical equilibria or just viscosity effects. It was also of interest to determine if eq 12 could be used to reduce the number of unknowns, since $f_T(\eta)$ is a known, in systems where the temperature dependences of T_{2M}^{-1} and T_{2O}^{-1} are not well defined.

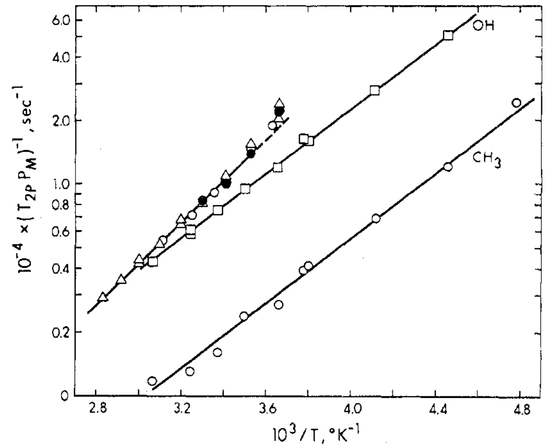


Figure 1. Temperature dependence of $(T_{2P}P_M)^{-1}$: upper curve, Co(*trans*-[14]diene)$^{2+}$ in water (ClO_4^-, (Δ) 60 MHz, (●) 100 MHz; BF_4^-, (○) 60 MHz); lower curves, Co(*trans*-[14]diene)(BF_4)$_2$ in methanol at 60 MHz.

In this work it must be decided whether exchange is slow and the results should be described by eq 4, or exchange is fast and the results should be described by eq 5. Clearly the decision must rest on a comparison of experimental to calculated values of $(T_{2P}P_M)^{-1}$. The calculations will be based on previous measurements of τ_r, measurements of τ_{e2} where possible, and estimated r_i and d_0 values.

It might be added that the observation of a shift of the solvent resonance provides strong evidence for fast exchange. Shifts due to second coordination sphere interactions are normally too small to be observed. In the fast exchange limit the observed chemical shift is given by

$$\Delta\omega_{\text{obsd}} = -P_M\Delta\omega_M \tag{14}$$

where $\Delta\omega_M$ is the shift of the solvent proton in the first coordination sphere of the metal ion, and a downfield shift gives a positive $\Delta\omega_{\text{obsd}}$. The well-known expression for $\Delta\omega_M$[14] can be used to calculate the scalar coupling constant ($A/\hbar$ radians sec^{-1}) when the effective magnetic moment of the paramagnetic ion (μ_{eff}) is known. If μ_{eff} is independent of temperature then the temperature dependence of the observed shift may be expressed as

$$\Delta\omega_{\text{obsd}}/P_M = -\Delta\omega_M = C_\omega/T \tag{15}$$

Co(*trans*-[14]diene)$^{2+}$ in Water. The magnetic susceptibility of a 7.34 × 10^{-2} *m* solution of Co(*trans*-[14]diene)(ClO_4)$_2$ in water, with 10% acetone as an internal standard, was measured between −10 and 90°. An effective magnetic moment of 2.07 μ_B was calculated from $\mu_{\text{eff}} = 2.839\cdot(\chi_{M(\text{cor})}(T + 42))^{1/2}$, where $\chi_{M(\text{cor})}$ has been corrected for the diamagnetism of the Schiff base ligand (213 cgs units).[15] The value of μ_{eff} is consistent with a low-spin cobalt(II) complex.[16]

The temperature dependence of $(T_{2P}P_M)^{-1}$ for this system is shown in Figure 1. The data below 10°C deviate somewhat from a simple exponential temperature dependence. The NMR line widths are independent of frequency, therefore these deviations cannot be ascribed to $\tau_M\Delta\omega_M^2$ contributions to $(T_{2P}P_M)^{-1}$. Since μ_{eff} does not change in this temperature range it seems most probable that the deviation is due to the nonexponential temperature dependence of the viscosity of water near the freezing point.

The viscosity of water from 0 to 90°[17] can be fitted, to better than 0.5%, by eq 12b, and the parameters are given in Table I. If this $f_T(\eta)$ is used in eq 13 then E is within 15% of that for the pure solvent. This difference in E is not considered significant because the data can be calculated to within 5%

Table I. Temperature Dependence Fitting Parameters

Metal complex	Solvent	Viscosity, cP		$(T_{2P}P_M)^{-1}$, sec^{-1}	
		$10^2 \times \eta_\infty$	E^a	$10^4 \times C$	E^a
Co(*trans*[14]diene)$^{2+}$	H_2O^b	9.039	4.106×10^7	21.6	6.850×10^7
Co(*trans*[14]diene)$^{2+}$	CH_3OH^c	0.861	1.233×10^3	1.34^d 0.329^e	$1.515 \times 10^{3\,d}$ $1.515 \times 10^{3\,e}$
Co(*trans*[14]diene)$^{2+}$	CH_3CN^c	1.52	9.260×10^2	1.36	1.120×10^3
CoCR^{2+}	$(CH_3)_2NCHO^c$	1.99	1.102×10^3	1.915^f	$1.535 \times 10^{3\,f}$
CuCR^{2+}	H_2O^b	9.039	6.016×10^7	3.54	5.657×10^7
CuCR^{2+}	$(CH_3)_2NCHO^c$	1.99	1.102×10^3	$2.52^{f,g}$	$1.173 \times 10^{3\,f,g}$

[a] Units are °K, except °K^3 for H_2O. [b] Equation 12b was used. [c] Equation 12a was used. [d] For the OH proton. [e] For the CH_3 protons. [f] For the CH proton. [g] For results above 0°C.

Table II. Summary of Results and Analysis

Complex	Co(*trans*-[14]diene)$^{2+}$				Co-CR^{2+}	CuCR^{2+}	
Solvent	H_2O	CH_3OH		CH_3CN	DMF	H_2O	DMF
Proton	OH	OH	CH_3	CH_3	CH	OH	CH
$10^{-3}(T_{2P}P_M)^{-1}$, sec^{-1} [a]	9.30	7.30	1.80	2.25	10.8	10.0	4.30
$10^{-3}(T_{2M})_D^{-1}$, sec^{-1} [b]	6.55	4.86	0.89	0.23	9.10	4.53	2.60
$10^{-3}(T_{2M})_S^{-1}$, sec^{-1} [b]		0.90^c		1.71			
$10^{-3}(T_{2O})^{-1}$, sec^{-1} [b]	2.75	1.55	0.90	0.31	1.70	5.50	1.70
r_i, Å^d	2.90	2.95	3.90	5.30	3.20	3.09	3.95
d_0, Å^d	4.65	4.00	4.80	9.40	5.75	4.65	5.75
$10^{11}\tau_r$, sec	4.5	3.7	3.7	6.2	11.5	4.5	11.5
$10^9 T_{2e}$, sec	1.2			1.4	0.3		

[a] Experimental value at 25° assuming $n = 2$ for Co(*trans*[14]-diene)$^{2+}$, and $n = 1$ for CoCR^{2+} and CuCR^{2+}. [b] $(T_{2M})_D$, $(T_{2M})_S$, and (T_{2O}) are the calculated dipolar, scalar, and outer-sphere contributions, respectively. [c] Estimated by difference. [d] Values estimated from models and previous work (ref 18 and 19).

with a pre-exponential factor of 2.75×10^5 K sec^{-1} and an exponential factor of 6.016×10^7 K^3.

Calculations based on a primary solvent coordination number of 2, with interaction distances and correlation times, listed in Table II, indicate that $(T_{2P}P_M)^{-1}$ is due to the sum of inner- and outer-sphere dipolar contributions. This result shows that the water proton exchange is rapid with a rate constant $>2 \times 10^4$ sec^{-1} at 0°C.

The EPR spectrum of Co(*trans*-[14]diene)$(ClO_4)_2$ in water, in the absence of oxygen, showed eight hyperfine lines due to coupling to the cobalt nucleus, with a coupling constant of 82 G. The line width of the narrowest hyperfine line was 43 G yielding $T_{2e} = 1.2 \times 10^{-9}$ sec. Since $T_{1e} \geq T_{2e}$ the apparently negligible scalar contribution to $(T_{2P}P_M)^{-1}$ implies that $(A/\hbar)$ is small. This is consistent with our failure to observe shifts in this system.

From the observation that $T_{2e} > 10^{-10}$ sec it is reasonable to conclude that the dipolar correlation time given in Table I is actually τ_r. The value is in good agreement with the τ_r of 4.1×10^{-11} sec obtained from an analysis of the EPR spectrum of VO^{2+} in water.[18]

Co(*trans*-[14]diene)$^{2+}$ in Methanol. The temperature dependences of $(T_{2P}P_M)^{-1}$ for the hydroxyl (OH) and methyl (CH_3) protons are shown in Figure 1. Calculations of the inner- and outer-sphere dipolar contributions can be based on interaction distances and the rotational correlation time was found previously for vanadyl in methanol.[19] These calculations (Table II) clearly show that there must be both inner- and outer-sphere dipolar broadening, and therefore the rate of inner-sphere solvent molecule exchange must be rapid with a rate constant $>5 \times 10^4$ sec^{-1} at −50°.

It must be noted however that the calculated dipolar contribution falls short of accounting for the observed $(T_{2P}P_M)^{-1}$ for the OH proton. The difference may be due to a scalar contribution if $(A/\hbar)_{OH} \approx 6 \times 10^6$ radians sec^{-1}, and $T_{1e} = T_{2e} = 1 \times 10^{-9}$ sec. For the concentrations used this value of $(A/\hbar)_{OH}$ predicts a negligible OH proton shift. The scalar contribution for the CH_3 protons appears to be much less because of a smaller coupling constant. If $(A/\hbar)_{CH_3}$ is 20 times smaller than $(A/\hbar)_{OH}$, as observed for cobalt(II) in methanol,[8] then the scalar relaxation of the methyl protons would be <1% of the observed $(T_{2P}P_M)^{-1}$. This estimate is admittedly questionable because cobalt(II) is high spin in methanol, whereas Co(*trans*-[14]diene)$^{2+}$ is low spin.

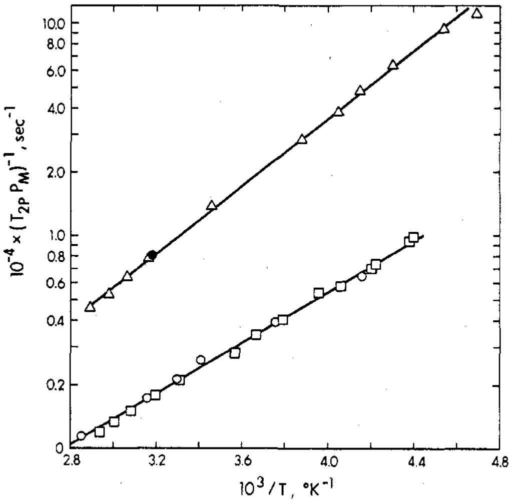


Figure 2. Temperature dependence of $(T_{2P}P_M)^{-1}$: lower curve, Co(*trans*-[14]diene)$^{2+}$ in acetonitrile at 60 MHz (ClO_4^- (□); BF_4^- (○)); upper curve, CoCR$(ClO_4)_2$ in DMF ((△) 60 MHz; (●) 100 MHz).

The variation of the viscosity of methanol[20] with temperature, between 45 and −50°, can be described by eq 12b, with the parameters given in Table I. The results of fitting the $(T_{2P}P_M)^{-1}$ data to eq 13 are given also in Table I. The difference between the E values is just outside the estimated error of ±0.10 and ±0.14 K, respectively. The discrepancy does not seem large enough to merit extensive comment. Possible reasons for the difference are noted in the discussion of CoCR^{2+} and CuCR^{2+} in DMF where the effect is more significant.

Co(*trans*-[14]diene)$^{2+}$ in Acetonitrile. The temperature dependence of $(T_{2P}P_M)^{-1}$ for this system is shown in Figure 2. Upfield shifts in the range of 10 to 20 Hz, shown in Figure 3, are given by

$$\Delta\omega_{\text{obsd}} = \frac{1.27 \times 10^6}{T} + 7.54 \times 10^2 \qquad (16)$$

The temperature-independent term is not predicted by eq 15, but could result from temperature-independent paramagnetism.[21] For purposes of estimating the scalar contribution to $(T_{2P}P_M)^{-1}$ the scalar coupling constant $(A/\hbar)$ of -2.24×10^6 radians sec^{-1} was calculated from $\Delta\omega_{\text{obsd}}$ at 25° and μ_{eff} of 2.07.

The calculated inner- and outer-sphere dipolar contributions

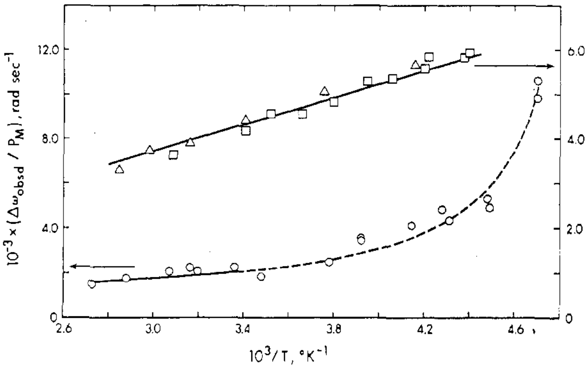


Figure 3. Temperature dependence of $(\Delta\omega_{obsd}/P_M)$: Co(*trans*-[14]diene)$^{2+}$ in acetonitrile at 60 MHz (ClO_4^- (□); BF_4^- (△)). $CuCR(BF_4)_2$ in DMF at 60 MHz (○).

to $(T_{2P}P_M)^{-1}$ (Table II) account for only 25% of the observed value. The remainder is easily explained by the scalar interaction with the $(A/\hbar)$ value calculated above, and $T_{1e} = T_{2e} = 1.36 \times 10^{-9}$ sec at 25°.

The EPR spectrum of Co(*trans*-[14]diene)$(BF_4)_2$ in acetonitrile has the expected eight lines with a coupling constant of 70 G. The line width of the narrowest line is 48 G, giving $T_{2e} = 1.4 \times 10^{-9}$ sec. The latter is in excellent agreement with the value needed to explain the scalar contribution to $(T_{2P}P_M)^{-1}$.

For acetonitrile the viscosity[22] from 45 to −40° can be described by eq 12a with the parameters given in Table I. The E value obtained from temperature dependence of the NMR line broadening (Table I) is in satisfactory agreement with that obtained from the viscosity in that it is probably within the experimental error on each quantity.

With the limiting condition that $\tau_M < T_{2M}$ a lower limit of 1×10^4 sec^{-1} is calculated for the solvent exchange rate at −45° in this system.

$CoCR^{2+}$ in *N,N*-Dimethylformamide. The magnetic susceptibility of a 2.52×10^{-2} *m* solution of the perchlorate salt of this complex was measured[7] at 35°. A magnetic moment of 1.85 μ_B was found after applying a diamagnetic correction of −163 cgs units.[15] The magnetic moment of $CoCR^{2+}$ in DMF is typical of low-spin cobalt(II).

The temperature dependence of $(T_{2P}P_M)^{-1}$ for the solvent formyl proton is shown in Figure 2. The value of $(T_{2P}P_M)^{-1}$ at 25° is consistent with fast exchange and proton relaxation controlled by both inner- and outer-sphere dipolar interactions (Table II). It should be noted that a primary solvation number (n) of one gives a more reasonable $\langle r_i \rangle$ of 3.2 Å compared to 3.58 if $n = 2$. Of course this is poor evidence for five coordinate cobalt(II), but is consistent with the observation[4] that $CoCR^{2+}$ does not form bis adducts with strong Lewis bases.

The absence of observable chemical shifts prevents the calculation of a scalar coupling constant and the scalar contribution to relaxation. However, if a maximum shift of 2 Hz were assumed, then $|A/\hbar| < 6 \times 10^6$ radians sec^{-1}.

The EPR spectrum of $Co(CR)(ClO_4)_2$ in DMF at 25° gave only a broad unresolved line from which $T_{2e} \approx 3 \times 10^{-10}$ sec. This combined with the above estimate of $(A/\hbar)$ predicts that the scalar contribution is 10% of the observed $(T_{2P}P_M)^{-1}$.

The viscosity of DMF from 15 to 120°[23] is described by eq 12a and the parameters in Table I. However, application of eq 13 to the relaxation data yields an E value 0.14 K greater than that for viscosity. This difference would seem to be significant especially since the difference is only 0.07 K for the CuCR system discussed subsequently. A temperature-dependent five–six-coordinate equilibrium might explain the higher exponential factor of $CoCR^{2+}$ in DMF. The six-coordinate species, with two solvent molecules in the first coordination sphere, might show about twice as much line broadening as the five-coordinate species. If the equilibrium shifts toward the six-coordinate species at low temperature then a higher than expected exponential factor would be found.

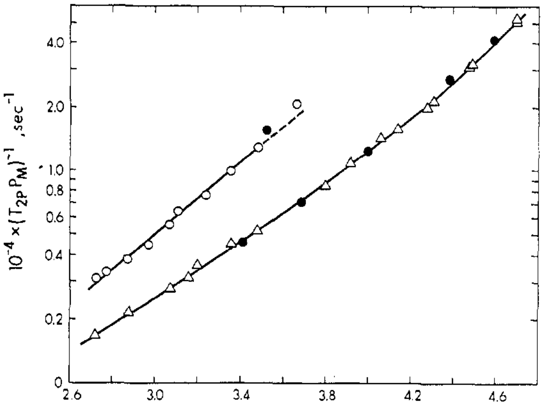


Figure 4. Temperature dependence of $(T_{2P}P_M)^{-1}$: upper curve, $CuCR(BF_4)_2$ in water ((○), 60 MHz; (●), 100 MHz); lower curve, $CuCR(BF_4)_2$ in DMF ((△) 60 MHz; (●) 100 MHz).

The results predict a lower limit of 1×10^5 sec^{-1} for the DMF exchange rate constant of $CoCR^{2+}$ at −60°.

$CuCR^{2+}$ in Water. The temperature dependence of $(T_{2P}P_M)^{-1}$ for this system is shown in Figure 4. No shifts could be detected, and one measurement at 100 MHz failed to indicate any frequency dependence of $(T_{2P}P_M)^{-1}$. A slightly nonexponential temperature dependence of $(T_{2P}P_M)^{-1}$ (indicated by a dotted line on Figure 4) is expected for the viscosity of water. The similarity of the exponential factor E in Table I to that for the solvent viscosity indicates the latter is the controlling factor in the temperature dependence of $(T_{2P}P_M)^{-1}$.

The observed $(T_{2P}P_M)^{-1}$ at 25° can be accounted for by one rapidly exchanging solvent molecule with the parameters given in Table II. The value of τ_R obtained here is in reasonable agreement with that for VO^{2+} (4.1×10^{-11} sec) and Co(*trans*-[14]diene)$^{2+}$ (4.5×10^{-11} sec).

The absence of chemical exchange effects on $(T_{2P}P_M)^{-1}$ only allows a lower limit for the solvent exchange rate constant of $>2 \times 10^4$ sec^{-1} at 0° to be estimated.

$CuCR^{2+}$ in *N,N*-Dimethylformamide. The temperature dependence of $(T_{2P}P_M)^{-1}$ and $(\Delta\omega_{obsd}/P_M)$ is shown in Figures 4 and 3, respectively. Measurements at 60 and 100 MHz indicate that $(T_{2P}P_M)^{-1}$ is independent of frequency. This shows that a $\tau_M\Delta\omega_M^2$ term is not causing the upward bend of the curve in Figure 4. The shifts (Figure 3) show an unusual temperature dependence, increasing much more rapidly than predicted by eq 15 at temperatures below ~0°.

These features are at least consistent with the equilibrium

$$CuCR(DMF)^{2+} + DMF \rightleftarrows CuCR(DMF)_2^{2+} \qquad (17)$$

with the latter species favored at lower temperatures. Unfortunately since a low-temperature limiting region is not reached it is not possible to calculate the $(T_{2P}P_M)^{-1}$ and $\Delta\omega_{obsd}$ for the proposed $CuCR(DMF)_2^{2+}$. However, the shifts above 0° obey eq 15 and permit calculation of a scalar coupling constant of 1.28×10^6 radians sec^{-1} for $CuCR(DMF)^{2+}$ if μ_{eff} is assumed to have the spin only value.

The $(T_{2P}P_M)^{-1}$ data above 0°C were fitted to eq 12a and the exponential factor is quite close to that found for the viscosity of pure DMF (Table I).

The value of $(T_{2P}P_M)^{-1}$ at 25° can be explained on the basis of inner- and outer-sphere dipolar relaxation[24] due to one rapidly exchanging solvent molecule. The inner-sphere interaction distance r_i of 3.95 Å is considerably larger than the value of 3.1 Å for VO^{2+} in DMF,[24] or 3.2 Å for Co(*trans*-[14]diene)$^{2+}$.[25] The longer distance for $CuCR(DMF)^{2+}$ could be due to tetragonal distortion with elongation of the Cu–DMF bond.

A lower limit of 5×10^4 sec^{-1} at −60° is estimated for the solvent exchange rate constant in this system.

Discussion

For all the systems described here the solvent exchange rate appears to be larger than the solvent proton relaxation rate in the first coordination sphere of the metal ion ($\tau_M^{-1} > T_{2M}^{-1}$). The alternative, that exchange is slower, would require that the observed line broadening is entirely due to outer-sphere effects. This seems unlikely because it requires that the $(T_{2O})^{-1}$ values in Table I be increased by ~30%. The latter can only be done by making d_0 unreasonably short (by a factor of ~1.5), or by increasing the correlation times by about a factor of 3. Such a change is considered unlikely because the correlation times used here are consistent with the EPR spectral line widths of various vanadyl complexes[18] in various solvents, and have been used successfully in the interpretation of other NMR systems.[26–28]

The estimates of the lower limit of the solvent exchange rates do not indicate that these systems are very labile. However, the limits given are conservative in that they apply at the lowest temperature attained in the particular solvent. If a rather low activation energy for exchange of 5 kcal mol^{-1} is assumed, then the exchange rates at 25° for Co(*trans*-[14]diene)$^{2+}$ in methanol, acetonitrile, and DMF are calculated to be $>9 \times 10^5$ sec^{-1}, $>1.3 \times 10^5$ sec^{-1}, and $>3 \times 10^6$ sec^{-1}, respectively. These values are about an order of magnitude greater than those for high-spin, hexasolvated, cobalt(II) complexes. However, the estimates are too uncertain to permit any discussion of the effect of the Schiff base and the low-spin configuration on lability.

The results in water, methanol, and acetonitrile, at least, indicate that eq 12 and 13 can be used to describe the temperature dependence of $(T_{2P}P_M)^{-1}$ in the absence of exchange effects (i.e., T_{2M}^{-1}). The added $1/T$ factor in eq 13 does not affect the fitting of the results, but makes the exponential factor smaller, and in much better agreement with that predicted from the temperature dependence of the solvent viscosity. It would appear that ambiguities encountered in fitting previously studied systems[28,29] could be significantly reduced by the use of eq 13 with the temperature dependence of the viscosity $(f_T(\eta))$ treated as a known function.

Acknowledgment. Support for this research by the National Research Council of Canada is gratefully acknowledged. L.R. wishes to thank the National Research Council for support through a postgraduate scholarship.

Registry No. Co(*trans*-[14]diene)$(ClO_4)_2$, 15387-88-9; $CoCR(ClO_4)_2$, 57066-21-4; $CuCR(BF_4)_2$, 57066-22-5; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CN, 75-05-8; DMF, 68-12-2; Co(*trans*-[14]diene)$(BF_4)_2$, 57066-23-6.

References and Notes

(1) N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).
(2) K. M. Long and D. H. Busch, *Inorg. Chem.*, **9**, 505 (1970).
(3) L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **10**, 2199 (1971).
(4) L. L. Rusnak, Ph.D. Thesis, Department of Chemistry, University of Alberta, Edmonton, Canada, 1971.
(5) R. E. Kitsen, *Anal. Chem.*, **22**, 664 (1950).
(6) L. R. Rich and G. L. Stucky, *Inorg. Nucl. Chem. Lett.*, **1**, 61 (1965).
(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(8) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).
(9) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(10) N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).
(11) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).
(12) K. J. Johnson, J. P. Hunt, and H. W. Dodgen, *J. Chem. Phys.*, **51**, 4493 (1969).
(13) T. A. Litovitz, *J. Chem. Phys.*, **20**, 1088 (1952).
(14) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).
(15) A. E. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, N.Y., 1967, pp 4–8.
(16) E. K. Barefield, D. H. Busch, and S. M. Nelson, *Q. Rev., Chem. Soc.*, **22**, 457 (1968).
(17) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties", Pergamon Press, New York, N.Y., 1965.
(18) N. S. Angerman and R. B. Jordan, *J. Chem. Phys.*, **54**, 837 (1971).
(19) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 1824 (1969).
(20) P. G. Sears, R. R. Holmes, and L. R. Dawson, *J. Electrochem. Soc.*, **102**, 145 (1955).
(21) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1966, p 281.
(22) J. P. Karnes, *Diss. Abstr.*, **26**, 1367 (1965).
(23) "DMF Product Information Bulletin", E. I. du Pont de Nemours, Wilmington, Del.
(24) R. B. Jordan and N. S. Angerman, *J. Chem. Phys.*, **48**, 3983 (1968).
(25) The scalar interaction will not be significant as long as $T_{2e} = T_{1e} < 10^{-9}$ sec.
(26) L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **10**, 2686 (1971).
(27) L. L. Rusnak, J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.*, **11**, 199 (1972).
(28) L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **14**, 988 (1975).
(29) L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **11**, 196 (1972).

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Aqueous Complexes of Gallium(III)

WESLEY R. HARRIS and ARTHUR E. MARTELL*

Received July 31, 1975 AIC50565Y

The dilute aqueous coordination chemistry (25 °C, $\mu = 0.10$) of gallium(III) is described with 16 multidentate ligands which include various polyaminopolycarboxylic acids, hydroxyalkylaminocarboxylic acids, polycarboxylic acids, and phenolic aminocarboxylic acids. Quantitative interactions have been measured and equilibrium constants calculated through spectrophotometric determination of metal–metal competition, potentiometric measurement of hydrogen ion displacement, and ligand–ligand competition determined by potentiometric measurement of hydrogen ion concentration. Depending on the ligand and pH, the metal-containing species formed were found to fall within the bounds of the following stoichiometry: $Ga_a(OH)_bH_cL_d$, where $1 < a < 3$, $0 < b < 4$, $0 < c < 3$, $1 < d < 3$. The conditions and limitations for the applicability of each method are delineated and the results are discussed in terms of both internal consistency and relevance to previously published work.

Introduction

Since it has been reported that the gallium(III) ion exhibits considerable anticancer activity,[1,2] the possibility of using various ligands as metal carriers in chemotherapy has increased the need for a more extensive study of the aqueous coordination chemistry of gallium. The literature on this subject is very limited and in most cases inconsistent and contradictory. For these reasons the protonation, stability, and hydrolysis constants of the gallium chelates of the multidentate ligands *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED), ethylene-1,2-bis(*o*-hydroxyphenylglycine) (EHPG), triethylenetetraaminehexaacetic acid (TTHA), diethylene-