

molecular correlation time (τ_c)^{2,3} which may be considered a measure of the rate of molecular tumbling. Using a simple spherical model, τ_c can be expressed in terms of eq 1 in

$$\tau_c = 4\pi\eta a^3 / 3kT \quad (1)$$

which η is the viscosity, a is the radius of the sphere, k is Boltzmann's constant, and T is the absolute temperature.⁶ In the four cases reported here, we may assume that η shows the same dependence on temperature (see above discussion) and any significant difference in spectral behavior is due most likely to a change in molecular volume ($4\pi a^3/3$; eq 1). As τ_c increases due to an increase in molecular volume, quadrupole-induced ¹⁰B and ¹¹B spin-state interconversion becomes more efficient and ¹H-^{10,11}B spin decoupling occurs. It is clear from a consideration of eq 1 that τ_c will be greater for the larger halocarboranes than for the smaller unsubstituted carboranes. Thus, more efficient quadrupole-induced ¹H-^{10,11}B spin decoupling in the halocarboranes is manifested by spectral sharpening at higher temperatures (Figures 2-4) as compared to the unsubstituted compounds (Figure 1).

An additional mechanism for ¹⁰B and ¹¹B nuclear spin relaxation which must be considered involves direct intramolecular or intermolecular interaction of the nuclear spins with tumbling dipoles in solution.³ Indeed, the significantly greater dipole moment for *o*-carborane ($\mu = 4.3 \text{ D}^7$) as compared to *m*-carborane ($\mu = 2.8 \text{ D}^7$) necessitates some consideration of this mechanism. Assuming an essentially spherical geometry for *o*- and *m*-carborane,⁸ para B-C and B-B distances of 3.3 Å, B-H and C-H bond lengths of 1.1 Å, and a van der Waals radius for hydrogen of 1.2 Å, a molecular radius of 4.0 Å is calculated for both compounds. Thus, in applying eq 1 to *o*- and *m*-carborane at a given temperature, it may be assumed that η , a , and T have the same respective values for both compounds and, therefore, τ_c is the same for both species. Since all the ¹H chemical shifts in *o*- or *m*-carborane are essentially identical and the ¹H-^{10,11}B spin-spin coupling constants in both compounds are very similar,² the almost coincident coalesced ¹H nmr spectra for *o*-carborane at -108° (see ref 4, Figure 3) and *m*-carborane at -110° (Figure 1) reveal the boron nuclear spin relaxation rates for the two compounds to be quite close at essentially the same temperature. This observation is consistent with the calculated identical τ_c values (eq 1). If dipolar interactions were a significant factor in boron nuclear spin relaxation, very different spectra at a given temperature would be expected for these two compounds of different dipole moment. Thus, it may be assumed that under these experimental conditions boron quadrupolar relaxation provides the principal nuclear spin relaxation mechanism for boron nuclei in these two compounds.³ It should be noted at this point that the ¹H nuclear spin relaxation rate should also be affected by dipolar interactions. However, the sharp carborane C-H resonances observed to very low temperatures (Figures 1-4) indicate that this effect is not very important in the temperature range of interest in this study and is consistent with our conclusions regarding the dominant mechanism of boron nuclear spin relaxation. A similar approach may be applied to 9,12-dibromo-*o*-carborane ($\mu = 7.2 \text{ D}^{7a,9}$) and 9,10-dibromo-*m*-carborane ($\mu = 5.4 \text{ D}^9$). In order to estimate " a " (eq 1) for

the two dibromo compounds, the distances across all six pseudo-fivefold rotation axes were averaged assuming para B-C and B-B distances of 3.3 Å, B-H and C-H bond lengths of 1.1 Å, a B-Br bond length of 2.0 Å, and van der Waals radii for hydrogen and bromine of 1.2 and 1.95 Å, respectively. This results in an average molecular radius (a ; eq 1) of 4.3 Å for both compounds. The higher nmr coalescence temperatures for the two dibromocarboranes (Figures 2 and 3) as compared to *o*- and *m*-carborane (Figure 1) are consistent with increasing molecular volume and increasing τ_c (eq 1). However, it should be noted that the nmr spectrum of 9,12-dibromo-*o*-carborane with the higher dipole moment sharpens at slightly higher temperatures (Figure 2) as compared to 9,10-dibromo-*m*-carborane (Figure 3). This observation may indicate an increasing importance of dipolar mechanisms for boron nuclear spin relaxation in these compounds of high dipole moment. An average radius of 4.7 Å is calculated for 8,9,10,12-tetrabromo-*o*-carborane. No dipole moment data are available although the higher coalescence temperature (Figure 4) as compared to *o*- and *m*-carborane is consistent with both increased molecular volume and dipole moment.

Thus, in any variable-temperature ¹H nmr study of carborane derivatives, increasing molecular volume will lead very likely to ¹H-^{10,11}B spin-spin coupling coalescence at increasing temperatures due to increasingly efficient ^{10,11}B nuclear spin relaxation.

Experimental Section

The dnmr spectra were recorded using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.⁹ Heteronuclear spin decoupling was performed using an NMR Specialties SD-60B heteronuclear spin decoupler.

9,12-Dibromo-1,2-dicarba-*closo*-dodecaborane(12) and 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12) were prepared by the methods of Smith, Knowles, and Schroeder.¹⁰ 8,9,10,12-Tetrabromo-1,2-dicarba-*closo*-dodecaborane(12) was prepared by an analogous procedure.

Acknowledgment. We are grateful for Public Health Service Research Grant No. CA12025-01 and to Olin Mathieson Chemical Corp. for samples of *o*- and *m*-carborane.

Registry No. 1, 16986-24-6; 3, 17702-36-2; 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12), 17032-20-1; 8,9,10,12-tetrabromo-1,2-dicarba-*closo*-dodecaborane(12), 20755-68-4; ¹⁰B, 14798-12-0; ¹¹B, 14798-13-1.

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Contribution from the Department of Chemistry,
North Texas State University, Denton, Texas 76203

Synthesis and Magnetic Properties of Copper(II) Complexes of *N*-(Hydroxyalkyl)pyrrole-2-carboxaldehydes

C. R. Pauley and L. J. Theriot*

Received December 21, 1973

AIC309131

Spin-spin coupling in polynuclear copper(II) complexes remains of considerable interest and significant developments have been reported. Bertrand and Kelley¹ have recently

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Table I. Analytical Data for the Complexes

Complex	% C		% H		% N		% Cu	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Cu(pyrr-propanolamine)	44.96	44.36	4.72	4.65	13.11	13.15	29.73	29.70
Cu(pyrr-ethanolamine)	42.15	41.45	4.04	3.97	14.03	13.91	31.85	31.73
Cu(pyrr-isopropanolamine)	44.96	45.15	4.72	4.96	13.11	12.65	29.73	29.00

reported the structures and room-temperature magnetic moments of Cu(acac-propanolamine) and Cu(acac-ethanolamine). The structures and properties of these two complexes are quite different. Cu(acac-propanolamine) is dimeric with a room-temperature moment of 0.41 BM and Cu(acac-ethanolamine) is tetrameric with a moment of 1.87 BM at room temperature. We have been interested in the factors associated with these dramatic changes in magnetic properties. Schiff base ligands prepared from pyrrole-2-carboxaldehyde and alcoholamines provide the possibility of investigating the effect of ring size on the structure and magnetic properties of complexes of this type.

Experimental Section

Chemicals. Pyrrole-2-carboxaldehyde and isopropanolamine were obtained from the Aldrich Chemical Co. Propanolamine was obtained from the Eastman Organic Chemical Co. Ethanolamine was obtained from the Matheson Coleman and Bell Co. Copper(II) acetate monohydrate and sodium hydroxide were obtained from the J. T. Baker Chemical Co.

Preparation of Complexes. Cu(pyrr-propanolamine). This complex has been prepared by Bertrand and Kirkwood² and we have followed their procedure. Pyrrole-2-carboxaldehyde (0.025 mol) was dissolved in 50 ml of anhydrous methanol. Propanolamine (0.025 mol) was added to the solution which was stirred at reflux for 30 min. The resulting yellow Schiff base was slowly added to copper(II) acetate monohydrate (0.025 mol) in 100 ml of anhydrous methanol. The mixture was stirred at reflux for 24 hr after which it was filtered, depositing a brown solid. The powder was washed with anhydrous methanol and dried in a vacuum desiccator at 100° for several hours. The yield is 80%. The complex was recrystallized from chloroform giving brown needlelike crystals.

Cu(pyrr-ethanolamine). This complex was prepared as above with the exception that 0.050 mol of sodium hydroxide was also added to the mixture. The complex was recrystallized from chloroform giving olive green microcrystals.

Cu(pyrr-isopropanolamine). This complex also required the addition of 0.050 mol of sodium hydroxide. The complex was recrystallized from pyridine giving green microcrystals.

Physical Measurements. Magnetic susceptibilities were determined by the Gouy method. The precision of the magnetic moments is $\pm 2\%$ or better. All measurements were calibrated with $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the standard. The diamagnetic corrections for the ligand and metal atoms were computed using a standard source.³ The susceptibilities were corrected for TIP using a value of 60×10^{-6} cgsu. Electron spin resonance spectra were obtained with a Varian V-4502-12 X-band spectrometer using 100-kc modulation and a 9-in. electromagnet. Cylindrical quartz sample tubes and a rectangular cavity were employed. For liquid nitrogen temperatures a quartz dewar which fitted into the cavity was used. Each sample contained a minute sample of finely powdered DPPH as an internal reference. The frequency was monitored with a Hewlett-Packard Model 5340A automatic microwave frequency counter. Infrared spectra were obtained on a Perkin-Elmer Model 621 instrument. Both Nujol and Fluorolube mulling techniques were employed. The electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. Solid-state spectra were obtained in Nujol mulls and solution spectra were obtained in chloroform using 1-cm matched quartz cells. Molecular weight measurements were obtained in chloroform at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. Several concentrations were used in the measurements.

Analyses. Copper analyses were determined on a Sargent-Welch electrolytic analyzer by plating copper onto a platinum electrode.

Carbon, hydrogen, and nitrogen analyses were obtained from PCR, Gainesville, Fla. Analytical data are presented in Table I.

Results and Discussion

The lack of $\nu(\text{OH})$ band in the infrared spectra indicates that the complexes are solvent free and do not have coordinated water. Molecular weight measurements indicate that Cu(pyrr-propanolamine) is dimeric in Spectral Grade chloroform, having a molecular weight of 449 compared to a calculated molecular weight of 427. The preparation and structure have recently been reported and the coordination around each copper is essentially square planar.² The electronic spectrum of the complex exhibits a broad absorption band around $17,900 \text{ cm}^{-1}$ in both Nujol and chloroform solutions ($\epsilon 129 \text{ l. mol}^{-1} \text{ cm}^{-1}$). On the basis of the magnetic data presented in Table II the complex exhibits antiferromagnetic interactions. The J value determined from the Bleaney and Bowers equation⁴ by averaging the results at each temperature was found to be -830 cm^{-1} . Recently a relationship between J and the bridging Cu-O-Cu angle has been established⁵ where as the bridging angle decreases, the magnitude of J increases. The reported structure and magnetic properties of Cu(pyrr-propanolamine) and Cu(acac-propanolamine) are consistent with this relationship.^{1,2} The esr of Cu(pyrr-propanolamine) is typical of a spin triplet,^{6,7} exhibiting four lines at 700, 1625, 5000, and 6200 G. These lines are assigned to H_{z_1} , $\Delta M_s = 2$, H_{1_2} , and H_{z_2} , respectively. In addition there is an absorption at 3300 G which is attributed to a spin-doublet monomeric copper(II) impurity in this complex.

Molecular weight measurements indicate that Cu(pyrr-ethanolamine) and Cu(pyrr-isopropanolamine) are tetrameric in chloroform (calcd 799, found 795; and calcd 855, found 848, respectively). The one band observed in the electronic spectrum of Cu(pyrr-ethanolamine) at $15,750 \text{ cm}^{-1}$ ($\epsilon 114 \text{ l. mol}^{-1} \text{ cm}^{-1}$) reflects distortion toward a trigonal-bipyramidal structure assuming the structure of these complexes are analogous to Cu(acac-ethanolamine).¹ The position of the band is similar to the reported spectrum of Cu(sal-ethanolamine).⁸ Similarly Cu(pyrr-isopropanolamine) has a broad band at $15,960 \text{ cm}^{-1}$ ($\epsilon 143 \text{ l. mol}^{-1} \text{ cm}^{-1}$). The magnetic moments of these complexes increase with decreasing temperatures, indicating some ferromagnetic coupling. Cu(acac-ethanolamine) has been cited as an example of a complex having both antiferromagnetic and ferromagnetic coupling with a singlet ground state.⁹ Without measurements down to liquid helium temperatures we cannot confirm a singlet ground state for these complexes. Moreover the bridging angle associated with the antiferromagnetic coupling in Cu(acac-ethanolamine) is 97.8° which is close to the crossover

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Table II. Magnetic Susceptibility Data for the Complexes

Complex	Temp, °K	$10^6 \times \chi_M^{\text{corr}}$, cgsu	μ_e , BM
Cu ^{II} (pyrr-propanolamine)	294	78	0.44
	265	44	0.34
	228	23	0.24
	189	16	0.20
	120	4	0.11
Cu ^{II} (pyrr-ethanolamine)	293	1521	1.89
	265	1731	1.92
	228	2090	1.96
	189	2645	2.00
	152	3396	2.03
	120	4348	2.05
	78	6958	2.08
Cu ^{II} (pyrr-isopropanolamine)	296	1370	1.80
	261	1628	1.84
	223	1856	1.82
	184	2408	1.88
	148	3056	1.90
	117	3915	1.91
	78	6163	1.96

angle to ferromagnetic coupling as represented in the work of Hatfield, *et al.*⁵ The possibility exist that all four copper(II) ions could be ferromagnetically coupled in our complexes. The interpretation of tetramers is not without controversy even when the structure is known.^{10,11} The use of the Bleaney and Bowers equation to approximate the true situation is fairly successful in the case of the weakly tetrameric acetyl-acetonemono(*o*-hydroxyanil)copper(II) complex. In this case this leads to J values of +22 and +124 cm⁻¹ for Cu-(pyrr-ethanolamine) and Cu(pyrr-isopropanolamine), respectively. The esr spectra of the tetramers are similar to the spectrum of dimeric Cu(pyrr-propanolamine). Cu-(pyrr-isopropanolamine) has bands at 750, 1680, 3300, 5000, and 6560 G. Resolution is not as good in the case of Cu(pyrr-ethanolamine) but the spectrum is similar. There has been little work with the spin quintet; however a recent report is available.¹² The transitions observed in these spectra could be associated with the $M_s = 0$ and ± 1 part of the spin quintet. The transitions associated with $M_s = \pm 2$ of the spin quintet, when seen, are usually at higher fields than employed with this spectrometer. The transition at 1680 G is assigned to $\Delta M_s = 2$.

In conclusion the important difference brought about by changes in the aminoalkoxide chain on the properties of Cu(acac-alcoholamine) complexes is retained in the Cu-(pyrr-alcoholamine) complexes. The change to a five-member ring has affected these properties only in changes of bond angles. The effect of the bond angles on the magnitude of the interaction is consistent with the correlation recently refined by Hatfield, *et al.*⁵ in that the magnitude of J increases as the bond angle decreases. The spectral changes are consistent with going from a square-planar to a distorted trigonal-bipyramidal arrangement of atoms around copper.

Acknowledgments. This research was supported by the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund. The authors wish to acknowledge preliminary discussions with Professor J. A. Bertrand at the start of this work.

Registry No. Cu(pyrr-propanolamine), 37820-94-3; Cu(pyrr-ethanolamine), 51380-64-4; Cu(pyrr-isopropanolamine), 51380-65-5.

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Contribution from the Department of Chemistry,
San Diego State University, San Diego, California 92115

Kinetics of the Reduction of Hexaammineruthenium(III) Ion by Vanadous Ion

Charles A. Jacks and Larry E. Bennett*

Received January 7, 1974

AIC40004R

The relative Marcus theory¹ has proven remarkably successful in rationalizing the rates of a substantial number of outer-sphere redox reactions between transition metal complexes.^{2,3} For reactions satisfying the Marcus relationship, the rate ratio for the reactions of two reductants with a common oxidant should depend only on the self-exchange rates and the difference in reduction potentials for the reductant couples (if small f terms are neglected).^{2,4} Thus, reduction by $V(H_2O)_6^{2+}$ has been found to be 10–60 times faster than by $Cr(H_2O)_6^{2+}$ with a number of oxidants.⁴ Heretofore, a notable exception appeared to be $Ru(NH_3)_6^{3+}$, with a reported rate of reaction with $V(H_2O)_6^{2+}$ ($80 M^{-1} sec^{-1}$, $I = 0.176 (ClO_4^-)$)⁵ being slightly lower than with $Cr(H_2O)_6^{2+}$ ($99 M^{-1} sec^{-1}$, $I = 0.079 (ClO_4^-)$).⁶ In connection with other studies we have investigated the vanadium reaction and measured a rate constant which yields a ratio to the chromous reaction of 13, *i.e.*, within the range observed with other oxidants.

Experimental Section

Materials. Solutions of vanadyl perchlorate were obtained by the reduction of reagent grade vanadium pentoxide at a platinum electrode in excess perchloric acid or from R. G. Linck, who prepared it by ion exchange from vanadyl sulfate (negative barium sulfate test). Reduction to $V(H_2O)_6^{2+}$ using either solution, under nitrogen or argon and either by electrolysis at a mercury cathode or with amalgamated zinc, gave indistinguishable kinetic results.

Initial concentrations of $V(H_2O)_6^{2+}$ were determined by spectrophotometry after reaction with excess $Co(NH_3)_5Cl^{2+}$ in perchloric acid or by assaying the remaining CrO_4^{2-} in alkaline solution ($\epsilon_{372} 4815^7$) after oxidation to VO_2^+ with excess $HCrO_4^-$ in perchloric acid, with good agreement between the methods.

The $Ru(NH_3)_6Cl_3$ salt was obtained from Matthey Bishop, recrystallized by the Armor procedure,⁸ and tested spectrophotometrically for purity.

Kinetic Measurements. The desired ionic strength was obtained by addition of standardized perchloric acid and dilution with doubly distilled water, making allowance for the production of Zn^{2+} and the consumption of acid during reduction to $V(H_2O)_6^{2+}$. The initial acidities of $V(H_2O)_6^{2+}$ solutions ranged from 0.040 to 0.099 M while those of $Ru(NH_3)_6^{3+}$ solutions ranged from 0.094 to 0.100 M . For runs at pH 3, VO_2^+ was reduced to $V(H_2O)_6^{2+}$ in acidic solutions followed by adjustment with concentrated sodium hydroxide. The $Ru(NH_3)_6^{3+}$ solutions were made up initially at pH 3 using sodium perchlorate and perchloric acid. In all cases, chloride was present only from the ruthenium salt. Vanadium(II) solutions were used within 2 hr to minimize oxidation by perchlorate ion; results with the older solutions were identical with those obtained 15 min after complete reduction.

Syringe techniques were used to transfer deoxygenated (with chromous-washed nitrogen or argon) solutions to a Durrum-Gibson

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