Acknowledgment. Robert G. Bowman was the recipient of an E. I. du Pont Graduate Fellowship (1974–1975) and a National Science Foundation Energy Traineeship during the academic years 1975–1977.

References and Notes

(1) R. H. Holm, *Acc. Chem. Res.*, **10**, 427 (1977).
(2) A. Schwartz and E. E. van Tamelen, *J. Am. Chem. Soc.*, **99**, 3189 (1977).
(3) B. A. Averill and W. H. Orme-Johnson, *J. Am. Chem. Soc.*, **100**, 5234 (1978).
(4) R. J. Butt, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 940 (1976).
(5) R. L. Burwell, Jr., *Chemtech*, **4**, 370 (1974).
(6) G. L. Ellman, *Arch. Biochem. Biophys.*, **82**, 70 (1959).
(7) The infrared spectrum of the modified gel was measured on a Beckman IR-5 spectrometer by placing gel wet with carbon tetrachloride between rock salt plates in one arm of the spectrometer and a similar sample of unmodified gel in the other arm. A band at 2550 cm^{-1} was assigned to the S–H stretch and bands at 2900 and 2800 cm^{-1} to C–H stretches in C–H and OCH_3 groups.
(8) B. A. Averill, T. Hershovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).
(9) D. L. Anderson, Doctoral Dissertation, Northwestern University, Evanston, Ill., 1975.
(10) L. Que, Jr., J. R. Angelis, M. A. Bobrick, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 6042 (1974).
(11) R. L. Burwell, Jr., and K. S. Stec, *J. Colloid Interface Sci.*, **58**, 54 (1977); R. L. Burwell, Jr., and A. Brenner, *J. Mol. Catal.*, 1, 77 (1976).
(12) A. P. Schaap, A. L. Thayer, E. C. Blossey, and D. C. Neckers, *J. Am. Chem. Soc.*, **97**, 3741 (1975).
(13) T. C. Bruice, R. Maskiewicz, and R. Job, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 231 (1975).
(14) R. W. Johnson and R. H. Holm, *J. Am. Chem. Soc.*, **100**, 5338 (1978).
(15) T. A. Egerton and F. S. Stone, *Trans. Faraday Soc.*, **66**, 2364 (1970).
(16) S. R. Ely and R. L. Burwell, Jr., *J. Colloid Interface Sci.*, **65**, 244 (1978).
(17) For example, hydrogen is adsorbed from flowing helium passing through Linde zeolite 5A at −196 °C but released upon warming; see ref 11.

Low-Temperature NMR Studies of a Single Crystal of *trans*-Cu(DL-ala)$_2$·H$_2$O

T. Sandreczki, D. Ondercin, and R. W. Kreilick*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received December 5, 1978*

Abstract: Low-temperature NMR spectroscopy has been used to investigate a single crystal of *trans*-Cu(DL-ala)$_2$·H$_2$O. The lines in the NMR spectra are shifted by both the electron-nuclei dipole-dipole and Fermi contact interactions and we obtained well-resolved spectra. Analysis of these spectra yield both Cu-proton distances and proton isotropic coupling constants. The metal-proton distances obtained from this NMR study are in good agreement with distances obtained from other metal-amino acid complexes by X-ray crystallography. The isotropic coupling constants determined in this study were accounted for by a mechanism involving spin delocalization from the copper's $d_{x^2-y^2}$ orbital through the σ bonds of the amino acid. The investigation demonstrates the utility of low-temperature NMR spectroscopy for the study of the structure of transition-metal complexes.

Introduction

Low-temperature nuclear magnetic resonance investigations of solid paramagnetic molecules allow one to obtain information about both the electron–nuclei dipolar and Fermi contact (isotropic) interactions.[1,2] These interactions shift the NMR lines of nuclei in the ligands of transition-metal complexes and well-resolved spectra are observed when these shifts become large compared to the intrinsic line width of solid samples. Exchange is normally rapid in concentrated solids and the nuclei experience an averaged electron spin polarization. The spin polarization and shifts vary inversely with temperature when the susceptibility follows a Curie law and if the experiments are carried out at low enough temperature well-resolved spectra are observed. The dipolar interaction depends on the separation of the electron and nuclear spins (r_i) and on the angle between the electron–nucleus vector and the external field (θ_i). Analysis of the angular dependence of shifts from single crystals may therefore be used to obtain information about the position of ligand nuclei with respect to the central metal ion. Nuclei within about a 1-6-Å radius of the metal ion have appreciable shifts at low temperatures while more distant nuclei experience smaller dipolar fields and their shifts are small compared to the width of the signals. An NMR study therefore produces information on the local structure of ligand nuclei near the metal ion which is of particular interest for relatively large biologically important complexes in which one is interested in the structure of ligands near the metal ion.

Fermi contact interactions (isotropic hyperfine couplings) may also be obtained through an analysis of the NMR spectra of metal complexes. This term is independent of orientation and can readily be separated from the angularly dependent dipolar term. Isotropic couplings from protons in the ligands of metal complexes are generally not resolved in ESR spectra as the line width is large compared to the magnitude of these couplings. Solution NMR studies of metal–amino acid complexes are generally complicated by multiple equilibria and isotropic coupling constants cannot be obtained directly. Evaluation of isotropic coupling constants from a series of ligand nuclei allows one to obtain information on the mechanism of spin delocalization from the metal atom into the ligand. Variations in the magnitudes of these couplings with the structure of the ligand are of value in identification of the coordinated amino acid in higher molecular weight complexes. We have initiated an NMR investigation of a series of metal–amino acid and metal–peptide complexes. This paper reports the results from a study of a single crystal of *trans*-Cu(DL-ala)$_2$·H$_2$O.

Theoretical

Spin exchange is normally rapid in concentrated samples of metal complexes and the nuclear spins experience an averaged electron spin polarization $\langle S \rangle$. In samples in which the magnetic susceptibility follows a Curie–Weiss law the averaged electron spin polarization is given by

0002-7863/79/1501-2880$01.00/0

$$\langle S\rangle = -\frac{g\beta HS(S+1)}{3k(T-\theta)} \qquad \theta = \text{Curie temperature} \quad (1)$$

Both the dipolar and Fermi shifts are proportional to $\langle S\rangle$ and the shifts increase linearly with the inverse of temperature until one approaches the Curie temperature. A given nuclear spin may experience dipolar fields from both the metal atom of the parent molecule and from metal atoms on neighboring molecules in the crystal. The shift of the signal from a given nuclear spin reflects the sum of these dipolar interactions and the Fermi contact interaction. The Fermi contact term is generally dominated by intramolecular interactions but in some cases it is possible for a neighboring electron spin to contribute to this interaction.

The expression for the shift (ΔH) of a given nuclear resonance line in a concentrated paramagnetic solid is given by

$$\Delta H = \langle S\rangle g\beta \sum_i \left(\frac{3\cos^2\theta_i - 1}{r_i^3}\right) + \langle S\rangle \sum_i A_i \qquad (2)$$

In this expression the summation extends over i electron spins, r_i is the separation between the nuclear spin and a given electron spin, θ_i is the angle between the vector connecting the electron and nuclear spins and the external magnetic field, and A_i is the isotropic coupling constant. If a molecule fixed coordinate system is selected so that the principal values of the internal field lie along the coordinate system's axes, the equation for the shift may be written as[1]

$$\Delta H = \langle S\rangle(H_1 \sin^2\theta' \cos^2\phi' + H_2 \sin^2\theta' \sin^2\phi' + H_3 \cos^2\theta') \qquad (3)$$

In this expression H_1, H_2, and H_3 are the principal components of the total internal field experienced by the nuclear spin reflecting the magnitude of both the isotropic and dipolar interactions. The polar angles θ' and ϕ' give the direction of the external field with respect to this molecule fixed coordinate system. The isotropic coupling constant is equal to $1/3$ of the sum of the principal components of the internal field:

$$A = \tfrac{1}{3}(H_1 + H_2 + H_3) \qquad (4)$$

The separation between the nuclear spin and a given electron spin cannot be obtained directly from the principal components in all cases as the nuclear spin may experience comparable dipolar fields from more than one electron spin if the metal atoms of neighboring molecules are separated from the nucleus by about the same distance as the metal in the parent molecule. One can define an effective distance (r_{eff}) by[1]

$$r_{\text{eff}} = \left[\frac{3g\beta}{H_3 - H_1}\right]^{1/3} \qquad (5)$$

The distance gives the separation a single electron spin would have to be from the nuclear spin to produce the observed dipolar shift. In previous studies[1] we have shown that r_{eff} is a good measure of the separation of the nucleus from the nearest electron spin when the second closest electron spin is more than a factor of 2 more distant than the nearest electron. A measure of the contribution of neighboring electron spins to the dipolar interaction is the asymmetry parameter (Δ) defined by[1]

$$\Delta = \frac{H_2 - H_3}{H_1 - H_3} \qquad (6)$$

When the value of Δ is close to 1 a single electron generally dominates the dipolar interaction, while when Δ is close to 0 more than one electron contributes to the dipolar interaction. The dipolar interactions for most of the protons in the copper–amino acid complexes are dominated by the interaction with the nearest electron spin and r_{eff} is a good measure of the metal–proton separation.

The shifts of NMR signals from a single crystal of a paramagnetic molecule depend on the orientation of the crystal with respect to the external magnetic field. If one rotates the crystal around three orthogonal crystal fixed axes (laboratory coordinate system) and records the shifts at a series of angles one is able to evaluate the elements of the internal field matrix in this coordinate system. Diagonalization of this matrix yields the principal components of the internal field in the molecular coordinate system. If one defines the experimental rotation angle as ϵ one obtains the following equations for the shifts as the crystal is rotated around the x, y, and z axes.

$$x \text{ axis } \Delta H = \langle S\rangle[H_{zz}\cos^2\epsilon + 2H_{yz}\sin\epsilon\cos\epsilon + H_{yy}\sin^2\epsilon] \qquad (7)$$

$$y \text{ axis } \Delta H = \langle S\rangle[H_{zz}\cos^2\epsilon + 2H_{xz}\sin\epsilon\cos\epsilon + H_{xx}\sin^2\epsilon]$$

$$z \text{ axis } \Delta H = \langle S\rangle[H_{xx}\cos^2\epsilon + 2H_{xy}\sin\epsilon\cos\epsilon + H_{yy}\sin^2\epsilon]$$

These equations can be reduced to the general form

$$\Delta H = A + K\cos 2(\epsilon - \alpha) \qquad (8)$$

in which the constants A, K, and α are related to the elements of the internal field by

$$\begin{aligned} \langle S\rangle H_{ii} &= A + K\cos 2\alpha \\ \langle S\rangle H_{ij} &= K\sin 2\alpha \\ \langle S\rangle H_{jj} &= A - K\cos 2\alpha \end{aligned} \qquad (9)$$

A nonlinear least-squares fit of experimental data to eq 8 allows one to evaluate the constants A, K, and α, which can then be used to determine the elements of the internal field. Diagonalization of the resulting matrix allows one to obtain the principal components, which can then be used to determine isotropic coupling constants and effective distances. The diagonalization procedure rotates the coordinate system from the laboratory frame into the molecular frame and the rotation matrix obtained by this procedure can be used to determine the relative orientation of the electron–proton vectors for different types of nuclei if a single electron dominates the dipolar interaction.

Experimental Section

trans-Cu(DL-ala)$_2$·H$_2$O was prepared by the reaction of DL-alanine with copper hydroxide.[3] A large single crystal of this material was grown by placing a seed crystal in a saturated solution of the complex with subsequent slow evaporation of the solvent. The partially grown crystal was removed from the solution and rinsed with distilled water when smaller crystals began to grow near it. It was subsequently placed in a new solution of the complex and allowed to grow further. A dark blue prism was obtained which was about 3 mm on the long edge. The long axis was assigned as the z axis for the NMR study.

The NMR spectra were taken with a pulsed field swept spectrometer operating between 90 and 100 MHz.[4] The field was modulated with a 2-kHz oscillator and a lock-in amplifier was used as a final detection stage. Special probes were constructed to fit in the 1.2-cm opening of a Janis Research[5] Super Varitemp liquid helium Dewar in which the temperature could be varied from 2 K to room temperature. The temperature was monitored with a Lakeshore Cryogenics[6] carbon-glass resistance thermometer which was mounted directly above the sample coil. The temperature stability was within about ±0.1 K during the period necessary to record an NMR spectrum. The crystal was mounted at the end of a long glass rod which could be rotated from outside the Dewar. Spectra were taken at 5° rotational intervals along three orthogonal axes.

Results and Discussion

Well-resolved NMR spectra were observed from the crystal at temperatures below about 40 K. The temperature dependence of the shifts with an arbitrary crystal orientation was measured over the temperature interval between 40 and 3 K to determine the variation in the magnetic susceptibility with temperature. A plot of reciprocal of the shifts vs. temperature was linear down to about 18 K. This plot began to show cur-

Table I. Principal Components, Effective Distances, Asymmetry Parameters, and Isotropic Coupling Constants for *trans*-Cu(DL-ala)$_2$·H$_2$O

line	type proton	H_1, G	H_2, G	H_3, G	R_{eff}, Å	R_{lit}, Å^a	Δ	A
A	NH$_2$	−2706	−1485	1445	2.46 ± 0.04	2.53	0.73	−1.4 ± 0.1
I	NH$_2$	−2653	−1704	1158	2.46 ± 0.04	2.53	0.73	−1.4 ± 0.1
H	NH$_2$					2.53		−1.7 ± 0.1
J	NH$_2$					2.53		−1.7 ± 0.1
B	CH	−803	479	798	3.37 ± 0.05	3.44	0.24	0.3 ± 0.06
F	CH	−594	468	874	3.37 ± 0.05	3.44	0.24	0.3 ± 0.06
C	CH$_3$	−981	−34	733	3.35 ± 0.1	3.5–4.8	0.44	−0.1 ± 0.04
G	CH$_3$	−786	37	652	3.35 ± 0.1	3.5–4.8	0.44	−0.1 ± 0.04
D	CH$_3$	−386	−217	485	4.4 ± 0.2	3.5–4.8	0.60	−0.06 ± 0.04
E	CH$_3$	−371	−16	235	4.4 ± 0.2	3.5–4.8	0.60	−0.06 ± 0.04

[a] Literature values for metal–proton distances of other metal–amino acid complexes. See ref 8.

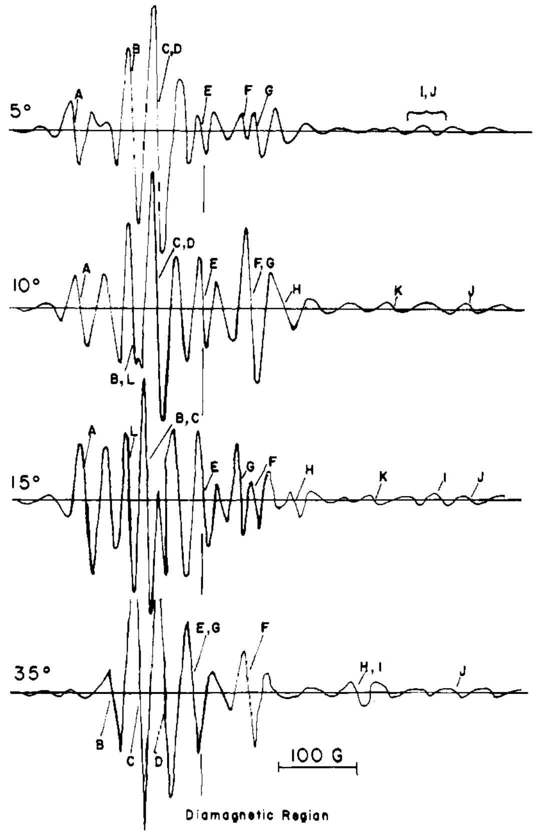

Figure 1. NMR spectra of *trans*-Cu(DL-ala)$_2$·H$_2$O as a function of rotation angle around the z axis.

vature below 18 K and the shifts became almost independent of temperature at temperatures below about 10 K. Extrapolation of the straight-line section of this plot gave a Curie temperature of 6.5 K indicating a ferromagnetic lattice interaction. The deviation from the Curie–Weiss law at lower temperatures may be explained by a strong exchange interaction between pairs of molecules with formation of a diamagnetic (singlet state) dimer. A temperature of 11.2 K was chosen for the studies involving rotation of the crystal as the temperature dependence of the shifts was almost flat at this temperature and small temperature fluctuations produced minor errors in the experimental data. The electron spin polarization, $\langle S\rangle$, is −0.1277 at this temperature.

The crystal was rotated around three mutually perpendicular axes and spectra were recorded as a function of rotation angle. Figure 1 shows NMR spectra as a function of rotation angle about the z (long) axis. Twelve lines were observed when the crystal was mounted along the z axis while only ten lines could be observed when the crystal was mounted along the x or y axes. The spectra taken with the crystal mounted along the y axis has significantly poorer signal to noise than those obtained from the other two axes as the thin edge of the crystal was in the receiver coil and the net sample volume was reduced. A plot of shifts vs. rotation angle for rotation about the z and x axes is shown in Figure 2. A phase angle adjustment of about 10° was necessary to make these two axes connect correctly because of small errors in alignment of the crystal before rotation. This figure indicates that the unit cell has a twofold axis of symmetry (i.e., lines A and I).

Preliminary X-ray studies of this molecule indicate that there is a minimum of two molecules per unit cell which are related by a twofold symmetry axis.[7] One expects methyl group rotation to be rapid on the NMR time scale and a single methyl resonance should be observed from each molecule if the methyl groups on the two sides of the molecule are in equivalent magnetic environments. We observe two signals from the methyl groups on the two sides of a given complex showing that these groups experience different dipolar fields. The spectra taken with the crystal mounted along the z axis showed two lines from the amine protons, a single line from the methylene protons, and two lines from the water protons in addition to the signals from the methyl groups. The second molecule in the unit cell showed a second set of lines which appears to be a reflection of the first set. The plane of reflection can be seen at a line drawn through approximately 50° on the z axis.

A nonlinear least-squares program was used to fit the experimental data to eq 8, from which the elements of the internal field matrix could be calculated. All of the matrix elements except H_{xz} could be calculated from data taken from the x and z axes and data from the y axis was used only to evaluate H_{xz}. Diagonalization of the matrix yields the principal components from which isotropic coupling constants and effective distances were calculated. A complete X-ray structure of this complex has not been completed and our results are the first measurement of metal–proton distances for this molecule. The lines were assigned to the various protons in the complex by comparison of the distances determined in the NMR experiment with metal–proton distances determined in X-ray studies of other Cu–amino acid complexes.[8] Table I gives the line assignment, principal values of the internal field matrix, effective distances, crystal structure distances, asymmetry parameters, and isotropic coupling constants.

Lines A and I are a symmetry-related pair of signals assigned to amine protons. The effective distance determined from the NMR experiment was very close to the value determined by X-ray crystallography, indicating that the dipolar interaction is dominated by the nearest copper atom (intramolecular distance). Lines H and J were assigned to the second pair of amine protons. We were unable to obtain good data for these lines when the crystal was aligned along the y axis (poor

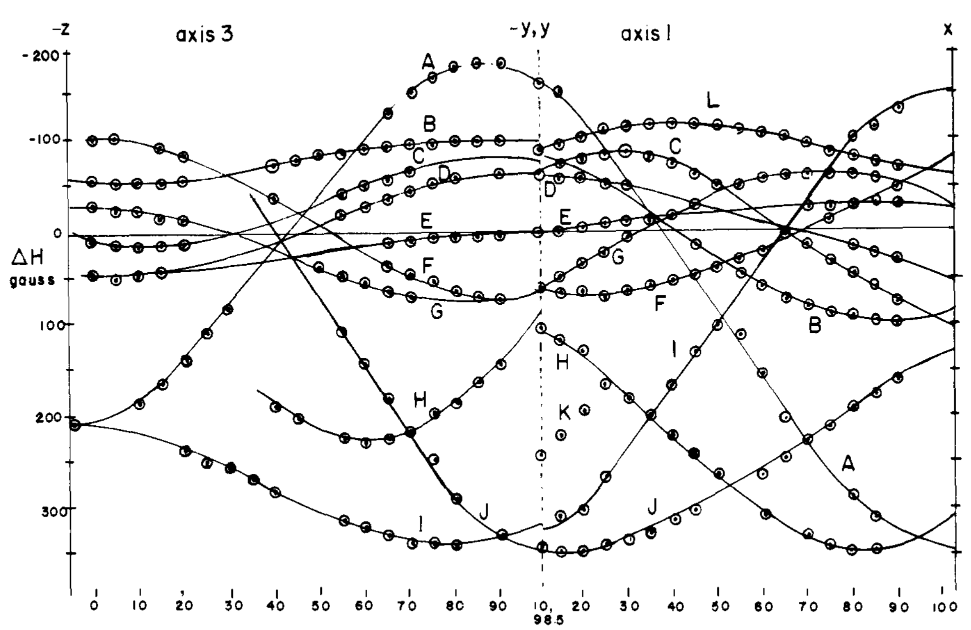

Figure 2. Shifts of NMR lines as a function of rotation angle about the z and x axes.

signal to noise) and consequently we were unable to determine distances for these protons. Isotropic coupling constants for these protons could be calculated from the data from two axes as the isotropic interaction is traceless and it is unnecessary to diagonalize the matrix to obtain these couplings. Lines B and F are related by a twofold symmetry axis and are assigned to the methylene protons. The metal-proton distance for these atoms is close to that predicted by crystallographic results but these protons have a relatively small asymmetry parameter indicating that the dipolar interaction receives some contribution from neighboring metal atoms. Lines C,G and D,E are two symmetry-related pairs of signals which are assigned to the methyl protons. The distances determined from these lines are of the same order as predicted from crystallographic results but the distances from the two sets of protons differ from one another by about 1 Å, indicating that the methyl protons on two sides of a given molecule experience significantly different dipolar fields. These groups are trans with respect to one another and relatively distant from the central metal atom. If the two molecules in the unit cell are nearly coplanar the methyl groups on the inside would experience a larger dipolar interaction from a neighboring copper atom than methyl protons pointed away from the second molecule in the unit cell. The smaller effective distance determined for one set of methyl protons probably reflects the interaction of this group with the second copper atom in the unit cell. Lines K and L were assigned to the water protons. Unfortunately we were only able to observe these signals when the crystal was mounted along the z axis and are therefore unable to determine either distances or coupling constants. These signals were weak and relatively broad and were not observed from the x and y axes either because of poor signal to noise or because of overlapping with other lines in the spectrum. Line L appears to be a superposition of the signals from two symmetry-related protons as it is symmetric about the reflection plane at about 50° on the z axis. The signals from two protons may be superimposed in line K as well but our data is insufficient to be certain. Both lines K and L have large shifts indicating relatively small distances and/or large isotropic coupling constants.

Isotropic coupling constants were determined for most of the protons in this complex (Table I). The mechanism for the isotropic interaction of the amino acid protons appears to be spin delocalization from the $d_{x^2-y^2}$ orbital of the copper atom through the σ bonds of the amino acid.[9] This mechanism predicts negative coupling constants for the amine protons, positive couplings for the methylene protons, and negative couplings for the methyl protons (Figure 3). These signs are observed experimentally. The magnitude of the coupling constants is expected to decrease as a function of the number of σ bonds through which the spin must be delocalized. The coupling constants of the amine protons are about a factor of 7 larger than those of the methylene protons, showing the attenuation of spin density as it moves through the σ bonds. The coupling constants of the methyl protons are in turn about a factor of 5 smaller than the methylene couplings. The two amine protons on a given molecule have slightly different coupling constants. These differences probably reflect variations in the N-H bond geometries with respect to the copper's $d_{x^2-y^2}$ orbital.[10] The coupling constants of the two types of methyl protons are nearly identical, although the effective distances differ by about 1 Å. This result indicates that the intermolecular contribution to the isotropic coupling constant is small even when there is a relatively large contribution to the dipolar interaction.

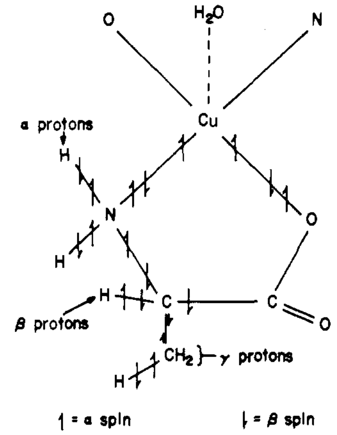

Figure 3. Spin polarization of *trans*-Cu(DL-ala)$_2$·H$_2$O.

Conclusions

Low-temperature NMR studies of transition-metal complexes provide a useful technique for obtaining both structural information and isotropic coupling constants. The metal-proton distances obtained from our study of *trans*-Cu(DL-ala)$_2$·H_2O are in good agreement with corresponding distances determined for other amino acid complexes by X-ray crystallography. Isotropic coupling constants for these molecules are not resolved in ESR spectra and our study gives the first direct measurement of these coupling constants. The sign and relative magnitude of these coupling constants can be explained by a mechanism involving spin delocalization from the $d_{x^2-y^2}$ orbital of the copper through the σ bonds of the chelate. This technique probes short-range metal-nuclei interactions without interference from more distant nuclei. It should be of value in studies of the local structure of higher molecular weight biologically important complexes in which knowledge of the ligand structure near the metal ion is of importance.

Acknowledgment. This work was supported in part by National Institutes of Health Grant GM-22793.

References and Notes

(1) T. Sandreczki, D. Ondercin, and R. W. Kreilick, *J. Magn. Reson.*, in press; D. Ondercin, T. Sandreczki, and R. W. Kreilick, *ibid.*, in press; T. Sandreczki, Ph.D. Thesis, University of Rochester, 1978; D. Ondercin, Ph.D. Thesis, University of Rochester, 1978.

(2) A. R. King, J. P. Wolfe, and R. L. Ballard, *Phys. Rev. Lett.*, **28,** 1099 (1972); J. P. Wolfe, *Phys. Rev. B*, **16,** 128 (1977); N. Bloembergen and T. J. Rowland, *Acta Metall.*, **1,** 731 (1953); N. J. Poulis and G. E. Hardeman, *Physica* (*Utrecht*), **18,** 201 (1952); N. Bloembergen, *ibid.*, **16,** 95 (1950).

(3) A. W. Herlinger, S. L. Wenhold, and T. V. Long, *J. Am. Chem. Soc.*, **92,** 6474 (1970).

(4) G. F. Hatch, J. W. Neely, and R. W. Kreilick, *J. Magn. Reson.*, **16,** 408 (1974).

(5) Janis Research Co., Stoneham, Mass.

(6) A Lakeshore Cryogenics Model CGR-1-1000 carbon–glass resistance thermometer was used (Lakeshore Cryogenics, Columbus, Ohio).

(7) Preliminary X-ray measurements of this crystal were made by T. Baker in the Chemistry Department. We also wish to thank W. Bernhard and K. Mercer of the Department of Radiation Biology and Biophysics of the University of Rochester for valuable discussions about the crystal structure. R. D. Gilliard, H. M. Irving, R. M. Perkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc. A*, 1159 (1966); A. V. Ablov, L. F. Chapurina, I. A. D'yakon, and V. Ivanova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **11,** 1407 (1966).

(8) R. D. Gilliard, R. Mason, N. C. Prayne, and G. B. Robertson, *J. Chem. Soc. A*, 1864 (1969); H. C. Freeman, M. R. Snow, and K. Tomita, *Acta Crystallogr.*, **17,** 1463 (1964).

(9) R. S. Milner and L. Pratt, *Discuss. Faraday Soc.*, **34,** 88 (1962); R. W. Kreilick. *J. Am. Chem. Soc.*, **90,** 5991 (1968); F. Yamauchi and R. W. Kreilick, *ibid.*, **91,** 3429 (1969).

(10) Y. Ellinger and R. Subra, *J. Chem. Phys.*, **62,** 10 (1975).

Kinetic Studies of the Reactions of *N,N*-Dimethylformamide and *N,N*-Dimethylacetamide with Sodium in Liquid Ammonia[1]

Clifton A. Young and Robert R. Dewald*

Contribution from the Department of Chemistry, Tufts University, Medford, Massachusetts 02155.
Received December 19, 1977

Abstract: The reactions of *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) with sodium in liquid ammonia were found to obey the fourth-order rate law $-d(e^-_{am})/dt = k(e^-_{am})^2(\text{amide})(\text{Na}^+)$. A negative activation energy was observed for the reaction of DMF with the ammoniated electron, while the rate of the DMA reaction was not significantly influenced by temperature. A mechanism involving ion pairing is presented to explain the results of this study.

Introduction

Dissolved metal nonaqueous solutions have long been known to constitute powerful reducing systems of considerable synthetic utility.[2] The nature of the reducing species present in these solutions has been a matter of conjecture over the years. Both solvated electrons and alkali metal anions are now recognized as reducing species in dissolved metal systems.[3-5] The equilibria which are important in the metal solutions can be described by the following:[5]

$$2M(s) \rightleftharpoons M^+ + M^- \qquad (1)$$

$$M^- \rightleftharpoons M + e^-_{solv} \qquad (2)$$

$$M \rightleftharpoons M^+ + e^-_{solv} \qquad (3)$$

In liquid ammonia, equilibria in eq 2 and 3 are far to the right and hence for dilute metal-ammonia solutions the only significant reducing species present are the solvated electron and its ion pair.[4] Relatively few homogeneous kinetic studies have been reported for reactions involving the ammoniated electron in contrast to the extensive amount of kinetic data available for the hydrated electron.[6,7] However, based on limited data, reactions involving the ammoniated electron are generally several orders of magnitude slower than those for the hydrated electron.[6,8,9]

The reaction of *N,N*-dimethylformamide (DMF) with sodium in liquid ammonia has been reported[10] to proceed according to the equation

$$2Na + 2(CH_3)_2NCHO \rightarrow (CH_3)_2NCNaO + (CH_3)_2NCH_2ONa \qquad (4)$$

Also, the electrochemical reduction of higher amides in methylamine with lithium chloride as the supporting electrolyte has been reported.[11] In the presence of a proton donor (ethanol) the product after hydrolysis and workup was the corresponding aldehyde; in the absence of a proton donor the corresponding alcohol was isolated after acid hydrolysis and workup.[11]

Using the pulse-radiolysis technique, a second-order rate constant of $(5.2 \pm 1.3) \times 10^7$ M^{-1} s^{-1} has been reported[12] for the reaction of DMF with the hydrated electron. Unfortunately, no information concerning reaction products was reported.[12] Moreover, an attempt to generate the solvated electron in DMF itself by pulse radiolysis failed.[12]

We undertook the present study to obtain more information concerning the reactivities of amides toward solvated electrons since these compounds are used extensively as solvents in electrochemical studies,[13] and to better understand the kinetics of solvated electron reactions in nonaqueous solvents.

0002-7863/79/1501-2884$01.00/0