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Deuteron NMR Spectroscopy of Copper(II) Complexes in Solution. 1. (5,7,7,12,14,14,-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)-Copper(II) and its Derivatives in Nonaqueous Solvent

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Abstract

^{1}H and ^{2}H NMR spectra of the title copper(II) complexes and its derivatives have been measured. In contrast with their ^{1}H NMR spectra, ^{2}H NMR spectra gave well resolved sharp signals, and demonstrated that two diastereomers attributable to two asymmetric ligand nitrogens are readily resolved. The remarkable linewidth-narrowing was found in the peripheral methyl groups, which make ^{2}H NMR spectra very useful even for copper(II) complexes with a long electron spin relaxation time. By using ^{2}H NMR spectra, *meso*–racemate equilibrium was pursued and examined in aqueous and acetonitrile solutions.

Introduction

The electron-spin relaxation time of copper(II) ion is sufficiently long [1] that ^{1}H NMR signals are broadened to the point that potential structural information is lost. Consequently, ESR spectroscopy has been utilized as a pertinent technique for copper(II) complexes. It has been pointed out [2] that the deuteron magnetic resonance signals in a given paramagnetic environment should be narrower than the corresponding ^{1}H NMR signals by the factor $(\gamma(^2H)/\gamma(^1H))^2 = 0.024$, where $\gamma(^1H)$ and $\gamma(^2H)$ are the magnetogyric ratios of the ^{1}H and ^{2}H, respectively. Because the isotropic shift is proportional to γ and chemical shifts in Hz are smaller for ^{2}H NMR by the factor $\gamma(^2H)/\gamma(^1H) = 0.15$, the overall resolution of a ^{2}H NMR spectrum should be 6.5 times better than that of the ^{1}H NMR spectrum of the same compound if quadrupole broadening in ^{2}H NMR is neglected [3]. These conclusions have been examined by using deuterated acetylacetonate complexes of various paramagnetic metal ions [4]. In spite of no achievement of the theoretical linewidth ratio, the data clearly reveal a substantial reduction in linewidth in each deuterated complex. The copper(II) complexes are not the exceptional case. These results make evident the potential utility of ^{2}H NMR in stereochemical investigations, as well as those of equilibria in solution, of copper(II) complexes which have long electron-spin relaxation time. This manuscript is concerned with the characterization of stereoisomers of 4,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene ($Me_6[14]4,11$-dieneN$_4$) [5] and its analogs with copper(II) by ^{2}H NMR spectroscopy. These macrocyclic copper(II) complexes are free from chemical exchange effect due to their great stability constants, and the fixed structure of the ligands themselves. Hence, their NMR signals reflect the paramagnetic interaction without any averaging effect.

Experimental

Materials

$Me_6[14]4,11$-dieneN$_4$ diperchlorate and $Me_2[14]$-4,11-dieneN$_4$ diperchlorate were formed by the reaction [6] of diaminoethane monohydroperchlorate with acetone and methylvinyl ketone, respectively. Deuterated $Me_6[14]4,11$-dieneN$_4$-d$_{22}$ was obtained from acetone-d$_6$. Corresponding copper(II) complexes of them were synthesized according to the literature [7]. $[Cu(5,12\text{-}Me_2[14]4,11\text{-dieneN}_4)](ClO_4)_2$ was prepared according to ref. 8, using $Cu(CH_3COO)_2$. Racemic and *meso* diastereomers were separated from each other by utilizing the difference in their solubility.

NMR Measurements

^{1}H and ^{2}H NMR spectra were recorded on a Jeol FX 200 FT NMR spectrometer operating at 199.5 (^{1}H) and 30.6 (^{2}H) MHz. Sample concentration was 0.03–0.4 M both for ^{1}H and ^{2}H NMR. Deuterated and non-deuterated solvents were used for ^{1}H and ^{2}H NMR, respectively. For ^{1}H NMR measurements, 1000 transients were accumulated with the use of 14-μs pulses (90°), and 4 K data points were collected over a band width of 40 K Hz. For ^{2}H NMR measure-

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ments, 2000 transients were accumulated with the use of 38-μs pulses (90°), and 8 K data points were collected over a bandwidth of 6 KHz. The temperature was set at 23 °C. $(CH_3)_4Si$ was used as the internal standard for ^{1}H NMR spectra. Natural abundance signal of solvent CDH_2CN (1.96 ppm) was chosen as the internal standard for ^{2}H NMR spectra, whose reading is 1.96 ppm from TMS. Sample solutions were contained in a spinning tube (outside diameter 5 and 10 mm for ^{1}H and ^{2}H NMR, respectively).

X-ray Structure Determination

The approximate dimensions of the crystal of the *meso* complex were 0.3 × 0.3 × 0.3 mm. Intensities were measured with a four-circle diffractometer (Rigaku AFC6B) using graphite-monochromated Cu Kα radiation (λ = 1.45418 Å). Detailed data are as follows: $M = 542.87$, monoclinic, $P2_1/C$, $a = 10.315(6)$, $b = 10.620(9)$, $c = 11.004(8)$ Å, $\beta = 111.67(5)°$, $Z = 2$, $U = 1120.2$ Å^3, final $R = 0.059$ for 1448 observed reflections. This result is in good agreement with that reported by Lee [10].

Results and Discussion

^{1}H NMR Spectral Feature

The ^{1}H NMR spectrum of $[Cu(Me_6[14]4,11\text{-diene}N_4)]^+$ (1) exhibits three broad signals in the region of +30–−40 ppm (Fig. 1). They are attributable to six methyl signals of the ligand. All the ring methylene protons gave much broader signals than the methyl ones, and their detection was unsuccessful. This was examined by ^{2}H NMR spectra of selectively deuterated complexes. Among four coordinated nitrogen atoms in **1**, two of them are asymmetric. These asymmetric centers afford the possibility of two diastereomers such as racemate and *meso*. The present synthesis of **1** provides a mixture of diastereomers. According to X-ray structure of racemate [9] and *meso* [10] of Cu(II), the location of the geminal carbon atom produces an axial and equatorial distinction between the two geminal methyl groups. Thus, there are three types of methyl groups [11] associated with each isomer: (a) CH_3^i, the imine methyl group oriented in an equatorial manner and is essentially in the CuN_4 plane; (b) CH_3^a, the axial methyl groups of the geminal pairs lie over the CuN_4 plane; (c) CH_3^e, the equatorial geminal methyl groups lie out away from the metal ion center and their bond axes are roughly parallel to the CuN_4 plane.

$[Ni(Me_6[14]4,11\text{-diene}N_4)](SCN)_2$ [11] gives sharp methyl ^{1}H signals, owing to its diamagnetism, which distinguishes the two types of diastereomers. On the other hand, ^{1}H NMR spectra of Cu(II) diastereomers failed to separate each species due to the considerable paramagnetic broadening, as is well illustrated in Fig. 1a. The observed linewidth amounts to 0.6–several KHz. Therefore, it is impossible to gain structural information of macrocyclic Cu(II) complexes from ^{1}H NMR spectra.

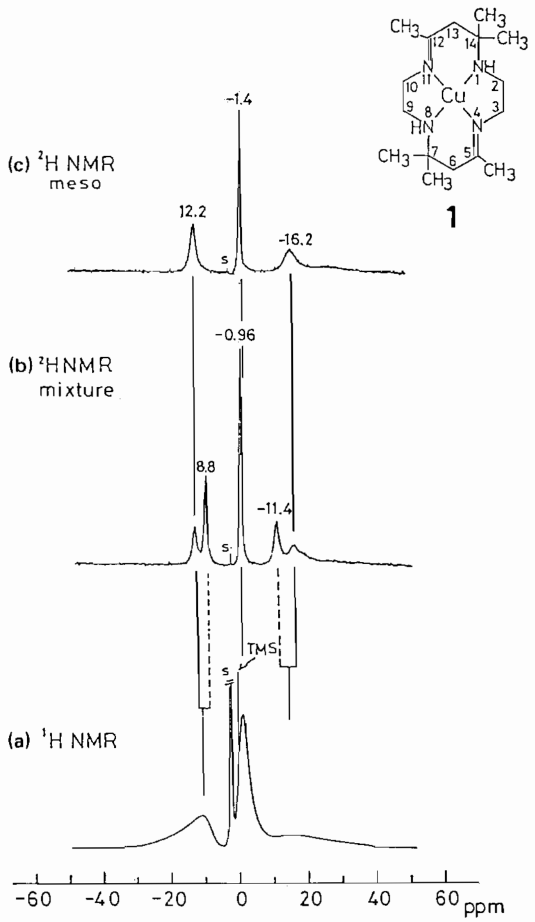

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Fig. 1. ^{1}H and ^{2}H NMR spectra at 24 °C of $[Cu(Me_6[14]\text{-}4,11\text{-diene}N_4)](ClO_4)_2$ in acetonitrile. (a) ^{1}H and (b) ^{2}H NMR spectra of a mixture, whose concentration was 0.020 and 0.22 M, respectively. In (b), deuterated diastereomers were used (c) ^{2}H NMR spectrum of 0.020 M pure deuterated *meso*. s indicates a solvent signal.

^{2}H NMR Spectral Feature

The linewidth-narrowing by a factor of $(\gamma(^2H)/\gamma(^1H))^2 = 0.024$ is expected on the basis of the Solomon–Bloembergen equation [12] for paramagnetic relaxation time. The ^{2}H NMR spectrum of deuterated **1** is presented in Fig. 1b. Each ^{2}H NMR signal, corresponding to both ^{1}H NMR signals at −15 and 11 ppm, splits into two signals, respectively (Fig. 1b). Clearly, this results from much less linewidth of ^{2}H signals than that of ^{1}H NMR signals. A central signal near −1 ppm is also separated into two signals even though the gap in the shift is very small, indicative of the usefulness of ^{2}H NMR spectro-

TABLE I. Observed ^{2}H NMR[a] Chemical Shifts[b] and Linewidth[c] at Half Height of [Cu(Me$_6$[14]4,11-dieneN$_4$-d$_{22}$)](ClO$_4$)$_2$

Compounds	Solvent	CH_3^{imine}	$CH_3^{equatorial}$	CH_3^{axial}	CH_2^{d}
Metal-free	CH_3CN	1.97	1.39	1.39	2.62
Racemate[e]	CH_3CN	−11.4	8.8	−0.96	−40[h]
		(89)	(42)	(28)	
Racemate[f]	CH_3OH	−11.1	8.8	−1.0[g]	–[i]
Racemate[f]	$(CH_3)_2CO$	−10.1	8.9	−1.0	–[i]
Racemate[f]	$(CH_3)_2SO$	−11.2	7.9	−1.2[g]	–[i]
Meso[e]	CH_3CN	−16.2	12.2	−1.4	−40[h]
		(137)	(62)	(22)	
Meso[f]	CH_3OH	−17.6	12.2	−1.0[g]	–[i]
Meso[f]	$(CH_3)_2CO$	−16.3	12.3	−1.4	–[i]
Meso[f]	$(CH_3)_2SO$	−14.8	11.2	−1.2[g]	–[i]

[a] Measured at 23 °C. [b] A solvent signal was used as internal standard. Chemical shift value in ppm from TMS. Error limit ±0.3 ppm. [c] The values in parentheses. Error limit for CH_3^{imine} and ($CH_3^{equatorial}$ and CH_3^{amine}) lower than ±5 and 2, respectively. [d] Methylene groups at 6 and 13-position. [e] A spectrum of pure complex obtained by resolving diastereomers. [f] A spectrum of mixture of two diastereomers. [g] Signals of racemate and *meso* in the corresponding solvent accidentally collapse with each other. [h] It is difficult to obtain the linewidth due to significant line-broadening. [i] Hard to read the chemical shifts.

scopy. The ratio of integrated intensity of the two signals is 3/2 for each pair. This indicates the presence of two species, which are attributable to racemate and *meso* [11]. In order to further determine which signals are racemate or *meso*, the *meso* complex was selectively isolated [13] because of the difference in solubility: *meso* has poorer solubility than racemate. The obtained crystal was examined by X-ray crystallography, and confirmed as *meso*. Detailed crystallographic parameters are given in 'Experimental'. *Meso* complex gives a spectrum of Fig. 1c, where signals at 8.8, –0.96, and −11.4 ppm in Fig. 1b disappear. Accordingly, three greater signals in Fig. 1b are assigned to racemate. The ratio of 3/2, thus, is that of racemate/*meso*. Whether this value of 3/2 corresponds to an equilibrium ratio or not will be discussed in the following section.

It is to be emphasized that the racemic signals are sharper than the *meso* ones. The linewidth ratio of racemate to *meso* is *ca.* 1/6–1/8 for each signal (Table I).

The proximity of the methyl protons (CH_3^i) to the imine group and the electron-withdrawing effect of the metal ion causes them to be acidic and to exchange for deuterium in basic D_2O [11]. Hence, the selective deuteration was made on CH_3^i. These ^{2}H signals of $C(^2H)_3^i$ appear at −11.4 and −16.2 ppm, exclusively assigned to racemate and *meso*, respectively. The analogous complex, [Cu(5,12-Me$_2$-[14]dieneN$_4$]$^+$ (**2**), also shows the ^{1}H signal of CH_3 at −13.7 ppm (Fig. 2b), characteristic of the imine methyl group oriented in an equatorial manner.

The ^{2}H signals at 12.2 and −1.4 ppm in Fig. 1c show an intensity equal to each other, and are thus assigned to two geminal methyls, CH_3^e and CH_3^a. In order to assign these signals, an analogous complex of [Cu(*rac*-(5,12)-Me$_6$[14]aneN$_4$](ClO$_4$)$_2$ (**3**) was used. **3** has four coordinated aliphatic amine nitrogens, whose bonding nature with Cu is similar to each other. Thus, their CH_3 signals resonate at the region close to those of CH_3^e and CH_3^a in **1**. The ^{1}H NMR spectrum in Fig. 2a shows that two signals with a 2:1 ratio in intensity appear at −2.2 and 11.5 ppm, respectively. It should be remembered that **3** has four axial and two equatorial methyl groups [14]. By considering that the paramagnetic shift is dependent on the position of observed nuclei if their metal–ligand bondings are similar to each other, the more intense signal at −2.2 ppm in Fig. 2 is assigned to the axial methyl group, indicating that the axial methyl resonates upfield more than the equatorial one. On this basis, ^{2}H signals at −1.4 and 12.2 ppm are ascribed to $C(^2H)_3^a$ and $C(^2H)_3^e$, respectively (Fig. 1c).

TABLE II. Observed ^{1}H NMR Chemical Shifts[a] of Methyl Groups

Compound	CH_3^{imine}	$CH_3^{equatorial}$	CH_3^{axial}
1 (racemate)	−13.1	10.0	−1.0
	(1500)[b]	(1200)[b]	(670)[c]
(*meso*)	−22.0	14.5	−1.4
	(2500)d	(2000)[d]	(600)[e]
(mixture)[f]	−15	11	−1.4
2	−13.7		
3	–	11.5	−2.2

[a] The value in ppm from TMS, measured at 24 °C. Acetonitrile was used as solvent and internal standard. The values in parentheses are the linewidths. [b] Error limit, ±300 Hz. [c] Error limit, ±45 Hz. [d] Error limit, ±500 Hz. [e] Error limit, ±22 Hz. [f] Peak maxima were read.

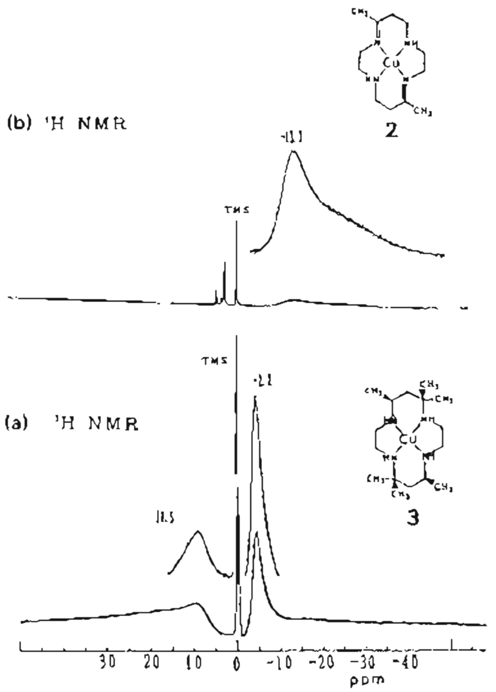

Fig. 2. ^1H NMR spectra of (a) [Cu(rac-(5,12)-Me_6[14]-aneN_4]$(ClO_4)_2$ and (b) [Cu((5,12)-Me_2[14]dieneN_4)]-$(ClO_4)_2$ in acetonitrile-d_3.

The ^1H NMR spectrum of Fig. 1a shows no signal of methylene protons, indicating that considerable broadening occurs in methylene protons. Methylenes at 6 and 13 position are deuterated when acetone-d_6 was utilized. Copper(II) makes these signals broad even in the ^2H NMR spectrum. Careful inspection of Fig. 1b and c reveals that very broad signals of 6- and 13-CH_2 are detected at near −40 ppm. The efficient deuteron relaxation of the methylene more than that of methyl is associated with the distributed spin densities [12].

The gain in resolution is quite evident in these ^2H NMR spectra. This is due to the narrowing of linewidth, and the narrowing ratio obtained here is close to the theoretical value of 0.024. Table III shows that the minimum value is 0.03, which is close to that found for copper(II) acetylacetonate [4]. The ratio of racemic CH_3^i is remarkably different from the others (Table III). This deviation from the theoretical ratio of γ_N^2 could be explained by assuming that proton and deuteron have a different hyperfine coupling constant A, which is associated with nuclei and its position in a molecule. At present, the experimental error significantly influences the linewidth data, and thus, precise data will be needed in order to discuss further details.

Equilibrium

By use of the ^2H NMR method developed here, the racemate–*meso* equilibrium of **1** has been examined.

TABLE III. The Ratio[a] of Linewidths at Half-height for Observed ^2H and ^1H NMR Signals

	$\Delta\nu_{1/2}(^2H)/\Delta\nu_{1/2}(^1H)$[b]	
	meso	racemate
CH_3^{imine}	0.03 ± 0.01	0.06 ± 0.01
$CH_3^{equatorial}$	0.03 ± 0.01	0.03 ± 0.01
CH_3^{axial}	0.036 ± 0.005	0.040 ± 0.005

[a] Theoretically obtained value is 0.024, corresponding to the ratio of $(\gamma(^2H)/\gamma(^1H))^2$. [b] $\Delta\nu_{1/2} = \nu_{1/2}(obs.) - \nu_{1/2}(dia.)$. $\nu_{1/2}(dia.)$ is obtained for the corresponding diamagnetic nickel(II) complexes: ^1H linewidths are 3.6, 3.7, and 3.6 Hz for CH_3^{imine}, $CH_3^{equatorial}$ and CH_3^{axial}, respectively. ^2H linewidths fall within 7 Hz, included in experimental error for copper(II) complexes.

Nickel(II) complexes [11] show this conversion in basic aqueous solution, and the attained racemate/*meso* ratio is 6 at 37 °C. As far as this isomerization is attributable to the lability of the secondary amine proton [11], complex **1** also encounters this isomerization. Firstly, the conversion to racemate does not occur in acidic solution (pH = 5). On the other hand, freshly prepared basic aqueous solution (pH = 11) of pure *meso* changes into the solution of racemate within a few hours. The ^2H NMR spectrum in Fig. 3b clearly demonstrates that the domi-

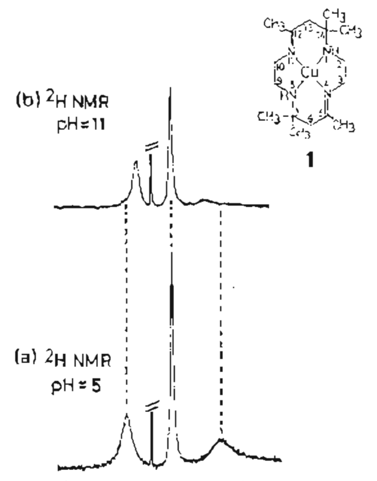

Fig. 3. ^2H NMR spectra at 24 °C of 0.01 M pure *meso*[Cu-(Me_6[14]4,11-dieneN_4]$(ClO_4)_2$ in aqueous solution. (a) No conversion occurred; (b) most of *meso* was converted into racemate (spectrum after 5 h from dissolution). Deuterated imine methyl group was selectively exchanged from proton under this condition, and its signal intensity significantly decreased.

nant methyl signals are characteristic of racemate and the *meso* signals become very weak. This shows that the conversion of *meso* to racemate readily occurs, and the equilibrium ratio of racemate/*meso* is much greater than that of the corresponding Ni(II) complex. Regarding this equilibrium, the effect of nickel(II) and copper(II) is different. As expected, no apparent conversion was observed within several hours in an aprotic solvent such as acetonitrile. It may take a long time to establish equilibrium. The racemate/*meso* ratio of 3/2 obtained from Fig. 1b, further from the equilibrium ratio, is associated with the ratio of the yield for each diastereomer upon metal-incorporation, which may be kept by the inert solvent system (methanol/water) to isolate **1**.

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