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Magnetic Phase Transitions in Dibromo(4*H*-1,2,4-triazole)copper(II) and Related Copper(II) Complexes As Studied by ^{14}N Nuclear Quadrupole Resonance and Magnetic Susceptibility Measurements

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The NQR spectra of nitrogen-14 in dibromo(4*H*-1,2,4-triazole)copper(II), dibromo(*N*-nitrosopiperidine)copper(II), and dibromo(dimethylnitrosamine)copper(II) were observed at various temperatures below liquid-N_2 temperature. In the temperature variation study, the unusual frequency shift or sudden disappearance of the observed resonance lines revealed the existence of phase transitions at 6.5, 1.90, and 29.5 K, for the complexes in the same order as above. Magnetic susceptibility measurements demonstrated that dibromo(4*H*-1,2,4-triazole)copper(II) shows a weak ferromagnetism below the transition temperature, indicating the appearance of a long-range-ordered state. From the temperature dependence of the ν^{I} frequency of the amino nitrogen atoms, it is found that the magnetism of this complex can be explained as a three-dimensional Ising ferromagnet below 6.5 K. The magnetic properties of the present complexes were discussed in comparison with those of the corresponding chlorine analogues.

Introduction

Previously, we reported the magnetic properties of dichloro(4*H*-1,2,4-triazole)copper(II), $C_2N_3H_3{\cdot}CuCl_2$, dichloro(dimethylnitrosamine)copper(II), $(CH_3)_2NNO{\cdot}CuCl_2$, and dichloro(*N*-nitrosopiperidine)copper(II), $(CH_2)_5NNO{\cdot}CuCl_2$, which were studied by ^{14}N nuclear quadrupole resonance (NQR) and magnetic susceptibility measurements.[1-3] In these compounds, $C_2N_3H_3{\cdot}CuCl_2$ and $(CH_3)_2NNO{\cdot}CuCl_2$ are known to form monoclinic crystals belonging to the space group $I2/c$ (C_{2h}^{6}) with $Z = 4$[4] and orthorhombic crystals belonging respectively to $Pnam$ (D_{2h}^{16}) with $Z = 4$.[5] It is a characteristic point of the crystal structure of these complexes that neighboring copper(II) ions are bridged by two chlorine atoms and one organic molecule to form an infinite linear chain. In conformity with this structural feature, the temperature dependence of the magnetic susceptibility of these complexes shows a broad maximum that is characteristic of a one-dimensional spin system coupled antiferromagnetically.[2,3,6] At extremely low temperatures, however, these two complexes undergo a magnetic phase transition from a paramagnetic into a long-range-ordered state, indicating that the magnetic interaction operative between those Cu(II) linear chains becomes nonnegligible. This interchain magnetic interaction is expected to play a more important role in the magnetic properties of the corresponding bromine complexes, which are obtained by replacing chlorine in the above complexes by bromine. For a confirmation of this, the present investigation of the ^{14}N NQR and magnetic susceptibility measurements of the bromine complexes has been undertaken.

Experimental Section

Materials. Dibromo(4*H*-1,2,4-triazole)copper(II), $C_2N_3H_3{\cdot}CuBr_2$, was prepared from 1*H*-1,2,4-triazole, copper(II) bromide, and concentrated hydrobromic acid according to the method described in the literature.[7] Large deep red crystals were obtained by slowly cooling the warm hydrobromic acid solution of the compound in a Dewar vessel. Dibromo(*N*-nitrosopiperidine)copper(II), $(CH_2)_5NNO{\cdot}CuBr_2$, and dibromo(dimethylnitrosamine)copper(II), $(CH_3)_2NNO{\cdot}CuBr_2$, were synthesized in a way similar to the method of preparation of the corresponding chlorine analogue.[8] *N*-Nitrosopiperidine or dimethylnitrosamine was added to solid copper(II) bromide, and then the mixture was dissolved in absolute ethanol. Slow evaporation of the ethanol solution at room temperature yielded deep red and green-black crystals for $(CH_2)_5NNO{\cdot}CuBr_2$ and $(CH_3)_2NNO{\cdot}CuBr_2$, respectively. The results of chemical analysis are listed in Table I.

Table I. Analytical Data for $C_2N_3H_3{\cdot}CuBr_2$, $(CH_2)_5NNO{\cdot}CuBr_2$ and $(CH_3)_2NNO{\cdot}CuBr_2$

compd		% Cu	% C	% H	% N	% Br
$C_2N_3H_3{\cdot}CuBr_2$	found	21.77	8.23	0.97	14.52	55.42
	calcd	21.73	8.21	1.03	14.37	54.65
$(CH_2)_5NNO{\cdot}CuBr_2$	found	19.05	17.90	2.98	8.32	46.24
	calcd	18.83	17.79	2.99	8.30	47.35
$(CH_3)_2NNO{\cdot}CuBr_2$	found	21.34	8.06	1.91	9.49	53.56
	calcd	21.36	8.08	2.03	9.42	53.73

Apparatus and Measurements. X-ray powder patterns were taken at room temperature by means of an X-ray diffractometer, Model D-3F, from Rigaku Denki Co. equipped with a copper anticathode.

^{14}N NQR spectra were observed by use of a modified Pound–Watkins type spectrometer operated in a frequency modulation mode.[9] Resonance frequencies were determined by employing a frequency counter, Model TR-5104, from Takeda Riken Co. The temperature below 4.2 K was obtained by using a conventional pumping system equipped with a manostat. Above 4.2 K, the temperature was controlled by adjusting by hand the current of a heater mounted in a cryostat. For the determination of the sample temperatures in this experiment, two germanium resistance thermometers were employed, which were N2G-28266, calibrated at Scientific Instruments, Inc., and CR 1000 from Cryocal, Inc., calibrated against the vapor pressure of liquid helium and also the ^{14}N NQR frequencies of hexamethylenetetramine.[10] The observed temperature was estimated to be accurate within ±0.01 K below 4.2 K, within ±0.05 K in the temperature range from 4.2 to ca. 10 K, and within ±0.5 K above ca. 10 K.

An ac bridge operated at 150 Hz[11] was employed for the determination of the magnetic susceptibility of the pulverized samples. As a standard sample, $CuSO_4{\cdot}5H_2O$ was employed.[12] The observed molar susceptibility was not corrected for diamagnetic contributions, because relatively large values were obtained for the susceptibilities in the temperature range studied. In this experiment, a carbon resistance thermometer calibrated by measuring the magnetic susceptibility of $CuSO_4{\cdot}5H_2O$ and a germanium resistance thermometer, CR1000-1.5-100, calibrated at Cryocal, Inc., were used above and below 4.2 K, respectively, for the determination of the sample temperature. The accuracy of the observed temperature was estimated to be within ±0.5

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Table II. ^{14}N NQR Frequencies and NQR Parameters of $C_2N_3H_3{\cdot}CuBr_2$ and Related Compounds in Their Paramagnetic States

compd (ref)	T/K	group	ν^I/kHz	ν^{II}/kHz	$eQqh^{-1}$/kHz	η
$C_2N_3H_3{\cdot}CuBr_2$	6.75	amino	1491.5			
	6.75	imino				
$C_2N_3H_3{\cdot}CuCl_2$ (1)	4.2	amino	1471.2	852.5	1549.1	0.7988
	4.2	imino				
$(CH_3)_2NNO{\cdot}CuBr_2$	30	amino	2304.4	1608.4	2608.5	0.5336
	30	nitroso	4379.0	3833.8	5475.2	0.1992
$(CH_3)_2NNO{\cdot}CuCl_2$ (2)	6.5	amino	2256.8	1537.1	2529.3	0.5691
	6.5	nitroso	4330.5	3808.6	5426.1	0.1924
$(CH_2)_5NNO{\cdot}CuBr_2$	1.95	amino				
	1.95	nitroso	4427.1	3856.3	5522.3	0.2067
$(CH_2)_5NNO{\cdot}CuCl_2$ (2)	2	amino	1851.9	1008.1	1906.7	0.8851
	2	nitroso	4208.0	3808.8	5344.5	0.1494

Table III. ^{14}N NQR Frequencies, ν^I, of the Amino Nitrogen Atoms of $C_2N_3H_3{\cdot}CuBr_2$ in Its Magnetically Ordered State

T/K	ν^I/kHz		
1.76	1511.62	1507.18	
2.98	1510.90	1506.68	
4.21	1508.76	1504.59	
5.26	1504.84	1501.19	
5.75	1501.64	1498.45	
6.12	1498.46	1495.84	
6.25	1497.46	1494.95	1491.55
6.32	1496.30	1494.37	1491.67
6.60			1491.43

and ±0.03 K above and below 4.2 K, respectively.

Results

Since ^{14}N nuclei have a nuclear spin I equal to unity, each of the crystallographically nonequivalent nitrogen atoms usually affords the following three resonance frequencies when the asymmetry parameter η is finite

$$\nu^I = \tfrac{3}{4}(eQqh^{-1})(1 + \eta/3) \tag{1a}$$

$$\nu^{II} = \tfrac{3}{4}(eQqh^{-1})(1 - \eta/3) \tag{1b}$$

$$\nu^{III} = \nu^I - \nu^{II} = \tfrac{1}{2}(eQqh^{-1})\eta \tag{1c}$$

where $eQqh^{-1}$ denotes the quadrupole coupling constant in frequency units. The ^{14}N NQR frequencies and the NQR parameters observed for the present dibromocopper(II) complexes in their paramagnetic state are listed in Table II. The assignment of observed resonance frequencies to amino and imino or nitroso nitrogen atoms can be made rather straightforwardly by comparing the frequencies of the dibromocopper(II) complexes with those of the corresponding dichlorocopper(II) complexes.

$C_2N_3H_3{\cdot}CuBr_2$. For this complex, only ν^I of the amino nitrogen could be observed. Figure 1 shows the temperature dependence of the ν^I frequencies. Above 6.5 ± 0.1 K, a single ν^I line was observed but it was split below 6.5 K into a doublet, each component line of which had almost equal intensity. This indicates the occurrence of a phase transition, possibly a magnetic one at the transition temperature T_c = 6.5 K. The observed ν^I frequencies below T_c are listed in Table III.

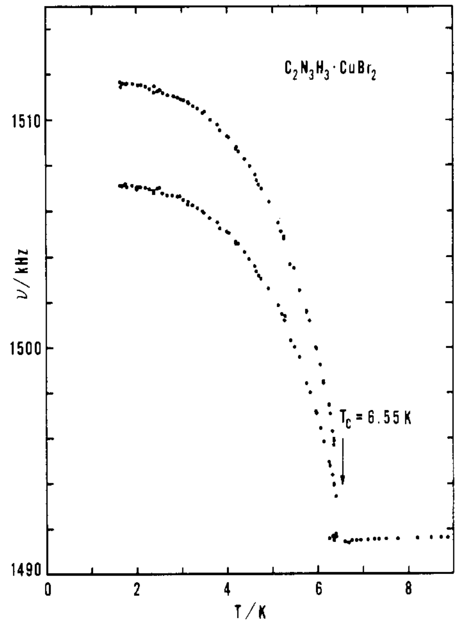

Figure 1. Temperature dependence of the ν^I NQR frequency of amino nitrogen atoms in dibromo(4*H*-1,2,4-triazole)copper(II).

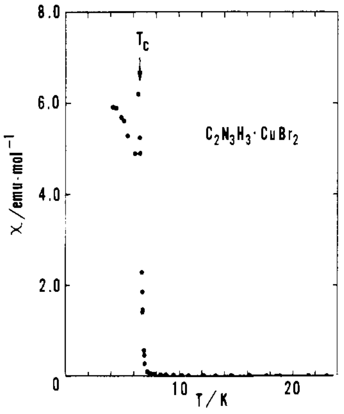

Figure 2. Temperature dependence of the ac powder susceptibility of dibromo(4*H*-1,2,4-triazole)copper(II).

When the sample was warmed from 4.2 K, each component line of the doublet decreased its frequency monotonously up to T_c. Near T_c, there happened rather complicated phenomena in the temperature dependence of resonance frequencies. At ca. 6.3 K, another resonance line appeared at 1491.6 kHz. Furthermore, the output level of a phase-sensitive detector became seriously dependent on temperature when the temperature became very close to T_c. This indicated that the oscillating conditions of the spectrometer strongly altered with changing temperature, resulting in a serious base line shift. Accordingly, it was impossible to determine the resonance frequencies between 6.4 and 6.6 K. At 6.6 K, a single ν^I line appeared at 1491.4 kHz and it was almost temperature independent up to ca. 20 K. The line could be observed even at 77 K.

The magnetic susceptibilities determined at various temperatures are shown in Figure 2. The susceptibility steeply increased with decreasing temperature and yielded a sharp maximum at T_c. Below this T_c, the experimental results strongly depended on the strength of the alternating magnetic field generated in the primary coil as in the case of $C_2N_3H_3{\cdot}CuCl_2$.[1]

From X-ray powder patterns, it was revealed that $C_2N_3H_3{\cdot}CuBr_2$ is isomorphous with $C_2N_3H_3{\cdot}CuCl_2$[4] and belongs to the monoclinic system having the lattice parameters a = 7.0 Å, b = 11.6 Å, c = 7.5 Å, and β' = 95.4°.

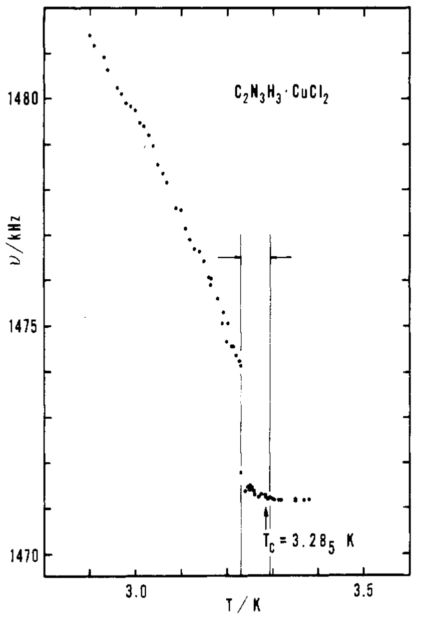

Figure 3. Temperature dependence of the ν^I NQR frequency of amino nitrogen atoms in dichloro(4*H*-1,2,4-triazole)copper(II) in the narrow temperature range near T_c. Complicated phenomena were observed (see text) in the temperature range indicated by arrows.

$C_2N_3H_3 \cdot CuCl_2$. For an evaluation of the critical exponent β in this complex, the temperature dependence of the ν^I frequency of the amino nitrogen atoms was reinvestigated more precisely. The sample that was prepared in the previous work[1] was used for the present measurements. The results are shown in Figure 3. In the temperature range between 3.29_5 and 3.23 K, several new lines appeared in the frequency range 1459–1485 kHz. The intensity of those lines was weakened when the external magnetic field of ca. 100 Oe was applied to the sample. The frequency and even the number of these new lines were changed in every experiment, although the original line always appeared at 1471.5 kHz. In Figure 3, the frequencies of only the original line are plotted.

$(CH_2)_5NNO \cdot CuBr_2$. In this compound, only the resonance frequencies attributable to nitroso nitrogen atoms could be observed, the temperature dependence of which is given in Figure 4. When the sample was cooled from 4.2 K, the ν^I and ν^{II} frequencies were observed to be shifted abruptly upward and downward, respectively, at 1.90 ± 0.02 K.

The temperature dependence of the magnetic susceptibility of $(CH_2)_5NNO \cdot CuBr_2$ is shown in Figure 5. The susceptibility went on increasing up to the lowest temperature, 1.65 K, attained in our experiment, and there was no detectable anomaly around 1.90 K.

$(CH_3)_2NNO \cdot CuBr_2$. From the X-ray powder analysis, it can be concluded that this dibromo complex is isomorphous with the chlorine analogue[5] and has an orthorhombic unit cell with $a = 6.6$ Å, $b = 15.1$ Å, and $c = 7.4$ Å.

It is interesting to note that NQR lines attributable to the nitroso nitrogen atoms could not be observed below 29.5 ± 0.5 K. Just above this temperature, however, the NQR lines of the nitroso nitrogen abruptly appeared. On the other hand, the NQR lines assignable to the amino nitrogen atoms could be observed even at 1.7 K. When the sample was warmed, the resonance frequencies of ν^I and ν^{II} of the amino nitrogen atoms decreased smoothly across 29.5 K with increasing temperature. However, the intensity of the signals became strong quite discontinuously when the sample was warmed above 30 K.

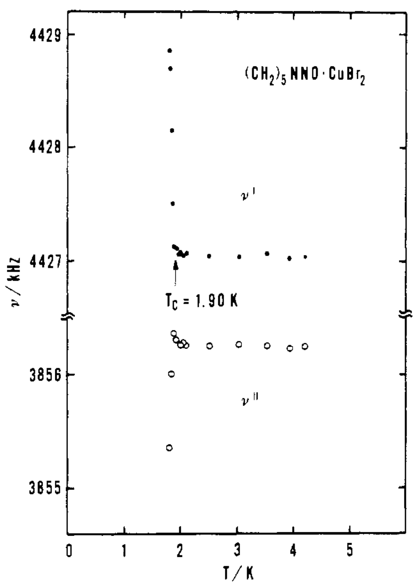

Figure 4. Temperature dependence of the nitroso nitrogen NQR frequencies, ν^I and ν^{II}, in dibromo(*N*-nitrosopiperidine)copper(II).

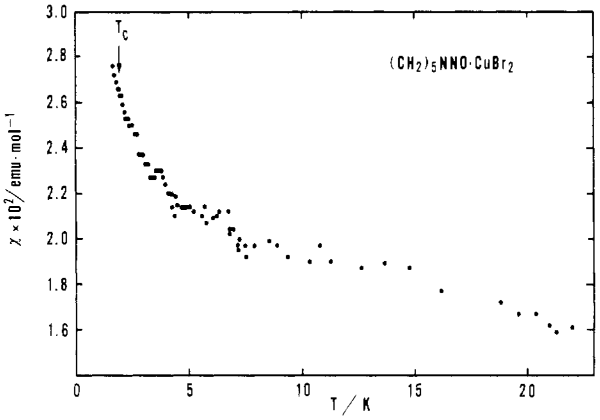

Figure 5. Temperature dependence of the ac powder susceptibility of dibromo(*N*-nitrosopiperidine)copper(II).

Discussion

$C_2N_3H_3 \cdot CuBr_2$ and $C_2N_3H_3 \cdot CuCl_2$. Since no NQR frequencies were detected between 6.4 and 6.6 K for $C_2N_3H_3 \cdot CuBr_2$, we could not determine T_c more accurately. However, it was noticed that the oscillating frequency of a Pound–Watkins type spectrometer employed for the experiment showed a remarkable temperature dependence near T_c; i.e., the oscillating frequency varied unusually only by changing the temperature of the sample near T_c. This means that there takes place around T_c an extraordinarily large change of the magnetic susceptibility of the complex, which is placed in the oscillating coil. The temperature-dependence curve of the oscillating frequency, thus, yielded a sharp minimum at 6.55 ± 0.02 K. We assumed this temperature to be a more accurate T_c.

Below T_c, the resonance frequency observed above T_c is shifted unusually and is split into a doublet as can be seen in Figure 1. The unusual frequency shift can be interpreted as resulting from the nuclear Zeeman interaction of ^{14}N nuclei due to an internal magnetic field at the nitrogen site produced by the polarized surrounding electron spins of Cu(II) ions. In this interpretation, we assume that the crystal structure of $C_2N_3H_3 \cdot CuBr_2$ is not altered by the magnetic phase transition. The frequency splitting, on the other hand, can be attributed to a magnetic dipole–dipole interaction operative between the amino nitrogen nucleus and a proton directly attached to it.[1]

Since only the ν^I frequency of the amino nitrogen in $C_2N_3H_3 \cdot CuBr_2$ was detected, the absolute magnitude of the internal field produced at the amino nitrogen nucleus could not be calculated. However, a relative magnitude of the internal

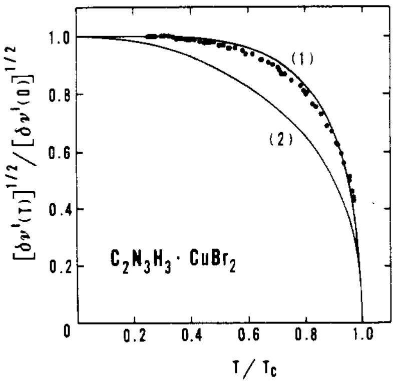

Figure 6. Reduced square root of the averaged ν^I NQR frequency shift of the amino nitrogen in dibromo(4*H*-1,2,4-triazole)copper(II) plotted against reduced temperature. The theoretical curves (1) and (2), respectively, calculated by assuming 3-D Ising bccub ferromagnets[15] and $S = 1/2$, 3-D Heisenberg scub ferromagnets,[16] were obtained from the literature.

field $H(T)/H(T')$ at different temperatures, T and T', could be estimated from the temperature dependence of the ν^I frequency alone. Since the magnitude of the Zeeman shift observed below T_c is sufficiently small as compared with the NQR frequency itself, a perturbation theory is applicable to solve this problem. When a perturbation magnetic field $H(T)$ is applied to a nitrogen nucleus at a given temperature T, let the ν^I frequency of the ^{14}N atom be shifted by $\delta(\nu^I(T))$. According to Pissanetzky,[13] $\delta(\nu^I(T))$ is given from second-order perturbation theory as

$$\delta(\nu^I(T)) = D^2\left[\frac{1}{2\eta A} - \frac{1}{\nu^I}\,\frac{3(1-\eta)}{(3-\eta)}\,g(\theta,\phi)\right] \quad (2)$$

where

$$D = \gamma(H(T))/2\pi \quad (3)$$

$$A = eQq/4h \quad (4)$$

and

$$g(\theta,\phi) = (\sin^2\theta)(3 - \eta + 2\eta\sin^2\phi)/2\eta \quad (5)$$

Here, θ and ϕ are angles that define the orientation of $H(T)$ with respect to the principal axis system of the electric field gradient tensor of the ^{14}N atom in question. If the quadrupole parameters and the orientation of $H(T)$ are assumed to be independent of temperature, one can obtain the relation

$$[\delta(\nu^I(T))]^{1/2}/[\delta(\nu^I(0))]^{1/2} = H(T)/H(0) \quad (6)$$

Here, $\delta(\nu^I(0))$ and $H(0)$ are values of the ν^I frequency shift and the magnitude of the internal field at $T = 0$, respectively, both of which are obtainable by extrapolation.

In Figure 6, the value of $[\delta(\nu^I(T))]^{1/2}/[\delta(\nu^I(0))]^{1/2}$ is plotted against a reduced temperature, T/T_c. Here, $\delta(\nu^I(T))$ is defined as a difference value of two frequencies, which are the averaged value of the two component frequencies of the ν^I doublet obtained at T and the ν^I frequency, 1491.51 kHz, obtained just above T_c. It is known that the internal magnetic field produced at a given position in a ferromagnetic or antiferromagnetic crystal is proportional to a spontaneous magnetization or a sublattice magnetization.[14] The theoretical curves calculated for the temperature dependence of the spontaneous magnetization are also given in Figure 6 for comparison.[15,16] The experimental values are in good agreement with the theoretical value, which is derived by assuming a three-dimensional Ising ferromagnet having a bccub lattice. Accordingly, it is concluded that an anisotropy of magnetic interaction plays a significant role in the manifestation of the weak ferromagnetism of $C_2N_3H_3 \cdot CuBr_2$ below T_c.

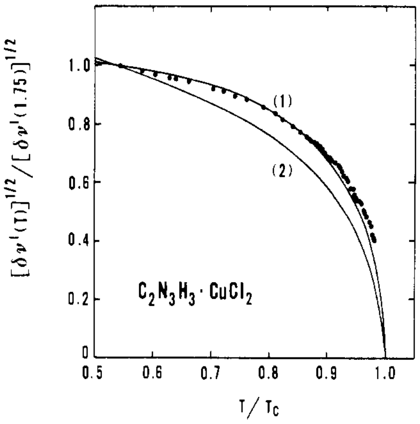

Figure 7. Plot of $[\delta(\nu^I(T))]^{1/2}/[\delta(\nu^I(1.75))]^{1/2}$ vs. T/T_c. The curves (1) and (2) are derived from the theoretical curves calculated for the 3-D Ising and 3-D Heisenberg ferromagnets, respectively, indicated in Figure 6.

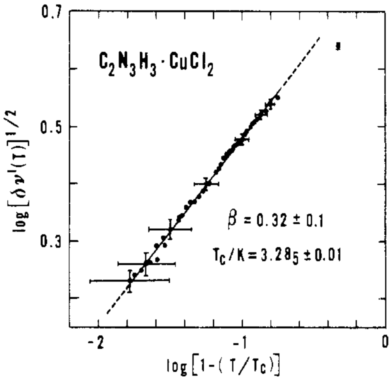

Figure 8. Plot of log $[\delta(\nu^I(T))]^{1/2}$ for the averaged ν^I NQR frequency shift of the amino nitrogen in dichloro(4*H*-1,2,4-triazole)copper(II) against log $[1 - (T/T_c)]$.

Because of the extremely low T_c value of 3.3 K,[1] $\delta(\nu^I(T))$ of $C_2N_3H_3 \cdot CuCl_2$ goes on increasing even at 1.75 K, which is the lowest temperature attained by our apparatus. Therefore, it was difficult to evaluate $\delta(\nu^I(0))$ very accurately. Then, we employed the ν^I frequency shift at 1.75 K in place of $\delta(\nu^I(0))$ to evaluate the ratio of the square root of the ν^I frequency shifts. Figure 7 shows the values of $[\delta(\nu^I(T))]^{1/2}/[\delta(\nu^I(1.75))]^{1/2}$ plotted against the reduced temperature. In this figure, T_c is taken as $3.28_5 \pm 0.01$ K, which was determined, as in the same way as for $C_2N_3H_3 \cdot CuBr_2$, from the sharp minimum temperature on the temperature dependence of the oscillating frequency of the spectrometer. The theoretical curves derived from those of Figure 6 are also included in Figure 7 for comparison. Again, the experimental values of $C_2N_3H_3 \cdot CuCl_2$ agree very well with the three-dimensional Ising model, indicating the presence of a crucial anisotropic magnetic interaction.

Since a precise determination of the temperature dependence of amino ν^I frequencies was made for $C_2N_3H_3 \cdot CuCl_2$ below 4.2 K in the present work (see Figure 3), a critical exponent β could be estimated for the magnetic phase transition.[17] Figure 8 shows log $[\delta(\nu^I(T))]^{1/2}$ values plotted against log $[1 - (T/T_c)]$. The value $[\delta(\nu^I(T))]^{1/2}$ is proportional to the internal field produced, that is, to the magnetization M.[13,14]

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Therefore, the slope of the straight line in Figure 8 gives the value of β defined by

$$M(T)/M(0) = B[1 - (T/T_c)]^{\beta} \tag{7}$$

where B is a constant. From Figure 8, the value of β can be estimated to be 0.32 ± 0.1, which is in good agreement with the theoretically predicted value of 0.312 for the three-dimensional Ising magnet.[17]

The magnetic susceptibility of $C_2N_3H_3{\cdot}CuCl_2$ and $C_2N_3H_3{\cdot}CuBr_2$ determined above T_c has been interpreted in terms of a one-dimensional Ising antiferromagnetic interaction.[6,7] In view of the crystal structure of these complexes and also of the magnetic susceptibility data, these complexes can be regarded as one-dimensional antiferromagnets at higher temperatures. However, the magnetic susceptibility of both complexes increases strikingly, when the temperature is lowered to T_c (see Figure 3 in ref 1 and the present Figure 2), indicating the existence of a weak ferromagnetism. This weak ferromagnetism is ascribable to spin canting in the antiferromagnetic state of these complexes.[18-21] From the symmetry considerations of these crystals, it is anticipated that there exists the Dzialoshinski–Moriya interaction,[21,22] which gives rise to spin canting between the neighboring Cu(II) sites along the Cu(II) magnetic chain. The weak ferromagnetism observed in the magnetic susceptibility of these complexes clearly indicates the occurrence of the phase transition from the paramagnetic state into the long-range-ordered state. When the temperature decreases to T_c, both $C_2N_3H_3{\cdot}CuCl_2$ and $C_2N_3H_3{\cdot}CuBr_2$ are no longer regarded as one-dimensional antiferromagnets but should be treated as three-dimensional weak ferromagnets with a considerable anisotropy.

The ratio of $kT_c/|J|$ can be employed as a measure of one-dimensionality,[17,23] where J denotes the exchange integral between the nearest-neighboring Cu(II) ions in a Cu(II) linear chain. Using the one-dimensional Ising model, Inoue et al. have estimated the J/k values as −8.3 and −17.9 K for $C_2N_3H_3{\cdot}CuBr_2$ and $C_2N_3H_3{\cdot}CuCl_2$, respectively.[6,7] The present results for T_c are 6.55 and 3.28_5 K for $C_2N_3H_3{\cdot}CuBr_2$ and $C_2N_3H_3{\cdot}CuCl_2$, respectively, indicating that the former complex has a greater $kT_c/|J|$ value. Therefore, it is concluded that the bromo complex is a less ideal one-dimensional antiferromagnet above T_c than the chloro complex.

$(CH_2)_5NNO{\cdot}CuBr_2$ and $(CH_3)_2NNO{\cdot}CuBr_2$. The sudden change of the ^{14}N NQR frequencies of the nitroso nitrogen in $(CH_2)_5NNO{\cdot}CuBr_2$ clearly indicates the occurrence of a phase transition at 1.90 K (see Figure 4). Because of the ^{14}N NQR anomaly appearing at extremely low temperature, the phase transition is assignable to a magnetic one although no anomaly was observed at around 1.90 K in the powder magnetic susceptibility measurements. The fact that the value of χT decreases monotonously with decreasing temperature indicates that antiferromagnetic interaction is dominant in the crystal. The temperature dependence of the magnetic susceptibilities seems essentially to bear the three-dimensional nature (see Figure 5).

The temperature dependences of the powder magnetic susceptibilities and the ^{14}N NQR frequencies observed for $(CH_2)_5NNO{\cdot}CuCl_2$ were already reported.[2] This chloro complex yields no phase transition down to ca. 2 K. The χ^{-1} vs. T curve shows the existence of a ferromagnetic coupling between Cu(II) ions in the chloro complex. However, the previously reported values of the susceptibility obtained above ca. 10 K are not so accurate that they are incapable of a more detailed theoretical analysis. Therefore, the magnetic susceptibility of $(CH_2)_5NNO{\cdot}CuCl_2$ was reinvestigated by using a larger amount of the sample. The results are shown in Figure 9. The magnetic susceptibilities obtained can be explained well by the model of a one-dimensional Heisenberg ferromagnet for $S = {}^1/_2$, where the exchange integral J/k is equal to 33 K within a chain.[24,25] In the calculation of the data plotted in Figure 9, the g value of 2.146 was used for the evaluation of the Curie constant

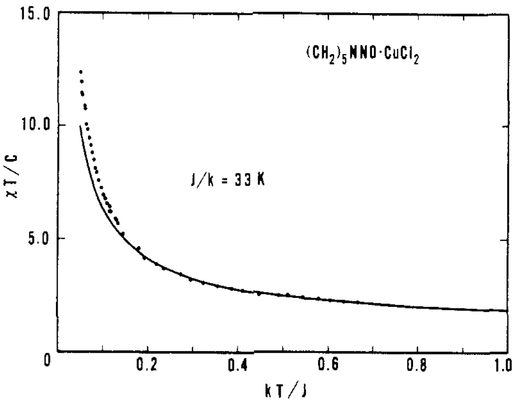

Figure 9. Plot of $\chi T/C$ vs. the reduced temperature (kT/J) for dichloro(N-nitrosopiperidine)copper(II). A theoretical curve calculated for $S = {}^1/_2$, 1-D Heisenberg ferromagnets is indicated.[26]

$$C = g^2\mu_B{}^2N/4k \tag{8}$$

where μ_B, N, and k are the Bohr magneton, the Avogadro number, and the Boltzmann constant, respectively. The g value was determined from ESR measurements carried out by use of a JEOL ES-SCXA X-band spectrometer. In view of the excellent agreement of the experimental curve with the theoretical one[25,26] as shown in Figure 9, it can be concluded that $(CH_2)_5NNO{\cdot}CuCl_2$ is a one-dimensional Heisenberg ferromagnet. Accordingly, it becomes apparent that the sign and the lattice dimensionality of the magnetic interaction operative in $(CH_2)_5NNO{\cdot}CuCl_2$ show a striking contrast to those in the corresponding bromo complex.

The abrupt disappearance of the ^{14}N NQR lines of the nitroso nitrogen in $(CH_3)_2NNO{\cdot}CuBr_2$ observed at 29.5 K with decreasing temperature can be attributed to the occurrence of a magnetic phase transition. Very similarly, the ^{14}N NQR lines of the nitroso nitrogen atoms of $(CH_3)_2NNO{\cdot}CuCl_2$ have not been observed below 6 K, where a three-dimensional ordering state is realized.[2] The fact that the bromo complex exhibits a higher T_c at 29.5 K than the chloro analogue suggests that the interchain magnetic interaction operative between Cu(II) chains plays a more significant role in the former complex than in the latter one.

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Registry No. $C_2N_3H_3{\cdot}CuBr_2$, 29502-81-6; $(CH_2)_5NNO{\cdot}CuBr_2$, 83547-90-4; $(CH_3)_2NNO{\cdot}CuBr_2$, 83547-92-6.

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