BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2232—2238 (1969)

ESR Studies of Bis-(*N,N*-diethylethylenediamine)copper(II) Perchlorate

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(Received February 10, 1969)

The ESR of bis-(*N,N*-diethylethylenediamine)copper(II) perchlorate has been examined in the polycrystalline state at three temperatures corresponding to the color change in the copper(II) complex due to thermochromism, in the glassy state of an aqueous solution at the temperature of liquid nitrogen, and in the magnetically-diluted state in diamagnetic bis-(*N,N*-diethylethylenediamine)nickel(II) perchlorate powder at three temperatures corresponding to the color change of the diluent due to thermochromism. The g and A values for square planar copper(II) complexes have been discussed in connection with the strength of the axial ligand field. The ESR results indicate that the structure of bis-(*N,N*-diethylethylenediamine)copper(II) perchlorate changes remarkably according to its circumstances, and possible mechanisms for the thermochromism have been suggested.

The bis-(*N,N*-diethylethylenediamine)copper(II) perchlorate was found to exhibit many interesting properties: (1) It is one of the few red copper(II) complexes, while it turns purplish-blue in an aqueous solution.[1,2] (2) The copper(II) complex exhibits thermochromism, a phenomenon which accompanies changes in crystal form and color.[1,3] (3) This copper(II) complex is known to be isomorphous to the diamagnetic nickel complex bis-(*N*,*N*-diethylethylenediamine)nickel(II) perchlorate, which also exhibits two steps of thermochromism.[3,4]

The copper(II) complex is *trans*-square coplanar, and two perchlorate anions are located at the axial position.[2,3] As to the structure of the complex, this is the only information so far reported. No satisfactory explanation for the structural mechanism of the thermochromism has yet been given. Therefore, more detailed and reliable information on the structure of the complex in various states is needed before we can understand the many interesting properties of the complex. The ESR technique is very useful for the study of the ligand field in metal complexes, and it has been widely applied to various copper(II) complexes.[5-9] The purpose of this paper is to discuss the ESR results on the copper(II) complex with the aim of estimating its structure and properties in various states, and their dependence on its molecular circumstances.

Experimental

The *N*,*N*-diethylethylenediamine, represented below, was a commercially-available substance. The bis-deen copper(II) perchlorate was prepared by the method in the literature[1] and was then recrystallized from methanol. In order to obtain magnetically-diluted samples, diamagnetic nickel complexes, bis-deen nickel(II) perchlorate, bis-deen nickel(II) tetrafluoroborate, diiodo-bis-deen nickel(II), and dinitrato-bis-deen nickel(II), were prepared using nickel(II) salt containing 1% of the cupric salt of the same anion, according to the method of the literature.[4] These samples are represented as Ni-ClO_4, Ni-BF_4, Ni-I, and Ni-NO_3 respectively. Although the amount of copper in each of these samples was not determined accurately in this investigation, proper magnetical dilution seemed to have been done for all the samples judging from the resolution of hyperfine structures and the S/N ratio of their ESR spectra, as shown, for example, in Figs. 2 and 3.

The ESR spectra were measured with a Hitachi X-band and a K-band ESR spectrometer, Model MES-4001, equipped with a 100 kc/s field modulation unit; furthermore, the second derivative ESR spectra were obtained using 100 kc/s-40 c/s field modulations in order to resolve the nitrogen super-hyperfine structure clearly. The field was calibrated with an NMR probe, and then with a benzene solution of vanadyl acetylacetonate. The ESR measurements were carried out at the temperatures of −196, 22, and 80—125°C for powdered samples and at −196°C in the glassy state for a *ca.* 0.01 M solution, using an equivolume mixture of water and methanol as the solvent. The ESR spectra thus obtained are shown in Figs. 1—5.

Results and Discussion

Polycrystalline State. The ESR line shapes for the polycrystalline samples of $S=1/2$ have been studied extensively by several authors.[10-12] From the ESR spectrum of the polycrystalline copper(II) complex, three approximate principal g values can be obtained, and a rough estimate for the line width along each of the principal axes may be made. The latter is, of course, connected with the spin interaction among neighboring cupric ions in a crystal.[13]

Figure 1 shows the ESR spectra of the polycrystal of bis-deen copper(II) perchlorate measured at three temperatures. This complex is brick red at room temperature and blue above 44°C. Furthermore, the complex has been found in this study to become pale red on cooling to the temperature of liquid nitrogen. This suggests that one more step of phase transition exists between room temperature and −196°C, although the phase-transition point was not determined precisely. This fact is also strongly supported by the clear differences in line shape among the three ESR spectra shown in Fig. 1, each being measured in the temperature range corresponding to each of the transition phases. These phases are called, in the order of temperature, the lower-temperature phase, the

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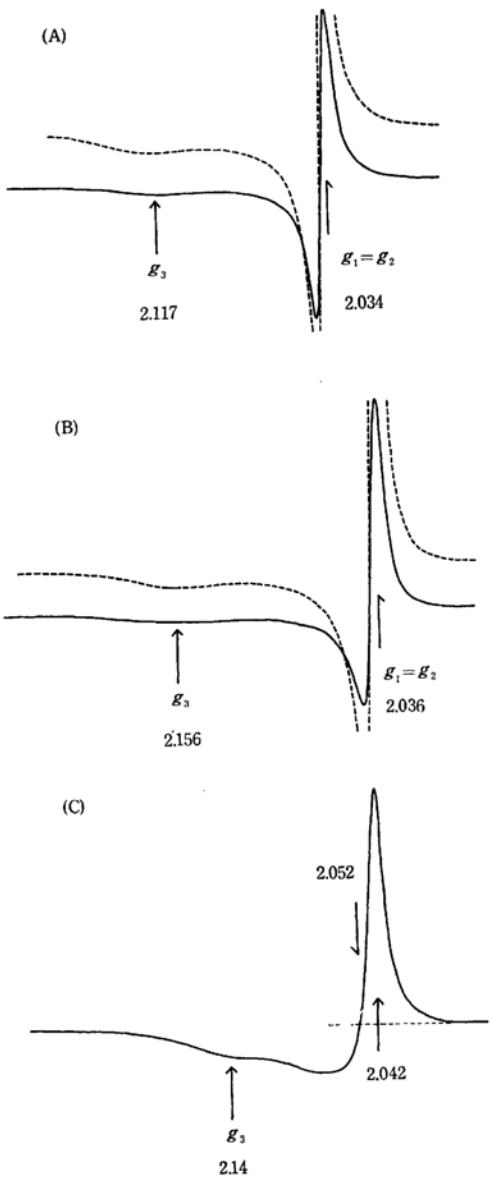

Fig. 1. The K-band ESR spectra of bis-(*N*,*N*-diethylethylenediamine)copper(II) perchlorate in poly-crystalline state. The spectra of dotted line are in case where amplification increased. The numbers represent g values.
(A) at −196°C, (B) at 22°C, (C) at 80°C

room-temperature phase, and the higher-temperature phase respectively.

The line shapes for all of the ESR spectra shown in Fig. 1 consist of one very intense absorption in the high-field part and one very weak and broad absorption in the low-field part, the latter being hardly observable by X-band measurement. This spectral feature apparently agrees with that of square planar copper(II) complexes, where the relation among three principal g values (assumed as $g_1 \leq g_2 \leq g_3$) is $g_1 \doteqdot g_2 < g_3$, which results from an axial or near axial symmetry in the ligand field. The numbers in the ESR spectra of Fig. 1 represent the results analyzed. Spectrum (A) in this figure is quite similar in line shape to (B) except that the g values are somewhat greater in (B) than in (A). However, Spectrum (C) is quite different in line shape from the (A) and (B) spectra, especially in the line shape of the intense absorption in the high-field part. A possible explanation for this is that the difference between the values of g_1 and g_2 is somewhat larger in (C) than in (A) and (B). In (C) the mean value of g_1 and g_2 could be estimated to be about 2.05. Furthermore, g_3 was smaller in (C) than in (B). Accordingly, although the phase-transition of the crystal is necessarily accompanied

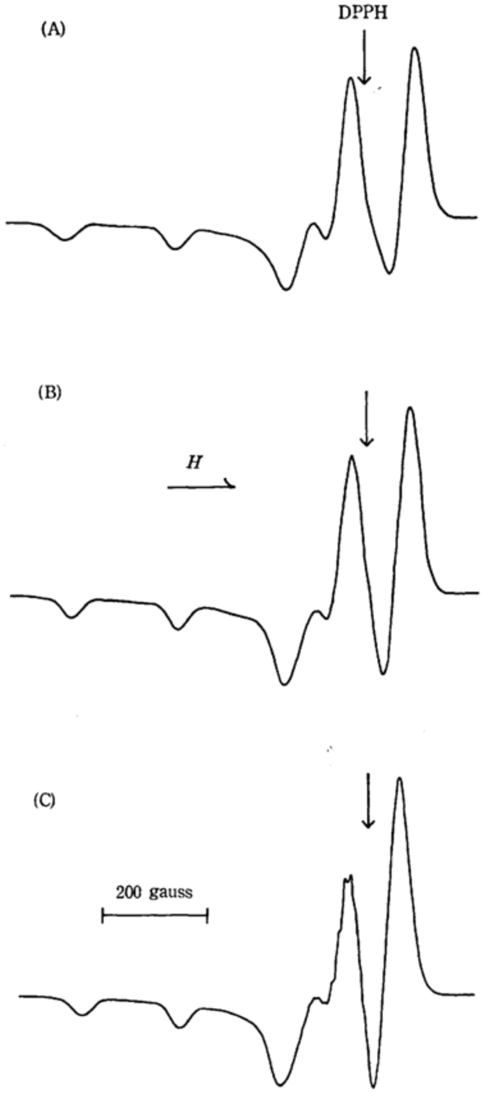

Fig. 2. The X-band ESR spectra of bis-(*N*,*N*-diethylethylenediamine)copper(II) perchlorate magnetically diluted in bis-(*N*,*N*-diethylethylenediamine) nickel(II) perchlorate powder.
(A) at −196°C, (B) at 22°C, (C) at 120°C

by some structural change in the constituent molecules, the structural change in this copper(II) complex from the room-temperature phase to the higher-temperature phase is not of the same type as that from the lower-temperature phase to the room-temperature phase.

Magnetically-diluted Powdered Samples. Bis-deen nickel(II) perchlorate is known to be isomorphous to bis-deen copper(II) perchlorate.³⁾ Interestingly, the nickel complex also exhibits two steps of thermochromism: it is reddish-orange above about 90°C, orange near room temperature, and pale yellow upon being cooled to the temperature of liquid nitrogen. Figure 2 shows the ESR spectra of the copper(II) complex magnetically diluted in diamagnetic bis-deen nickel(II) perchlorate, measured using the X-band in the three temperature ranges corresponding to the transition phases of the diluent. These ESR spectra are very similar to each other in line shape except that the super-hyperfine structure observed in the high-field part is clearly resolved as the transition phase becomes a higher-temperature phase. This property of the super-hyperfine structure is also clearly indicated in the second derivative spectra shown in Fig. 3. This tendency of the super-hyperfine structure is contrary to the general rule that the line width narrows, because of the lengthening of the spin-lattice relaxation time, with a lowering in the temperature. Accordingly, it seems most reasonable that the tendency is closely related to the fact that the resolution of this kind of super-hyperfine structure depends upon the relative values among the magnetic parameters of g, A, and A_N. The super-hyperfine structure under discussion is considered to be due to the interaction of a copper unpaired electron with ligand nitrogen nuclei.⁶⁻⁸⁾

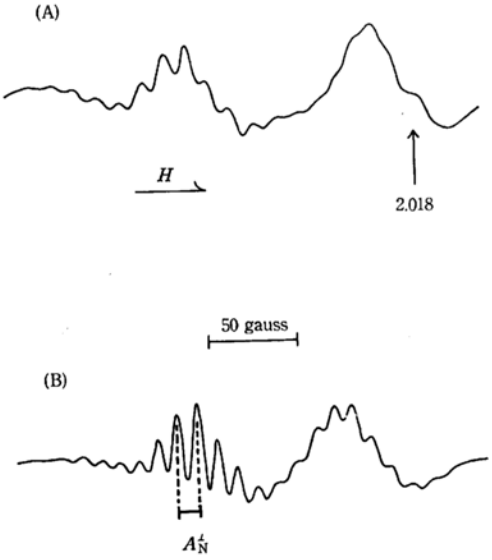

Fig. 3. The second derivative X-band ESR spectra enlarged at the high field part of the ESR spectra shown in Fig. 2.
(A) at 22°C, (B) at 120°C

The K-band ESR spectra for two temperature phases are shown in Fig. 4. These two spectra are similar to each other in line shape. The purpose of this K-band measurement is to eliminate as far as possible the complexity of absorption observed in the high-field part of the X-band spectra of Fig. 2. Judging from the line shape of these K-band ESR spectra of Fig. 4,¹¹⁾ it seems reasonable to determine the values of g_1 and g_2 in such a way as is indicated by the arrows in the figure. Then, g_1 differs from g_2 by about 0.03; therefore, axial symmetry in the ligand field decreases to a certain extent in Ni-ClO$_4$.

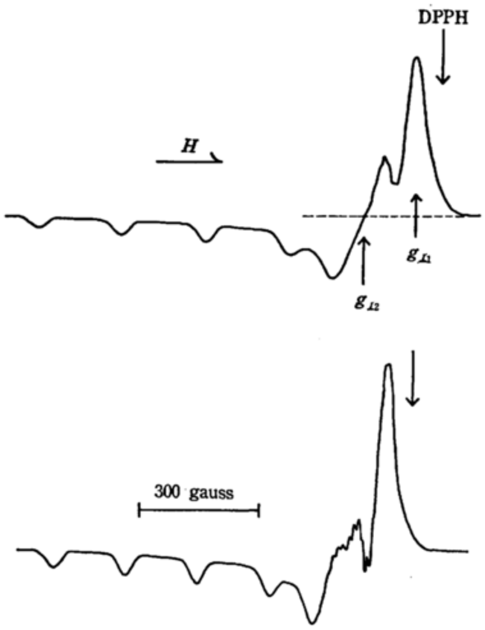

Fig. 4. The K-band ESR spectra of bis-(*N*,*N*-diethylethylenediamine)copper(II) perchlorate magnetically diluted in bis-(*N*,*N*-diethylethylenediamine)nickel(II) perchlorate powder.
(A) at 22°C, (B) at 120°C

Bis-deen nickel(II) tetrafluoroborate, diiodo-bis-deen nickel(II), and dinitrato-bis-deen nickel(II) are diamagnetic; all of these also exhibit two steps of thermochromism, much like bis-deen copper(II) perchlorate.⁴⁾ They were used as diluents in order to dilute magnetically the copper(II) complex of the same anion. The behavior of the ESR spectra for these samples, namely, Ni-BF$_4$, Ni-I and-NO$_3$, was almost the same as that of Ni-ClO$_4$. It is worth noting that the change in magnetic parameters for the copper(II) complexes takes place at the transition temperatures of diluents, for the change in bis-deen copper(II) perchlorate did not occur at its transition temperature of 44°C. This result indicates that the structural change in the copper(II) complexes takes place simultaneously

Table 1. The magnetic parameters of $[Cu(deen)_2]X_2$[a] magnetically diluted in the powder of $[Ni(deen)_2]X_2$

Temperature (°C)	Magnetic parameter	X			
		ClO_4^-	BF_4^-	I^-	NO_3^-
−196	$g_{//}$	2.171	2.172	2.178	2.170
	$A_{//}\times 10^4\,cm^{-1}$	213	213	202	212
22	$g_{//}$	2.172	2.175	2.179	2.171
	$g_{\perp 1}$	2.018	2.018	2.021	2.015
	$g_{\perp 2}$	2.045	2.046	2.049	2.049
	$A_{//}\times 10^4\,cm^{-1}$	206	205	198	206
	$A_N\perp\times 10^4\,cm^{-1}$	11.3	11.3	10.8	11.6
120	$g_{//}$	2.180	2.182	2.180	2.173
	$A_{//}\times 10^4\,cm^{-1}$	193	192	190	201
	$A_N\perp\times 10^4\,cm^{-1}$	10.6	10.7	11.0	11.0

a) For example, bis-(*N,N*-diethylethylenediamine)copper(II) perchlorate is expressed as $[Cu(deen)_2]X_2$ where $X=ClO_4^-$.

with those of the diluents. All of the magnetic parameters experimentally determined for the magnetically-diluted samples are listed in Table 1.

The results listed in Table 1 indicate that the g and A values gradually change in one direction as the phase changes from the lower-temperature phase to the higher-temperature phase. This fact implies that the structural changes accompanied by each of the phase transitions are of the same kind and increase in one direction with the transition from the lower-temperature phase to the higher. The super-hyperfine splitting constants decrease slightly for almost all of the samples as the phase transfers from the room-temperature phase to the higher-temperature phase. This suggests that the σ covalency of copper-ligand nitrogen bonds decreases somewhat with the same phase transition.[6-8] The table also reveals that all the anions of Ni-ClO_4, Ni-BF, Ni_4-I, and Ni-NO_3 have almost the same effect on the cupric ion.

Solution. Figure 5 shows the X-band and K-band ESR spectra of bis-deen copper(II) perchlorate in the glassy state of an aqueous-methanolic solution measured at the temperature of liquid nitrogen. When spectrum (B) in this figure is compared with the spectra of Fig. 4, the difference between g_1 and g_2 seems to be smaller in the former than in the latter; the ligand field for the copper(II) complex is nearer to being of an axial symmetry in solution than in the diamagnetic nickel(II) complex. The spectra of Fig. 5 were analyzed as follows:

$$g_{//}=2.212$$

$$g_{\perp}=2.048$$

$$A_{//}=184\times 10^{-4}\,cm^{-1}$$

Attention should be given to the point that the structure of the copper(II) complex changes considerably according to its circumstances.

Ligand Field and Magnetic Dilution. In this paragraph the structure of bis-deen copper(II) perchlorate will be discussed from the point of view of ESR. The copper(II) complex is known to be purplish-blue in an aqueous solution and red in crystal.[1,2] This color change has been speculated, on a simplified basis, to be due to the difference in strength of ligand field along the axis normal to the molecular plane.[2] Although the copper(II) complex is of a planar structure in both states, in an aqueous solution water molecules, being small in volume, can come close to the cupric ion, but in crystal perchlorate anions can not come so closely to the cupric ion as can water

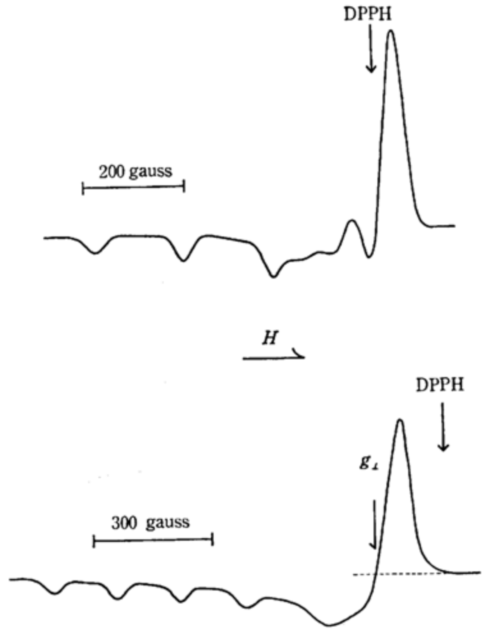

Fig. 5. The ESR spectra of bis-(*N,N*-diethylethylenediamine)copper(II) perchlorate in aqueous-methanolic solution at −196°C.
(A) X-band, (B) K-band

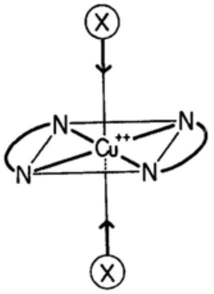

Fig. 6. The schematically represented structure of the copper(II) complex under discussion. X (ClO_4^- or H_2O) presents axial ligand field to cupric ion.

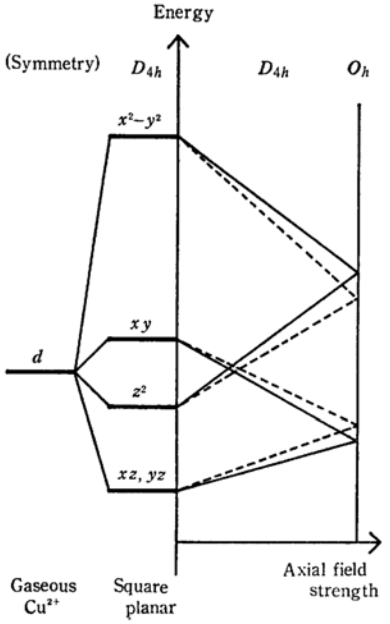

Fig. 7. Schematic representation of the energy levels cupric ion in axial ligand field of various streng of ths.

molecules because of the remarkable steric hindrance by ligand ethyl groups on the bulky anions.

In Fig. 6 the above situation is schematically pictured. Figure 7 also schematically represents, using, for convenience, the crystal field theory, the energy levels of the cupric ion of the square planar complex (D_{4h} symmetry) when two axial ligands coordinate to the cupric ion in various strengths. The dotted line in this figure represents the energy levels in a more practical case; when the axial coordination strengthens, the equatorial coordination weakens. In the planar copper(II) complex, the uppermost level of the $d_{x^2-y^2}$ orbital is half filled, and the other levels, completely occupied, with electrons, and the *d*–*d* absorption bands correspond to a one-electron transfer from the lower levels to the uppermost level. The fact that the bands shift to longer wavelengths as the axial coordination strengthens has been confirmed both theoretically and experimentally.[14]

It will be assumed that the following wave functions describe the system:

$$\left.\begin{aligned} \psi_{x^2-y^2} &= \alpha d_{x^2-y^2} - \alpha' \sigma_{\rm L}(x^2-y^2) \\ \psi_{xy} &= \beta d_{xy} - \beta' \phi_{\rm L}(xy) \\ \psi_{xz,yz} &= \beta_1 d_{xz,yz} - \beta_1' \phi_{\rm L}(xz,\ yz) \\ \psi_{z^2} &= \alpha_1 d_{z^2} - \alpha_1' \sigma_{\rm L}(z^2) \end{aligned}\right\} \qquad (1)$$

In each of the wave functions, the second term on the right-hand side represents the proper ligand orbital which can be mixed with the copper *d* orbital expressed in the first term. The relations between the ESR data and the covalency parameters, α, β, and β_1, can then be expressed approximately as follows:[5-9]

$$g_{//} = 2 - \frac{8\lambda}{\Delta E_{xy}}\alpha^2\beta^2 \qquad (2)$$

$$g_{\perp} = 2 - \frac{2\lambda}{\Delta E_{xz,yz}}\alpha^2\beta_1^2 \qquad (3)$$

$$A_{//} = P\left[-\frac{4}{7}\alpha^2 - \kappa + (g_{//}-2) + \frac{3}{7}(g_{\perp}-2)\right] \qquad (4)$$

where κ is the Fermi contact term, $\Delta E_{xy} = E_{x^2-y^2} - E_{xy}$, $\Delta E_{xz,yz} = E_{x^2-y^2} - E_{xz,yz}$, and $P = 0.036$ cm^{-1}.

It is interesting and important to learn how the *g* and *A* values change as the axial coordination varies in strength. The following theory may be derived from Fig. 7 and the three equations (2)—(4); All of the following discussion is concerned with the case in which the axial ligand field strengthens. α^2 increases remarkably, β_1^2 increases to a smaller extent, and the change in β^2 is quite small. $\Delta E_{xz,yz}$ decreases remarkably, and ΔE_{xy} decreases slightly. Therefore, $g_{//}$ remarkably increases. $g_{\perp}$ also increases, but the amount of increase is not large because of the small factor, 2, in the second terms on the right-hand side of Eq. (3). On the other hand, the situation for $A_{//}$ is rather complicated. When the axial coordination varies in strength, the change in the value of $|A_{//}|$ is dependent on the relative changes in the value of α^2, κ, and *g* in Eq. (4). However, it was experimentally indicated that, for some planar copper(II) complexes, the value of $|A_{//}|$ decreases as the axial coordination is strengthened.[15] Furthermore, cupric ions in MgO or CaO, which may be regarded as extreme cases in which the axial coordination becomes almost equal in strength to the equatorial coordination, have a very small value of $|A_{//}|$.[16] From the above-mentioned facts, it may be considered, as a general rule, that the value of $|A_{//}|$ decreases

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as the axial coordination strengthens.

The samples employed in this work are numbered as follows: the polycrystal at -196°C is I: the polycrystal are 22°C, II; the polycrystal at 80°C, III; Ni-ClO_4 at -196°C, IV: Ni-ClO_4 at 22°C, V; Ni-ClO_4 at 120°C, VI, and the aqueous-methanolic solution at -196°C, VII. For I, II, IV, V, VI, and VII, the $g_{//}$ or g_3 values are 2.117, 2.156, 2.171, 2.172, 2.180, and 2.212 respectively, and the $g_{\perp}$ values, or the mean values of g_1 and g_2, are 2.034, 2.036, 2.03—2.04, 2.03—2.04, 2.03—2.04, and 2.048 respectively. For IV, V, VI, and VII, the values of $|A_{//}|$ ($\times 10^4$ cm^{-1}) are 213, 206, 193, and 184 respectively. From these results it may reasonably be concluded that, among I, II, IV, V, VI, and VII, the difference in structure lies mainly in the axial coordination and that the axial ligand field is strengthened in this order of samples. The tendency of the super-hyperfine splitting constant for V and VI, which had already been discussed, also supports this conclusion indirectly. It is a very interesting suggestion that the phase transitions from I to II, from IV to V, and from V to VI accompany such a structural change as the access of the perchlorate anion to the cupric ion. However, the phase transition from II to III is of a different kind and possibily accompanies the structural change in the equatorial coordination. It may also be noted that IV, V, and VI in the above-mentioned series of samples decreases in axial symmetry to a slightly larger extent than the others.

It should be emphasized here that, as has been described, the properties of bis-deen copper(II) perchlorate vary to a larger extent according to its circumstances. Therefore, the meaning of magnetical dilution for the metal complex of a flexible structure is rather complicated.