ELECTRON PARAMAGNETIC RESONANCE AND DILATOMETRIC STUDY OF PENTA- AND TETRAMMINE COMPLEXES OF Cu^{2+} IN $[Cu(NH_3)_n](ClO_4)_2$

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EPR spectrum parameters are determined for copper (II) penta- and tetrammine perchlorates. Copper pentammine perchlorate is found to undergo a phase transition at 142 K with a twofold decrease in isotropic EPR linewidth and a simultaneous increase in the g-factor 2.130 to 2.136. For copper (II) tetrammine perchlorate, an anisotropic spectrum is observed with $g_{||} = 2.230$ and $g_{\perp} = 2.051$. At high temperatures observations reveal an activation process of rotation of the complex, as well as the initial stage of g-factor averaging. Dilatometric measurements reveal, at 140 K, a phase transition for $[Cu(NH_3)_5](ClO_4)_2$ but none for $[Cu(NH_3)_4](ClO_4)_2$.

1. Introduction

The authors report results of an EPR study of copper (II) ions in $[Cu(NH_3)_n](ClO_4)_2$ and draw conclusions regarding the structure and symmetry of the complex and the nature of the metal-ligand bonds. The dynamics of the complex is studied throughout a wide range of temperature. Especially interesting is the copper (II) pentammine perchlorate complex, which possesses a structure typical for hexamines with the symmetry Fm3m. Hexammines are compounds with the general formula $Me^{2+}(NH_3)_6X_2^{1-}$ where Me = Ni, Mn, Co, Zn, Cd and X = I, Br, Cl, NO_3, PF_6, BF_4, ClO_4. Depending on temperature, hexamines occur in two phases, differing i.a. as to the parameters of their EPR spectrum. The transition from one phase to the other is structural and takes place at a well defined temperature T_c dependent on the effective radii of the cations and anions [1]. Hitherto, such phase transitions have not been observed for copper (II) pentammine complexes.

2. Experimental

The compounds for investigation were obtained by the method described in Gmelin [2] and in a paper by Hathaway and Tomlinson [3].

Acting on $CuCO_3 \cdot CuOH_2 \cdot H_2O$ with the stoichiometric amount of 60% perchloric

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acid $HClO_4$, copper (II) perchlorate $Cu(ClO_4)_2 \cdot 6H_2O$ was obtained. The compound was dehydrated by drying to constant weight at 370 K. In order to obtain copper (II) pentammine perchlorate a flow of NH_3, purified and dried over NaOH, was applied. The pentammine, which is blue, changes to violet in air on losing one NH_3 molecule. Copper (II) tetrammine perchlorate is stable. Analysis by the Kjeldahl method shows that pentammine perchlorate contains 5.19 moles of NH_3 while the one mole of tetrammine contains 4.23 moles of NH_3.

The compound $[Cu(NH_3)_5](ClO_4)_2$ has a regular crystallographical structure of the type Fm3m, with a lattice constant $a = 11.31$ Å [3], whereas $[Cu(NH_3)_4](ClO_4)_2$ is of symmetry lower than regular, as shown by the powder diffractogram. From optical measurements [3] the band of maximal absorption is known to lie at $\Delta = 15.9 \times 10^3$ cm^{-1} for $[Cu(NH_3)_5](ClO_4)_2$ and $\Delta = 17.8 \times 10^3$ cm^{-1} for $[Cu(NH_3)_4](ClO_4)_2$.

EPR was studied with a microwave spectrometer, made by ITA Wrocław. The magnetic field was calibrated with an automatic digital JTM-2 magnetometer. Temperature was controlled and stabilized with an accuracy of 0.5 deg throughout the cavity by means of a flow of nitrogen gas. EPR was studied for both $Cu(ClO_4)_2 \cdot 4H_2O$, $[Cu(NH_3)_5](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)_2$. The EPR parameters measured at room temperature RT and liquid nitrogen temperature are given in Table I. Due to the presence of spin exchange,

TABLE I

	$g_{\|\|}$		$g_\perp$		$\bar{g}$	
	RT	77K	RT	77K	RT	77K
$Cu(ClO_4)_2 \cdot 4H_2O$	2.425		2.091		2.203	
$[Cu(NH_3)_5](ClO_4)_2$	—	—	—	—	2.136	2.130
$[Cu(NH_3)_4](ClO_4)_2$	2.230	2.228	2.051	2.049	2.111	2.109

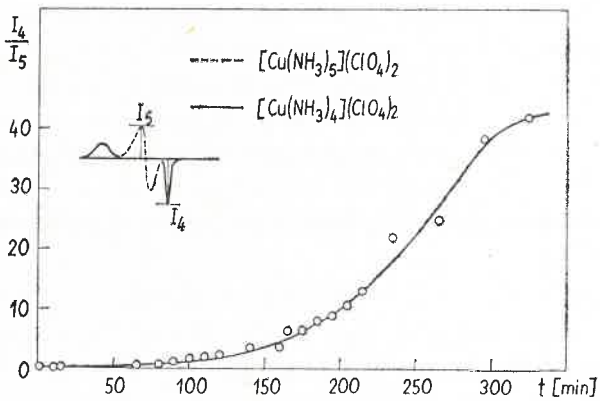


Fig. 1. Transition kinetics of $[Cu(NH_3)_5](ClO_4)_2$ into $[Cu(NH_3)_4](ClO_4)_2$

the EPR of the compounds fail to reveal a hyperfine structure related to the unpaired electron-copper nucleus interaction.

In $[Cu(NH_3)_5](ClO_4)_2$, copper is surrounded by an NH_3 square-based pyramid which, at room temperature, performs rotation. Thus, the anisotropy tensor values g cancel out by averaging and the line is symmetric, of width $2\Delta B_{1s} = 4.5$ mT. For the other compounds, a spectrum typical of polycrystals with lines of parallel and perpendicular orientation is observed. The ground state of Cu^{2+} in copper tetraqueus and tetrammine perchlorate is $d_{x^2-y^2}$, whereas the surroundings consists of a planar coordination square, composed of four H_2O or four NH_3. The compound $[Cu(NH_3)_5](ClO_4)_2$ is unstable and, in air, gives off one ammonia molecule. This is apparent by a gradual vanishing of the single line amplitude of $[Cu(NH_3)_5]^{2+}$ in place of which there emerges the spectrum of the polycrystalline $[Cu(NH_3)_4]^{2+}$ sample. The kinetics of the process is displayed in Fig. 1, where the axis of ordinaten gives the ratio of amplitudes of the line of perpendicular orientation for the tetrammine compound and the line originating in the pentammine complex.

A. $[Cu(NH_3)_5](ClO_4)_2$

To preserve the compound from losing NH_3 the sample was maintained in an air-tight ampoule. The linewidth (Fig. 2) and g-factor (Fig. 3) were measured from 4.2 to 350 K. Both parameters were found to undergo a change in value at 142 K, the linewidth decreas-

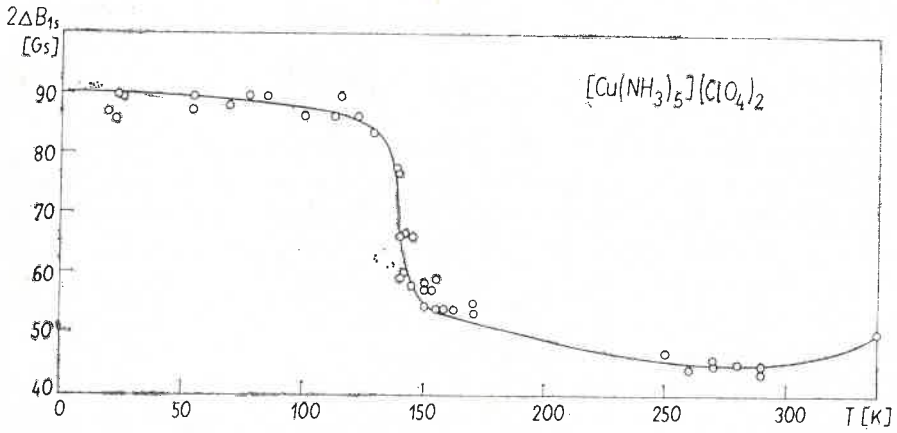


Fig. 2. $[Cu(NH_3)_5](ClO_4)_2$ EPR line width vs. temperature

ing to one half and the g-factor increasing slightly at higher temperature. Upwards of room temperature the linewidth begins to increase. A similar behaviour of $\Delta B(T)$ has been reported for hexammines with nickel cations and the complex anions PF_6[4], BF_4 [5], ClO_4[6] and NO_3[7]. All these compounds exhibit a structural phase transition with an anomaly of the specific heat at a temperature coinciding with, or close to that of the discontinuity in linewidth changes. The transition observed in hexammines consists in a change in structure from cubic at high temperatures to lower at $T < T_c$, involving an increase in density and hindering of NH_3 rotation. Hence, copper pentammine perchlorate can

also be presumed to undergo a phase transition of this type. This is additionally corroborated by the increase in g-factor at increasing temperature pointing to a distortion of the square-based pyramid enclosing the copper ion. In the case of copper ions, as a result of the static Jahn–Teller effect, distortion is present in either phase and should lead to an anisotropic spectrum i.e. two groups of lines at $g_{\parallel}$ and $g_{\perp}$ should appear from polycrystalline samples. The presence of a spin exchange and rotation is confirmed by the results

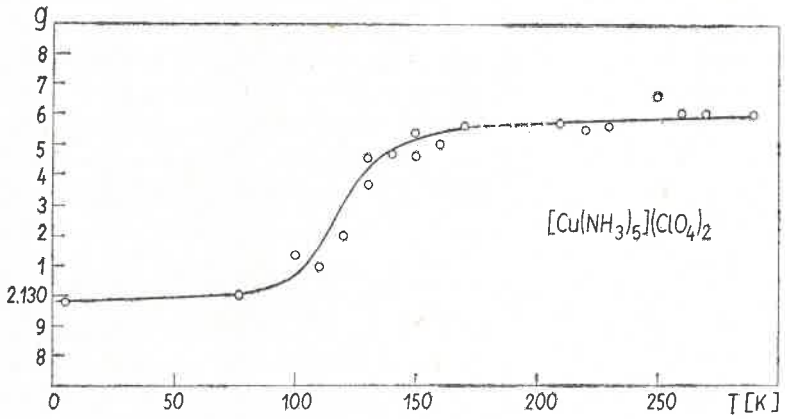


Fig. 3. Jump-wise change of the g-factor in the region of phase transition for $[Cu(NH_3)_5](ClO_4)_2$

[8] for a pentammine copper complex — doped $[Zn(NH_3)_4](ClO_4)_2$, where strong dilution of the copper ions removes exchange interaction permitting the observation of a hyperfine structure of the EPR spectrum. Below 155 K the spectrum exhibits g-factor anisotropy whereas at higher temperatures incipient pseudorotation causes the anisotropic spectrum to disappear and to be replaced by an averaged "liquid-like" spectrum. In $[Cu(NH_3)_5](ClO_4)_2$, irrespective of temperature, a single symmetric line is observed. Since the complex salt is a purely copper compound there is strong spin exchange, cancelling the anisotropy. Moreover, at temperatures higher than T_c, the tetragonal distortion axis of the complex begins to rotate leading to a narrowing of the line.

It has been found that the presence of NH_3 gas lowers the transition temperature to 130 K (of T_c in Fig. 3 and 2 for experiments performed in the presence and absence of gaseous ammonia) and causes the transition to become diffuse. The phase transition temperature of 100% copper pentammine perchlorate (142 K) lies slightly below than that of $Zn^{99\%}\ Cu^{1\%}\ (NH_3)_5(ClO_4)_2$(155 K) and the 100% Zn compound (163 K)[9].

B. $[Cu(NH_3)_4](ClO_4)_2$

"Aged" samples, stored without an atmosphere of NH_3, exhibit a typically anisotropic spectrum, with the parameters given in Table I. From 77 K to 420 K a slight increase in $g_{\parallel}$ and $g_{\perp}$ is observed (Fig. 4). Also, the linewidth increases slowly, corresponding to a shortening of the relaxation time T_1. Upwards of 380 K a transition from the anisotropic spectrum to an isotropic one becomes apparent. Hence, in this temperature region, tumbling of the

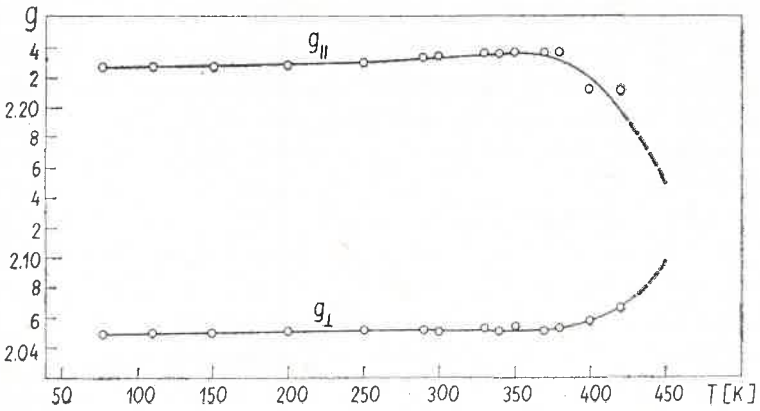
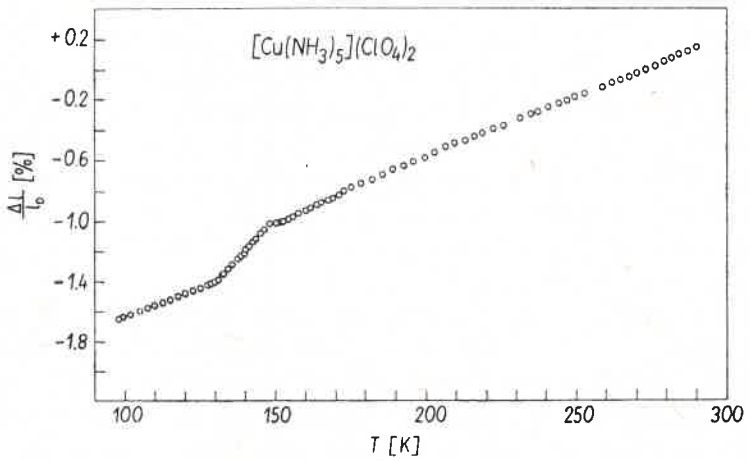


Fig. 4. Temperature-dependence of g-factor for $[Cu(NH_3)_4](ClO_4)_2$



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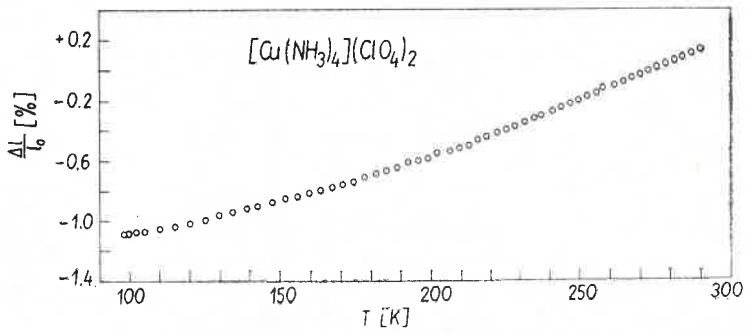

b

Fig. 5. Relative change in length of the sample for: a) $[Cu(NH_3)_5](ClO_4)_2$, b) $[Cu(NH_3)_4](ClO_4)_2$

complex $[Cu(NH_3)_4]^{2+}$ as a whole sets in. Hoffmann and Goslar [10] have observed an effect of this kind for $[Cu(NH_3]_4]^{2+}$ in $Cd(NH_3)_4(CH_3COO)_2$ crystal in the neighbourhood of 250 K. The difference in temperature of the emergence of isotropic tumbling is due to the much larger size of Cd^{2+} cation compared to Cu^{2+} ion. Hence, the complexes are much freer $[Cu(NH_3)_4]^{2+}$ in a cadmium lattice than in 100% copper tetrammine perchlorate. The spectrum observed below 380 K points to: (*i*) an absence of rotation, and (*ii*) weak spin exchange. The coordination surroundings of the Cu^{2+} ion, here, consists of a planar NH_3 square, and this lowering of the symmetry, compared with the square-based pyramidal symmetry of the copper pentammine complex, rules out rotation of the complex. Since the energies of the optical transitions between the ground state $d_{x^2-y^2}$ and the excited states are unavailable, we can but approximately assess the spin density on the central ion on the basis of $\bar{g}$ (2.111) and the frequencies corresponding to maximal absorption ($\Delta = 17.8 \times 10^3$ cm^{-1}):

$$\bar{g} = 2.0023 - \frac{4\lambda_0 \alpha^2 \beta^2}{\Delta},$$

where α is the spin density on the orbital $d_{x^2-y^2}$, β — that on the orbital excited, and λ_0 — spin-orbit coupling constant for the free ion. We hence obtain $\alpha^2\beta^2 = 0.58$ and, assuming $\beta^2 = 0.9$ derive $\alpha^2 = 0.64$ pointing to a large contribution from covalence bonding in the formation of the complex. Similar calculations performed for $[Cu(NH_3)_5](ClO_4)_2$ gave $\alpha^2 = 0.71$. This indicates the presence of covalence bonding. This is corraborated by the presence of hyperfine structure in the spectrum of Zn: $[Cu(NH_3)_5](ClO_4)_2$ [8]. The unpaired electron density on the NH_3 groups is nonzero and spin exchange is rendered possible by way of these groups.

In the case of $[Cu(NH_3)_4](ClO_4)_2$, there is a lack of one NH_3 group in each coordination surroundings of copper, leading to a decrease in spin exchange. Accordingly, the spectrum of the complex exhibits *g*-factor anisotropy although, on the other hand, spin exchange is sufficiently strong to eliminate hyperfine structure. Studies of the two compounds clarify the influence of spin exchange and molecular motions on the temperature-dependent change in EPR line width. The present observation is, to the best of our knowledge, the first one of the phase transition of a copper pentammine perchlorate permitting the insertion of one more point in Stankowski's graph [1], defining the dependence of the phase transition temperature on the lattice constant of the ammoniacate.

3. Dilatometric study

In order to verify the effects observed in EPR, we proceeded to the present thermal expansion measurements. The polycrystalline powders were compressed under 300 MPa to cylinders 8 mm in diameter and of lengths 12.95 and 16.43 mm, respectively. The $[Cu(NH_3)_5](ClO_4)_2$ sample was protected from losing NH_3 by a very thin layer of teflone. No such protection was needed in the case of $[Cu(NH_3)_4](ClO_4)_2$.

The dilatometric study was carried out with the dilatometer described in Ref. [11]. The changes in length of the samples were read with an accuracy of 10^{-4} mm while very

slowly cooling from room temperature down to 100 K and then raising the temperature slowly. The temperature was measured with a copper-constantan thermocouple placed within the sample. Deviations of the experimental points from the continuous line did not exceed 0.01 %.

For $[Cu(NH_3)_4](ClO_4)_2$, no sharp changes in the linear expansion coefficient were observed throughout the range of temperatures investigated. The coefficient was found to vary gradually from $(2.3 \pm 0.3) \cdot 10^{-5}$ K^{-1} at 100 K to $(8.2 \pm 0.2) \cdot 10^{-5}$ K^{-1} at 290 K.

For $[Cu(NH_3)_5](ClO_4)_2$, a change in the thermal expansion coefficient occurs at about 140 K. The hysteresis of about 10 deg observed in the entire temperature range at heating, was due to inertia of the experimental device. The mean linear expansion coefficient of $[Cu(NH_3)_5](ClO_4)_2$ amounts to $(8.2 \pm 0.2) \cdot 10^{-5}$ K^{-1} in the range from 150 to 290 K and to $(7.7 \pm 0.2) \cdot 10^{-5}$ K^{-1} from 100 to 130 K, and takes the value $(22.5 \pm 0.4) \cdot 10^{-5}$ K^{-1} in the region of the phase transition observed. The change in volume related with the structural phase transition was evaluated to be about 0.72 % i.e. about one half of that for $[Ni(NH_3)_6](ClO_4)_2$, studied by a similar method [11]. Dilatometric results are in agreement with those of EPR. They confirm the existence of a phase transition of the same temperature T_c for $[Cu(NH_3)_5](ClO_4)_2$ and the absence of one for $[Cu(NH_3)_4](ClO_4)_2$.

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