An ESR Study of Structural Phase Transitions of $(NH_4)_2Pb[Cu(NO_2)_6]$

Tetsuo Asaji, Laxman Shrikrishna Prabhumirashi *, and Daiyu Nakamura
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

Z. Naturforsch. **41 a,** 1154–1158 (1986); received May 3, 1986

The structural changes of $(NH_4)_2Pb[Cu(NO_2)_6]$ crystals during the phase transitions at 316, 287, and 95 K were studied by means of a single crystal ESR technique. Anisotropic g values ($g_{\parallel} > g_{\perp}$) were obtained in the lowest temperature phase IV, whereas the ESR spectra recorded in the intermediate phases III and II, in which the crystal is known to be tetragonally compressed along the c axis, could be interpreted by use of effective g values [$g(\parallel c) < g(\perp c)$]. In the highest temperature phase I an isotropic g value was obtained. The phases I, II, and III of the present complex can be assumed to be very similar to the corresponding phases observed above ≈ 250 K for the compounds $R_2Pb[Cu(NO_2)_6]$ with R = K, Rb, Cs, and Tl. However, the lowest temperature phase transition transforms the phase III with an antiferrodistortive order of the elongated $[Cu(NO_2)_6]^{4-}$ octahedra into the phase IV with a ferrodistortive one. This occurs only for the complex with R = NH_4 and is very unusual. The results of the ^{14}N NQR experiments already reported for the phases III and IV could be well explained by the present newly proposed model.

Key words: Magnetic Resonance (ESR, NQR), Phase Transition, Crystal Structure

Introduction

In our previous papers [1, 2], we reported the results of ^{14}N NQR and differential thermal analysis (DTA) measurements carried out for the complexes $R_2M[Cu(NO_2)_6]$ with R = K, Rb, Cs, NH_4, Tl and M = Pb, Ca, Sr, Ba. In these studies it was revealed that $(NH_4)_2Pb[Cu(NO_2)_6]$ undergoes three phase transitions at 316, 287, and 95 K. Although each crystal of the above $R_2Pb[Cu(NO_2)_6]$ type complexes shows successive phase transitions caused by a cooperative Jahn-Teller effect of $[Cu(NO_2)_6]^{4-}$ ions in a temperature range 250–390 K [3–6], the phase transition additionally found at the very low temperature of 95 K for the ammonium salt is rather exceptional. The ^{14}N NQR frequencies could be detected above and below this phase transition. This indicates that both phases are in a highly ordered state. However, when the temperature was raised from liquid helium temperature, the NQR lines of the other complexes studied disappeared at the lowest phase transition occurring above about 250 K or far below the transition temperatures. The present ESR investigation has been undertaken to obtain information about the structural changes occurring at the phase transitions of the ammonium salt.

Crystal Structure of the Usual $R_2Pb[Cu(NO_2)_6]$ Type Complexes

As for the structure of the lowest temperature phase of $K_2Pb[Cu(NO_2)_6]$, Harrowfield et al. [7, 8] assumed a ferrodistortive order in which all the $[Cu(NO_2)_6]^{4-}$ octahedra are tetragonally compressed along [001] axis. On the other hand, Reinen et al. [9–11] proposed an alternative model from their ESR results which have been explained by an antiferrodistortive ordered system consisting of two crystallographically nonequivalent $[Cu(NO_2)_6]^{4-}$ octahedra elongated along [100] and [010] crystal axes.

When exchange interactions operative between neighboring Cu^{2+} ions can be neglected, two ESR signals are expected to be observed for the crystal of the lowest temperature phase IV by applying the external field H_0 parallel to the (001) plane if the crystal is in the antiferrodistortive ordered state. However, only one signal may be observed in the (001) plane of the crystal when a strong exchange coupling is present [11–13]. By use of the model

---

Reprint requests to Dr. T. Asaji, Nagoya University, Faculty of Science, Department of Chemistry, Chikusa, Nagoya 464, Japan

* Present address: Chemistry Department, Poona University, Pune-411007, India.

0340-4811 / 86 / 0900-1154 $ 01.30/0. – Please order a reprint rather than making your own copy.

proposed by Reinen et al. [9–11], the ESR results for the usual complexes can be well interpreted and their model was proved to be adequate from the single crystal X-ray and neutron diffraction study of the low temperature phase of $K_2Pb[Cu(NO_2)_6]$ [4]. The intermediate phase of the potassium salt was established to be an incommensurate phase where the local Jahn-Teller distortion of the complex anions is modulated along the [110] direction [4]. The high temperature cubic phase of the $R_2Pb[Cu(NO_2)_6]$ type complexes is formed from the $[Cu(NO_2)_6]^{4-}$ octahedra showing a three-dimensional dynamic Jahn-Teller distortion [4].

Experimental

Crystals of $(NH_4)_2Pb[Cu(NO_2)_6]$ were prepared by slow cooling of an aqueous solution containing NH_4NO_3, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $NaNO_2$ and a few drops of CH_3COOH [1].

The ESR spectra recorded on a JEOL ES-SCXA X-band spectrometer were calibrated by using a spectrum of Mn^{2+} diluted in MgO. The tetragonal shaped crystal ($0.3 \times 0.3 \times 0.2$ mm^3) was mounted on the bottom or side of a quartz rod by use of silicone grease [14]. This rod was mounted in a usual ESR sample tube which was rotated in a sample holder having an angle scale attached to it. The accuracy of the observed angles for each sample setting was estimated to be ± 5°. A copper–constantan thermocouple was located close to the crystal but outside of the cavity. Temperatures were measured within an accuracy of ± 5 K.

Results

Through this paper, the four solid phases of $(NH_4)_2Pb[Cu(NO_2)_6]$ crystals, which appear in turn with decreasing temperature, are denoted as the phases I, II, III, and IV.

In the highest temperature phase I, which has a cubic structure [1], the isotropic g value (2.13 at 333 K) was obtained. On the other hand, anisotropic g values were observed for the remaining three phases in conformity with the foregoing structural consideration. In Fig. 1, the angular dependences of the g values observed in the phases II, III, and IV are shown when the crystal is rotated about the axis which is perpendicular to the square basal plane of a tetragonal-shaped crystal. The origin of the rotation angle φ was taken so that the maximum separation of the two g components observed for the phase II occurs at $\varphi = 90°$.

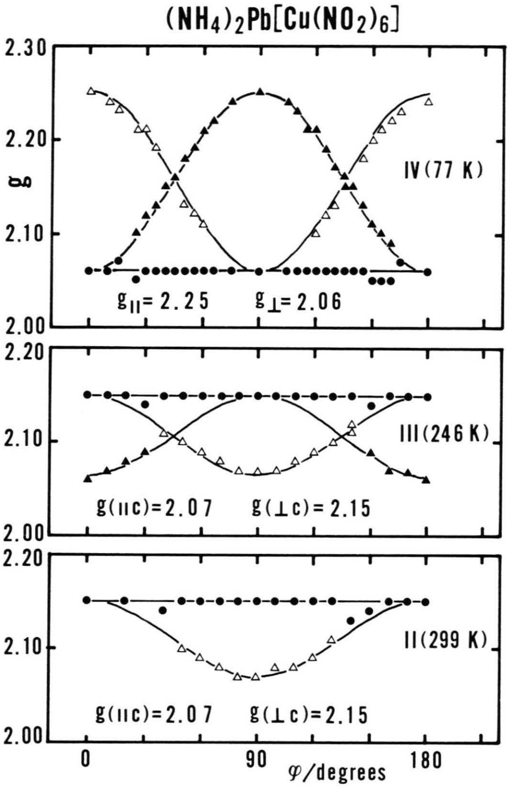

Fig. 1. Angular dependence of the g values observed for the phases II, III, and IV of $(NH_4)_2Pb[Cu(NO_2)_6]$. Signal components assigned to different domains are indicated by different symbols. Solid curves are theoretical as calculated with the formula for axial symmetry of the g tensor. The scale of rotation angles φ is described in text.

The spectra shown in Fig. 2 can be devided into two or three different Cu^{2+} spectral components. The crystal of the phase II, which was transformed from the phase IV or I, showed two spectral components with different relative intensities which differ from those of the same phase observed at room temperature without thermal treatment. However, practically no change in the relative intensities of the two components of the phase II was observed when the sample was transformed from the phase III. The phases II and III yielded approximately the same spectra.

A single crystal of the phase II gave only a single ESR signal even when the crystal was mounted at any orientation to H_0. The variation of the g values when this single crystal was rotated about the axis perpendicular or parallel to the square basal plane coincided exactly with one of the curves for the phase II given in Figure 1.

A fairly large angular dependence of the ESR linewidth was observed at 77 K in the phase IV (see Figure 2). The component appearing at a lower field was always broader than that appearing at a higher field.

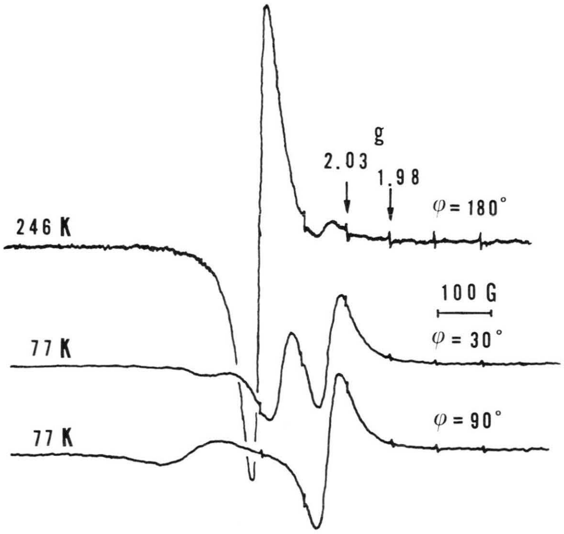

Fig. 2. X-band ESR spectra recorded using single crystals of $(NH_4)_2Pb[Cu(NO_2)_6]$. Room temperature spectra of Mn^{2+} diluted in MgO were simultaneously recorded as markers.

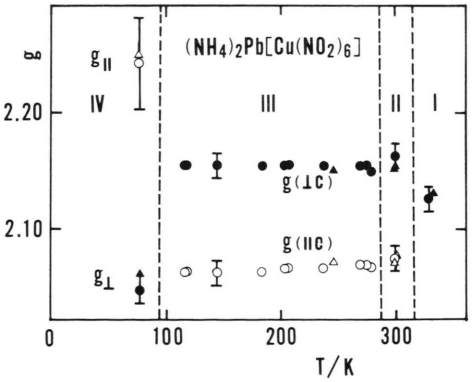

Fig. 3. Temperature dependence of g determined from the powder ESR spectra of $(NH_4)_2Pb[Cu(NO_2)_6]$. The parallel and perpendicular components observed in the phases II, III, and IV are indicated by open and full symbols, respectively. Data obtained from single crystals are indicated by triangles.

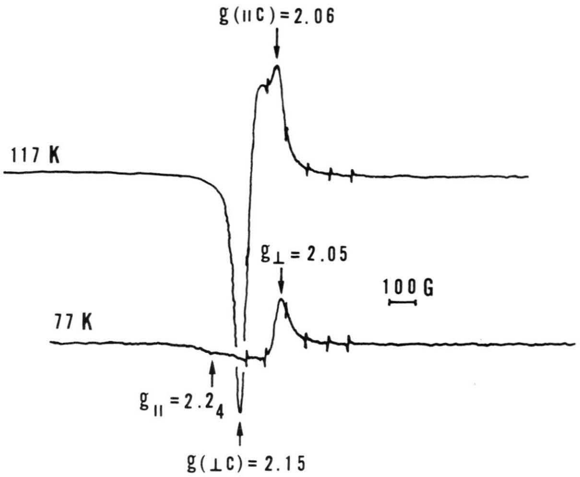

Fig. 4. X-band ESR spectra of polycrystalline samples of $(NH_4)_2Pb[Cu(NO_2)_6]$ at 77 and 117 K. Room temperature spectra of Mn^{2+} diluted in MgO were simultaneously recorded as markers.

The temperature dependence of g, determined from the powder spectra of the complex between 77 and 330 K, is shown in Figure 3. The g values are almost temperature independent in the temperature range of the phases II and III. In the powder spectra of the phase IV $g_\parallel > g_\perp$ was found, whereas the spectra of the phases II and III showed an apparent anisotropy with $g_\parallel < g_\perp$ (cf. Figure 4).

Discussion

Crystals of $R_2M[Cu(NO_2)_6]$ in their low temperature pseudotetragonal phase usually contain two or more crystalline lattice domains of different abundance [15–18]. Owing to this domain structure, two or three ESR signals are usually obtained [10]. The distortion axis of each domain within the pseudotetragonal phase of $K_2Pb[Cu(NO_2)_6]$ is approximately parallel to one of the three crystal axes of the high temperature cubic phase [7, 10].

Each component line observed in the ESR spectra of the phases II, III, and IV of the present ammonium salt can be assigned to Cu^{2+} ions in such a domain of the crystal. This assignment is supported by the fact that the relative intensities of these components changed somewhat or considerably when the sample once experienced phase transitions. Furthermore, the crystal obtained at room temperature gave a single ESR line. This clearly indicates that this crystal consists of a single domain.

Fitting calculations for the angular variation of the g values of each component were carried out by use of a formula assuming axial symmetry of the g tensor [19]:

$$g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta, \tag{1}$$

where θ is the angle between H_0 and the distortion axis of the g tensor.

Although it is expected that the exact symmetry of the crystal in the phases II, III, and IV is lower than tetragonal as in the case of $K_2Pb[Cu(NO_2)_6]$ [4], the distortion from tetragonal symmetry in the phase II is so small that X-ray powder patterns observed for the sample in this phase can be well explained by assuming a tetragonal symmetry [1]. The present X-band ESR spectra of the three phases could be interpreted by use of (1) even in the lowest temperature phase IV, as is shown by the solid curves in Figure 1. This indicates that the distortion of the complex anion from the tetragonal symmetry is fairly small in the three low temperature phases.

The angle between the two crystal orientations where the g value of each component line shows a maximum and a minimum is 90° within experimental errors. Furthermore, the maximum and minimum g values belonging to different component lines appear at the same φ. This indicates that the distortion axes of the different domains are orthogonal to each other. It is highly probable that these axes in the phases II and III are almost parallel to the three crystal axes of the cubic phase I as observed in the potassium salt [7, 10].

The temperature dependence of the g tensor obtained for the phases I, II, and III of the present complex is very similar to that obtained for the corresponding phases of $R_2Pb[Cu(NO_2)_6]$ (R = K, Rb, Cs, Tl), [6, 7, 10]. This strongly suggests that the crystal structure of these phases is very similar to the corresponding phases of $K_2Pb[Cu(NO_2)_6]$ [4]. However, the Cs salt is somewhat exceptional and exhibits two complicated intermediate phases II and II′ above 285 K [5, 10].

In the lowest temperature phase III of the potassium salt, there exist two crystallographically nonequivalent $[Cu(NO_2)_6]^{4-}$ octahedra which are elongated along [100] and [010], respectively (antiferrodistortive order) [4]. When a strong exchange interaction is operative between neighboring Cu^{2+} ions, they should have average values of $g(\parallel c)$ and $g(\perp c)$ which can be written by use of the g values of an elongated $[Cu(NO_2)_6]^{4-}$ octahedron, $g_\parallel$ and $g_\perp$, as

$$g(\parallel c) = g_\perp, \tag{2}$$

$$g(\perp c) = (g_\parallel + g_\perp)/2, \tag{3}$$

where c denotes the crystal axis along [001] [10, 11]. Simple crystal field theory predicts that the condition $g_\parallel > g_\perp > 2$ should be fulfilled [11] for a Cu^{2+} ion placed in a tetragonally elongated crystal field. Hence for the effective values of $g(\parallel c)$ and $g(\perp c)$ resulting from the exchange interactions we have the relation of $2 < g(\parallel c) < g(\perp c)$. A similar expectation can be obtained for the incommensurate phase II of the potassium salt [4], whereas an isotropic g value was observed in the phase I due to a three-dimensional dynamic Jahn-Teller effect [10].

When (1) is employed for describing the angular dependence of the g values in the phases II, III of $R_2Pb[Cu(NO_2)_6]$, $g_\parallel$ and $g_\perp$ in (1) should be read as the effective values of $g(\parallel c)$ and $g(\perp c)$. From the fitting calculations, $g(\parallel c) = 2.07$ and $g(\perp c) = 2.15$ were obtained for both phases II (at 299 K) and III (at 246 K) of $(NH_4)_2Pb[Cu(NO_2)_6]$. The arithmetic average of the three principal values of the g tensor obtained for the phase II gave the same value as the isotropic g value of the phase I. This suggests that dynamical averaging of the distortion of the octahedral complex anions takes place in the phase I of the ammonium salt.

In the phase IV of the ammonium salt, the ESR spectra can be explained as arising from a Cu^{2+} ion in a tetragonally elongated complex anion with $g_\parallel > g_\perp > 2$. The anisotropy of the linewidth observed in this low temperature phase may be due to an unresolved hyperfine structure originating from the copper nuclei [20].

The g values determined for the phase IV ($g_\parallel = 2.25$ and $g_\perp = 2.06$ at 77 K) coincide with the values $g_\parallel = 2.23$ and $g_\perp = 2.07$ calculated from (2) and (3) using the values of $g(\parallel c)$ and $g(\perp c)$ determined for the phase III. Therefore, it is concluded that the distortion axes of the elongated $[Cu(NO_2)_6]^{4-}$ octahedra are aligned in the same direction (ferrodistortive order) in the phase IV. This indicates that all the $[Cu(NO_2)_6]^{4-}$ octahedra in the crystal become crystallographically equivalent. No significant rotational displacement of the complex anions seems to be involved through the phase transition III → IV, since the maximum or minimum of the angular dependence curves of the g values in these phases occurs at the same orientation of the crystal (see Figure 1).

The temperature dependence of the ^{14}N NQR frequencies observed for $(NH_4)_2Pb[Cu(NO_2)_6]$ shows a discontinuity at 95 K, and the number of resonance lines decreases from four to two when the temperature is lowered across the transition point [1]. In the phase III abover 95 K, the two sets of NQR frequencies, ν^I and ν^{II} observed for $(NH_4)_2Pb \cdot [Cu(NO_2)_6]$ can be assigned to the two crystallographically nonequivalent axial nitrogen atoms placed in the different $[Cu(NO_2)_6]^{4-}$ octahedra elongated along [100] and [010]. In the ferrodistortive phase IV, all of the axial nitrogen atoms of the complex anions are assumed to be crystallographically equivalent, leading to the appearance of two ^{14}N NQR frequencies, ν^I and ν^{II}, as it was actually observed.

The most appropriate reason for the adequacy of the present assignment of the ^{14}N NQR frequencies to axial nitrogens in the complex anions is as follows: Only the axial nitrogens are assumed to be practically insensitive to the disturbance due to the unpaired electrons of Cu^{2+} ions through the superhyperfine interaction [21]. This is because the unpaired electrons occupy predominantly $d_{x^2-y^2}$ orbitals of Cu^{2+} in its electronic ground state. In the ESR study of Cu^{2+} doped $K_2Cd_2(NO_2)_6$, Ozarowski and Reinen reported that only the superhyperfine splitting due to the equatorial nitrogen atoms could be observed [22]. Furthermore, they concluded that the superhyperfine interaction operative between the axial nitrogen nucleus and the unpaired electron on the copper atom is several ten times smaller than that involving the equatorial nitrogen atoms. The broadening of the NQR lines due to superhyperfine interactions will make the signals from the equatorial nitrogens unobservable even if the signals from the axial nitrogens can be observed. This explanation of the NQR results of $(NH_4)_2Pb[Cu(NO_2)_6]$ is supported by the fact that a single set of the NQR lines was observed in $K_2Ba[Cu(NO_2)_6]$ [2], in the crystals of which all the elongated $[Cu(NO_2)_6]^{4-}$ octahedra are crystallographically equivalent [16]. The decrease of the number of NQR lines when the temperature was lowered from III to IV, therefore, indicates that all the $[Cu(NO_2)_6]^{4-}$ octahedra become crystallographically equivalent in phase IV of $(NH_4)_2Pb[Cu(NO_2)_6]$. This is the same conclusion as obtained from the present ESR investigation.

[1] T. Asaji R. Ikeda, and D. Nakamura, Z. Naturforsch. **34b**, 1722 (1979).

[2] T. Asaji, J. Ishikawa, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **54**, 2211 (1981).

[3] B. V. Harrowfield and R. Weber, Phys. Lett. A **38**, 27 (1972).

[4] Y. Noda, M. Mori, and Y. Yamada, J. Phys. Soc. Japan **45**, 954 (1978).

[5] M. Mori, Y. Noda, and Y. Yamada, Solid State Commun. **27**, 735 (1978).

[6] B. V. Harrowfield, A. J. Dempster, T. E. Freeman, and J. R. Pilbrow, J. Phys. C: Solid State Phys. **6**, 2058 (1973).

[7] B. V. Harrowfield and J. R. Pilbrow, J. Phys. C: Solid State Phys. **6**, 755 (1973).

[8] B. V. Harrowfield, Solid State Commun. **19**, 983 (1976).

[9] D. Reinen, C. Friebel, and K. P. Reetz, J. Solid State Chem. **4**, 103 (1972).

[10] C. Friebel, Z. anorg. allg. Chem. **417**, 197 (1975).

[11] D. Reinen, Solid State Commun. **21**, 137 (1977).

[12] H. Abe and K. Ono, J. Phys. Soc. Japan **11**, 947 (1956).

[13] M. Yokota and S. Koide, J. Phys. Soc. Japan **9**, 953 (1954).

[14] T. D. Waite and M. A. Hitchman, Inorg. Chem. **15**, 2155 (1976).

[15] S. Takagi, M. D. Joesten, and P. G. Lenhert, Acta Cryst. **B32**, 1278 (1976).

[16] S. Takagi, M. D. Joesten, and P. G. Lenhert, Acta Cryst. **B31**, 596 (1975).

[17] S. Takagi, P. G. Lenhert, and M. D. Joesten, J. Amer. Chem. Soc. **96**, 6606 (1974).

[18] D. Mullen, G. Heger, and D. Reinen, Solid State Commun. **17**, 1249 (1975).

[19] G. E. Pake and T. L. Estle, The Physical Principles of Electron Paramagnetic Resonance, 2nd Ed., p. 117, W. A. Benjamin, Inc., London 1973.

[20] P. R. Newman, J. L. Imes, and J. A. Cowen, Phys. Rev. B **13**, 4093 (1976).

[21] B. B. Wayland and M. D. Wisniewski, J. Chem. Soc. Chem. Commun. **1971**, 1025.

[22] A. Ozarowski and D. Reinen, Inorg. Chem. **24**, 3860 (1985).