CHEMISTRY LETTERS, pp. 579-582, 1978. Published by the Chemical Society of Japan

ESR g-ANISOTROPY INVERSION OBSERVED FOR Cu(II)-CROWN ETHER COMPLEX IN SOLUTION

Kazuhiko ISHIZU, Tokuhiro HARUTA, Kazuhiro NAKAI,
Kiyonori MIYOSHI* and Yukio SUGIURA**
Department of Chemistry, Faculty of Science, Ehime University,
Bunkyo-cho, Matsuyama, Ehime 790
* Department of Metallurgical Engineering, Niihama Technical College,
Niihama, Ehime 792
** Faculty of Pharmaceutical Science, Kyoto University, Kyoto 606

$CuCl_2$ solubilized by Benzo-15-crown-5 in dry $CHCl_3$ showed the anomalous g-anisotropy inversion ($g_{\parallel} < g_{\perp}$) in the ESR spectrum. The spin Hamiltonian parameters determined were $g_{\parallel}=1.995$, $g_{\perp}=2.294$ and $|A_{\parallel}|=129.8\times10^{-4}$ cm^{-1}. Based on the ESR parameters, the bonding parameters of Cu(II) were calculated with application of the Swalen's method. A weak bonding in the xy-plane of the paramagnetic site was assumed between the metal and the ligands, and a perturbation on the Cu(II) positive hole appears mainly due to the crystal field working along the z-axis, and the unpaired electron was suggested to occupy the d_{z^2} orbital at the ground state.

Under the usual square-planar ligand geometry distorted from the octahedral symmetry, the positive hole of Cu(II) occupies the $d_{x^2-y^2}$ orbital at the ground state, and the observed ESR $g_{\parallel}$ values were always larger than $g_{\perp}$ values.$^{1)}$ ESR of Cu(II) complexes for the pseudo-tetrahedral symmetry were extensively studied in solution, but the observed g-values never changed their order ($g_{\parallel} > g_{\perp}$).$^{2)}$ Anisotropy inversion of g-values., that is, $g_z < g_x$, g_y, were already reported for several Cu(II) complexes doped in the solid matrices, where d_{z^2} is the half-filled orbital in compressed tetragonal, compressed trigonal bipyramidal and cis-distorted octahedral systems.$^{3)}$ For ESR in solution, however, such as anisotropy inversion of g-values would be quite exceptional, since the geometry of the complex is more or less fixed by the coordinations of polar functional groups and of solvent molecules under usual experimental conditions. In connection with the studies of the paramagnetic active site of blue-copper proteins, the Cu(II) complexes of some crown-thioether have been regarded as a model complex.[4)] Recently, a possibility of g-anisotropy inversion has been also proposed for some macropolycyclic ligands.[5)]

In the present communication, we wish to report the fact of g-anisotropy inversion occurring in ESR of $CuCl_2$-crown-ether (Benzo-15-crown-5) complex dissolved in dry $CHCl_3$. Based on ESR parameters of Cu(II), the bonding nature of Cu(II) was investigated with aides of the Swalen's method, and the structure of the Cu(II) paramagnetic site was assumed.

Benzo-15-crown-5 was synthesized according to Pedersen's procedures.[6)] The pure materials were obtained by recrystallization in hexane; mp, 80~82°C (uncorrected). Elementary analysis, Calcd. C, 62.69%; H, 7.46% Found. C, 62.48%, H, 7.46% for $C_{14}H_{20}O_5$. The reagent grade $CHCl_3$, which was previously treated with conc. H_2SO_4 and washed with water, was stocked with anhydrous potassium carbonate in a refrigerator. It was then dehydrated with activated molecular sieves followed by vaccum distillation before use. The commercial anhydrous cupric chloride was dried by heating the material at 110°C for 6 hrs under vaccum. ESR measurements were carried out at 77 K using a JES-ME-3X spectrometer operating with 100 KHz magnetic field modulation. ESR operating frequencies were measured with a Takeda-Riken microwave frequency counter, and g-values were determined by taking Li-TCNQ (g=2.00252) as a standard. The magnetic fields were calibrated based on the splitting of Mn(II) in MgO (ΔH_{3-4}=86.9 gauss). $CuCl_2$ was hardly soluble in dry $CHCl_3$, but it gradually dissolved upon addition of the crown-ether; $CuCl_2$ (0.04 m mole) and crown-ether (0.4 m mole) was mixed in dry $CHCl_3$ (4 ml) under vaccum, and the mixture was kept in dark. After standing for one day, the solution colored to orange-yellow, displayed the single absorption maximum at 440 nm with extinction coefficient ε=380, which was calculated by assuming that the 1:1 complex forms between $CuCl_2$ and the crown-ether.[7)] The ESR spectrum (Fig.1) measured in a frozen matrix of $CHCl_3$ revealed a typical line shape for nonoriented systems ($S=1/2$, $g_\perp > g_\parallel$) with high axial symmetry. The ESR parameters determined are; $g_\parallel$ =1.995, $g_\perp$=2.294 and $|A_\parallel|=129.8\times10^{-4}$ cm^{-1}. The $A_\perp$ hyperfine splitting was not resolved, but it was assumed to be $|A_\perp|<40\times10^{-4}$ cm^{-1} from the $g_\perp$ line width. Calculations of bonding parameters were accomplished by the method of Swalen and coworkers, who wrote the ground-state Kramer's doublet wave functions as

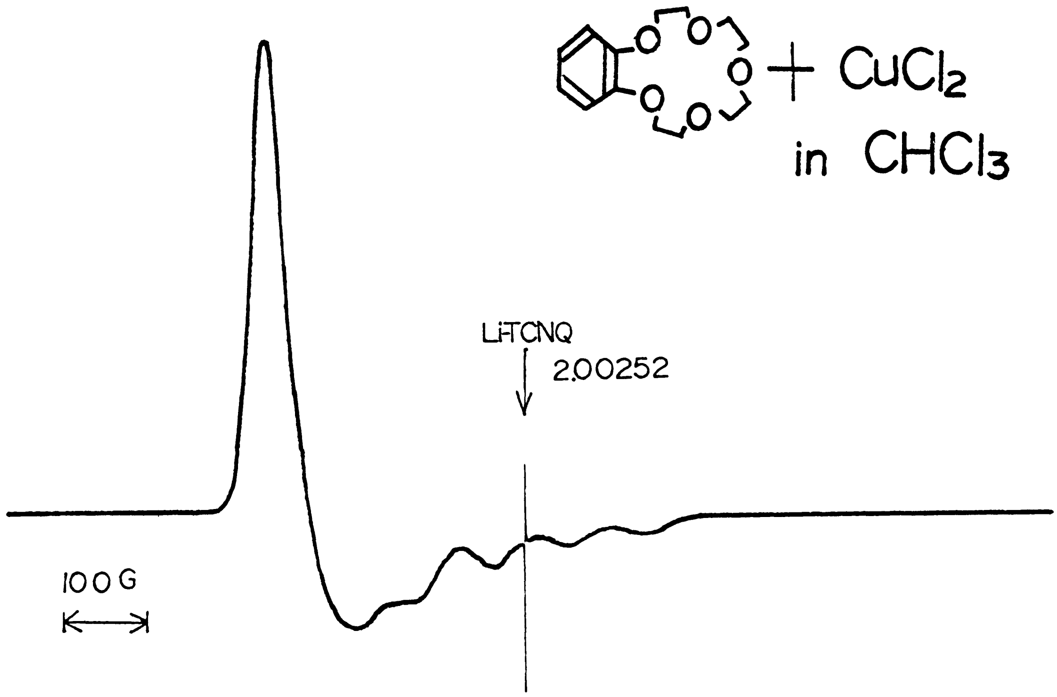

Fig. 1. ESR Spectrum of $CuCl_2$-Crown Ether measured at 77 K.

$$\Psi = a\phi_1\alpha + b\phi_3\alpha + ic\phi_2\alpha - id\phi_4\beta - e\phi_5\beta \quad (1)$$

$$\Psi^* = i(a\phi_1\beta + b\phi_3\beta - ic\phi_2\beta - id\phi_4\alpha + e\phi_5\alpha) \quad (2)$$

where $\phi_1=|d_{z^2}>$, $\phi_2=|d_{xy}>$, $\phi_3=|d_{x^2-y^2}>$, $\phi_4=|d_{yz}>$ and $\phi_5=|d_{xz}>$.[8)]

The expression for g-values were calculated as matrix elements of the type $<\Psi|\ \ell_j+2s_j\ |\Psi>$ for j=x, y, z; $g_z=2 - 4d^2 - 4e^2 + 8bc + 4de$ (3) $g_x=2 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd$ (4) $g_y=2 - 4c^2 - 4d^2 + 4\sqrt{3}ae - 4be + 4cd$ (5).

Equation 3-5 along with the normalization condition were solved for the four unknown a, b, c and d for e=d, assuming that the ground state is d_{z^2}. By taking $g_x \simeq g_y$, the sets of coefficients a, b, c, d and e were obtained from the g-values; that is, a=0.9981, b=c=0.0051, d=e=0.0433. The Cu(II) hyperfine parameters were calculated as function of p and k using the sets of coefficients a, b, c, d and e thus obtained from the g-values.

$$A_z = p\{8bc + 4de + (6\xi - k)(1 - 2d^2 - 2e^2) - 3\xi[4c^2 + 4b^2 - 4d^2 - 4e^2 + \sqrt{3}a(d + e) + 3(d - e)(c - b)]\} \quad (6)$$

$$A_x = p\{4\sqrt{3}ad - 4ec + 4bd + (6\xi - k)(1 - 2c^2 - 2e^2) - 3\xi[(\sqrt{3}a + b)^2 - c^2 + 4d^2 - e^2 - \sqrt{3}a(e + 2c) + 3dc - 3de]\} \quad (7)$$

$$A_y = p\{4\sqrt{3}ae + 4dc - 4bc + (6\xi - k)(1 - 2c^2 - 2d^2) - 3\xi[(\sqrt{3}a + b)^2 - c^2 + d^2 + 4c^2 - \sqrt{3}(d - 2c)a - 3ce + 3db + 3dc]\} \quad (8)$$

The coefficient ξ is related to the electronic configuration of the ion [2/21 for

Cu(II)]. The $A_\perp$ value was not known here, but numerous calculations were carried out by changing the values from 20×10^{-4} cm^{-1} to 50×10^{-4} cm^{-1}. Judging from the $g_\perp$ line width, the factor p and k are probably in the following range, 299×10^{-4} cm^{-1}< p<359×10^{-4} cm^{-1} and 0.100<k<0.173. With a tentative use of $|A_\perp|=30\times10^{-4}$ cm^{-1} assumed from the ESR line width, the observed ESR spectrum can be well understood in terms of the following p and k values; p=319×10^{-4} cm^{-1}, k=0.127 respectively. Since the p factor measures the mean radial distribution functions of the unpaired electron, the p-value close to the free atom value (360×10^{-4} cm^{-1}) concludes that the electron delocalization into the ligand or the expansion of the d-orbitals is not significant. The low k value obtained here probably means that a mixing of the 4s orbital into the d-orbital should be taken into account.[9)] Swalen's calculations of the coefficient ($a\simeq1$, $c\simeq0$) concludes that the ligand fields affecting on Cu(II) site in the xy-plane are very weak, and a perturbation on the positive hole can be mainly due to the coordination along the z-axis of the paramagnetic site. This is probably true, since the cavity radius of benzo-15-crown-5 (R=0.85~1.1 Å) is fairly larger than the ion radius of Cu(II) (r=0.72 Å), a weak chelation should be expected between the central metal ion and the crown oxygen atoms.[10)] A perturbation on the d_{z^2} positive hole appears to be due to the two chlorine atoms axially coordinated above and below of the pentagonal crown ring nearly in the axial symmetry.

References

1) A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions. pp. 455 (1970) Clarendon press, Oxford.

2) H. Yokoi and A. W. Addison, Inorganic Chemistry, 16, 1341 (1977).

3) R. Hirasawa and H. Kon, J. Chem. Phys., 56, 4467 (1972).

4) T. E. Jones, D. B. Rorabacher and L. A. Ochrymswcz, J. Am. Chem. Soc., 97, 7485 (1975).

5) A. H. Albert, R. Annuziata and J. M. Lehn, J. Am. Chem. Soc., 99, 8502 (1977).

6) C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).

7) ESR of $CuCl_2$ solubilized by a spin labeled benzo-15-crown-5 demonstrated existence of the triplet state with suggestion that $CuCl_2$ forms the 1:1 complex with crown-ether. cf. K. Ishizu, H. Kohama and K. Mukai, Chemistry Letters, 227 (1978).

8) J. D. Swalen, B. Johnson and H. M. Gladney, J. Chem. Phys., 52, 4078 (1970).

9) J. P. Sorzano and J. P. Fackler, JR., Inorganic Chemistry, 13, 38 (1974).

10) Dibenzo-18-crown-6 (R=1.30~1.60 Å), the crown-ether with a larger ring radius cannot solubilize $CuCl_2$ under the identical experimental condition.

(Received March 24, 1978)