Inorganica Chimica Acta, 45 (1980) L113–L114
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ESR Spectra of Seven-coordinated Pentagonal Bipyramidal Copper(II) Complexes

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Received April 28, 1980

It is known that the Schiff bases derived from 2,6-diacetylpyridine and semicarbazides (or organic acid hydrazine) (*cf.* Fig. 1) can act as planar pentadentate ligands [1]. The geometry around copper(II) ion in $[Cu(dapa)(H_2O)_2](NO_3)_2$ was found to be a pentagonal bipyramid by X-ray diffraction technique [2], where (dapa) represents 2,6-diacetylpyridinebis(semicarbazone). For the copper(II) complex of a pentagonal bipyramidal structure, it was predicted from the angular overlap model [3] that one unpaired electon is in d_{z^2} orbital. However, no experimental evidence has been reported so far.

Thus, in this study we have measured the ESR spectrum of $[Cu(dapa)(H_2O)_2](NO_3)_2$. We also prepared a new complex, $Cu(dapm)(H_2O)_2(PF_6)_2$, presumed to have a similar structure to the (dapa) complex, where (dapm) represents 2,6-diacetylpyridinebis(acetohydrazone). In fact ESR spectra of these complexes are quite similar to each other. This is the first report of ESR spectra of pentagonal bipyramidal copper(II) complexes.

Experimental

The copper(II) complex, $[Cu(dapa)(H_2O)_2](NO_3)_2$ was prepared by the method described in the literature [2].

Preparation of (dapm): 2,6-diacetylpyridine (0.82 g, 5 mmol) and acetohydrazide (0.74 g, 10 mmol) were dissolved in 75 ml of 95% ethanol, and one drop of concentrated hydrochloric acid was added. The solution was heated at 55 °C and stirred for about 15 minutes. Then colorless crystals began to precipitate. After heating for one hour, the mixture was allowed to stand at room temperature overnight. The solid was filtered and dried.

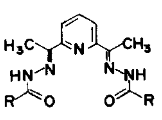

Fig. 1. Ligands used in this study. Abbreviations are: (dapa), R = NH_2; (dapm), R = CH_3.

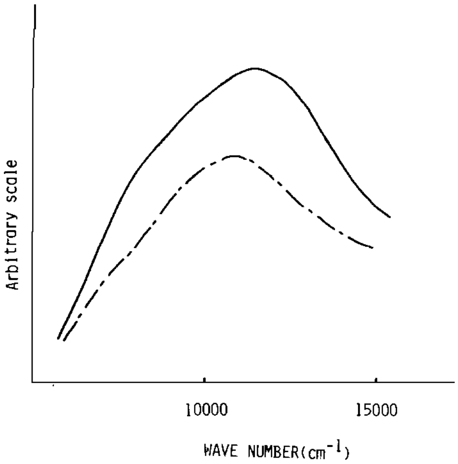

Fig. 2. Powder reflectance spectra of (———) $[Cu(dapa)(H_2O)_2](NO_3)_2$ and (– – – –) $[Cu(dapm)(H_2O)_2](PF_6)_2$.

Preparation of $Cu(dapm)(H_2O)_2(PF_6)_2$: The ligand (1 mmol) was suspended in 25 ml of water and the temperature was raised to 50 °C. The copper(II) nitrate, $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol) was dissolved in 25 ml of ethanol and added to the ligand suspension. The light-green transparent solution was obtained. To this solution was added NH_4PF_6 (1 g), and the solution was kept standing overnight at room temperature. Yellow needles deposited were filtered. *Anal.* Found: C, 23.00%, H, 3.47%, N, 10.34%; calcd. for $Cu(dapm)(H_2O)_2(PF_6)_2$: C, 23.49%, H, 3.18% and N, 10.53%.

ESR spectra were obtained with a JEOL ESR apparatus model JES-ME-3X using an X-band at 77 K. The complexes were dissolved in EtOH–H_2O (1:1) for ESR measurements. Powder reflectance spectra were measured with a Shimadzu Multipurpose spectrophotometer model MPS-5000 at room temperature.

Results and Discussion

In Fig. 2, the powder reflectance spectra of the complexes are shown. The spectrum of $Cu(dapm)(H_2O)_2(PF_6)_2$ is quite similar to that of $[Cu(dapa)(H_2O)_2](NO_3)_2$, the d–d bands being observed in the range 7–12 × 10^3 cm^{-1}. As shown in Fig. 3, the ESR spectrum of $Cu(dapm)(H_2O)_2(PF_6)_2$ shows a distinct axial symmetry. The ESR spectrum of $[Cu(dapa)(H_2O)_2](NO_3)_2$ was very similar to that of $Cu(dapm)(H_2O)_2(PF_6)_2$. The ESR parameters of

TABLE I. ESR Parameters of the Complexes.

Compound	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ ($\times 10^{-4}$ cm^{-1})	$\lvert A_\perp \rvert$
$[Cu(dapa)(H_2O)_2]^{2+}$	1.995	2.35	85	65
$[Cu(dapm)(H_2O)_2]^{2+}$	1.992	2.33	93	68
Calculated value[a]	1.99	2.33	90	−66

[a] Calculated on the assumption that $\nu = 0.058$, $P = 0.036$ cm^{-1} and $\kappa = 0.27$ (*cf.* text).

these copper(II) complexes are summarized in Table I. Based on the above results, it is concluded that $Cu(dapm)(H_2O)_2(PF_6)_2$ has a seven-coordinated pentagonal bipyramidal structure, similar to that of $[Cu(dapa)(H_2O)_2](NO_3)_2$.

The theoretical expressions for $g_\parallel$ and $g_\perp$ values were already given for the copper(II) complexes of the $(d_{z^2})^1$ ground state configuration [4, 5],

$$\begin{aligned} g_\parallel &= 2.002 - 3\nu^2 \\ g_\perp &= 2.002 + 6\nu - 6\nu^2 \end{aligned} \qquad (1)$$

where $\nu = -\lambda/\Delta$; λ and Δ represent the spin–orbit interaction parameter for Cu^{2+} (free ion value is -818 cm^{-1}) and the energy gap between d_{z^2} and d_π (= d_{xz}, d_{yz}) orbitals, respectively. As shown in Table I, the experimentally obtained *b*-values are in good agreement with the calculated values based on the equation (1) assuming $\lambda = -700$ cm^{-1} and $\Delta = 12000$ cm^{-1} (hence $\nu = 700/12000 = 0.058$).

The values of hyperfine structure due to the interaction between unpaired electron and the nuclear spin of copper atom can be calculated as follows [4, 5],

$$\begin{aligned} A_\parallel &= P[-\kappa + (4/7) - (6/7)\nu] \\ A_\perp &= P[-\kappa - (2/7) + (45/7)\nu] \end{aligned} \qquad (2)$$

where $P = g_e g_N \beta \beta_N \langle r^{-3} \rangle$, to which 0.036 cm^{-1} has been generally assigned in the case of copper(II) complexes [6]; g_e and g_N are the electron and nuclear *g* factors, and β and β_N are Bohr and nuclear magnetons, respectively. κ is a dimensionless quantity representing the contribution from s electrons to the hyperfine interaction and generally assuming a value near 0.3 [4]. As shown in Table I, the observed $A_\parallel$ and $A_\perp$ values for the present complexes agree with the calculated values on the assumption that $P = 0.036$ cm^{-1}, $\kappa = 0.27$, and that $A_\parallel$ and $A_\perp$ have opposite signs. The latter assumption was adopted by several authors in the interpretation of ESR parameters of copper(II) complexes of $(d_{z^2})^1$ ground state configuration [4, 5, 7]. Thus, the above discussion on the ESR spectra provides a strong evidence for the $(d_{z^2})^1$ ground state configuration of the present copper(II) complexes.

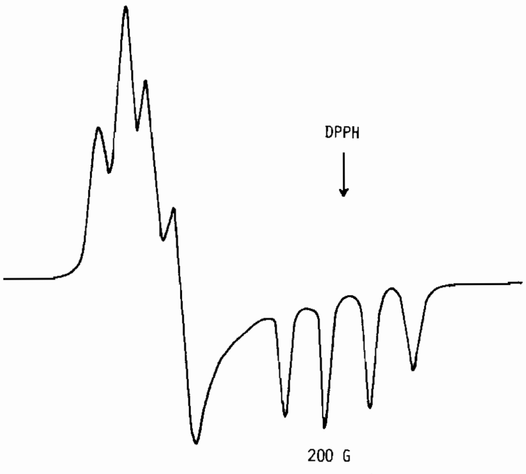

Fig. 3. ESR spectrum of $[Cu(dapm)(H_2O)_2](PF_6)_2$ (77 K).

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