

Studies on ESR Spectra of Some Polyamine-Cu(II) Complexes in Solution & Frozen Solution

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ESR spectral (solution and solid), and optical absorption studies have been made on (i) $[\text{Cu}(\text{tn})_2](\text{NCS})_2$ [$\text{tn}_2 = \text{bis}(1,3\text{-diaminopropane})$], (ii) $[\text{Cu}(\text{tn})_2\text{NCS}]\text{B}\phi_4(\text{III})$ [$\text{Cu}(\text{dpt})\text{NCS}]\text{B}\phi_4$ [$\text{dpt} = 3,3'\text{-diamino-dipropylamine}$] and (iv) $[\text{Cu}(\text{Me}_6\text{tren})\text{NCS}]\text{NO}_3$ [$\text{Me}_6\text{tren} = \text{tris}(2\text{-dimethylaminoethyl})\text{-amine}$]. The ESR spectra of the first three complexes indicate B_{1g} ground state to Cu(II) ion in pyridine solutions. These studies in pyridine and acetone solutions of Me_6tren complex support A_{1g} ground state to the Cu(II) ion. In all the complexes, the ESR and optical absorption data support the earlier conclusions on the coordination around Cu(II) ion arrived at on the basis of IR, molar conductivity and optical data. The strength of the σ and π metal-ligand bonds are estimated using the above data in solutions. In these complexes σ and in-plane π -bonding is moderately strong, disproving the earlier conclusions that aliphatic polyamines are incapable of π -bonding. Out-of-plane π -bonding is found to be absent in $(\text{tn})_2$ complexes.

UNLIKE the ESR studies of copper(II) ions having square-planar, square-pyramidal and elongated octahedron symmetries, ESR studies of Cu(II) ions having trigonal bipyramidal and compressed octahedron symmetries are relatively few. In the latter case the ground state will be A_{1g} and in the former, either it will be B_{1g} or B_{2g} . The symmetry of trigonal bipyramidal complexes dissolved in solvents is found to change, as revealed by ESR, to give either B_{1g} or B_{2g} ground state to the Cu(II) ion¹. To the best of our knowledge till now no ESR spectrum of Cu(II) ion with trigonal bipyramidal symmetry in frozen solution state is recorded. In the present investigation the authors have compared the shape of the ESR spectra of a series polyamine-Cu(II) complexes having A_{1g} with those of B_{1g} ground state and have also studied the metal-ligand bond strengths in solution state using ESR and optical data.

Materials and Methods

The copper(II) complexes studied in the present investigation are (i) $[\text{Cu}(\text{tn})_2](\text{SCN})_2$ [$\text{tn}_2 = \text{bis}(1,3\text{-diaminopropane})$], (ii) $[\text{Cu}(\text{tn})_2\text{NCS}]\text{NO}_3$, (iii) $[\text{Cu}(\text{dpt})\text{NCS}]\text{B}\phi_4$ ($\text{dpt} = 3,3'\text{-diaminodipropylamine}$) and (iv) $[\text{Cu}(\text{Me}_6\text{tren})\text{NCS}]\text{NO}_3$ [$\text{Me}_6\text{tren} = \text{tris}(2\text{-dimethylaminoethyl})\text{-amine}$]. These complexes were prepared by the methods described earlier^{2,3}. The symmetry of the cation $[\text{Cu}(\text{tn})_2\text{NCS}]^+$ in the complex $[\text{Cu}(\text{tn})_2(\text{NCS})]\text{ClO}_4$ in solid state is trigonal bipyramidal⁴. From the IR, conductivity and optical absorption data, it is found that in solution the solvent molecules substitute the thiocyanate². Above studies on dpt complexes indicate square-pyramidal structure. Whereas the crystal structure

studies of $[\text{Cu}(\text{dpt})(\text{NCS})]\text{ClO}_4$ gave evidence of a strongly elongated octahedron⁵. Tren and Me_6tren ligands have the characteristic tripod like shape which gives trigonal bipyramidal configuration around Cu(II) ions. The anions NO_3 and $\text{B}\phi_4$ are ineffective in bringing any change in the trigonal bipyramidal configuration². The crystal structure analysis of $[\text{Cu}(\text{tren})(\text{NCS})]\text{SCN}$ (ref. 6) and $[\text{Zn}(\text{tren})(\text{NCS})]\text{SCN}$ confirms the trigonal bipyramidal configuration⁷.

The ESR spectra of these complexes have been taken in 0.005M solutions of pyridine and acetone with the help of Varian E-4 X-band ESR spectrometer using DPPH as g-marker. A Unicam SP700 spectrophotometer was used to record the optical absorption peaks in solutions.

Results and Discussion

The ESR spectra of $(\text{tn})_2$ and dpt complexes at room temperature in pyridine (Fig. 1) solution consist of the usual four hyperfine lines of Cu(II) with spin-dependent line-widths. But the spectra of Me_6tren complex in pyridine and acetone (Fig. 1) show only one line perhaps due to small separation of hyperfine lines and large line-widths. The ESR spectra of $(\text{tn})_2$ and dpt complexes at liquid nitrogen temperature (Fig. 1) are identical with those of $\text{Cu}(\text{tn})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{tren})(\text{SCN})_2$ in N,N-dimethylformamide (DMF)⁸. From the computer stimulations the above spectra are found to fit the tetragonal symmetry. Due to one to one correspondance of shape of the ESR absorption curves, in both the cases we have taken the Cu(II) ion in the complexes to possess tetragonal symmetry. The g_{\parallel} and A_{\parallel} values of the Cu(II) ion in the present case are directly obtained

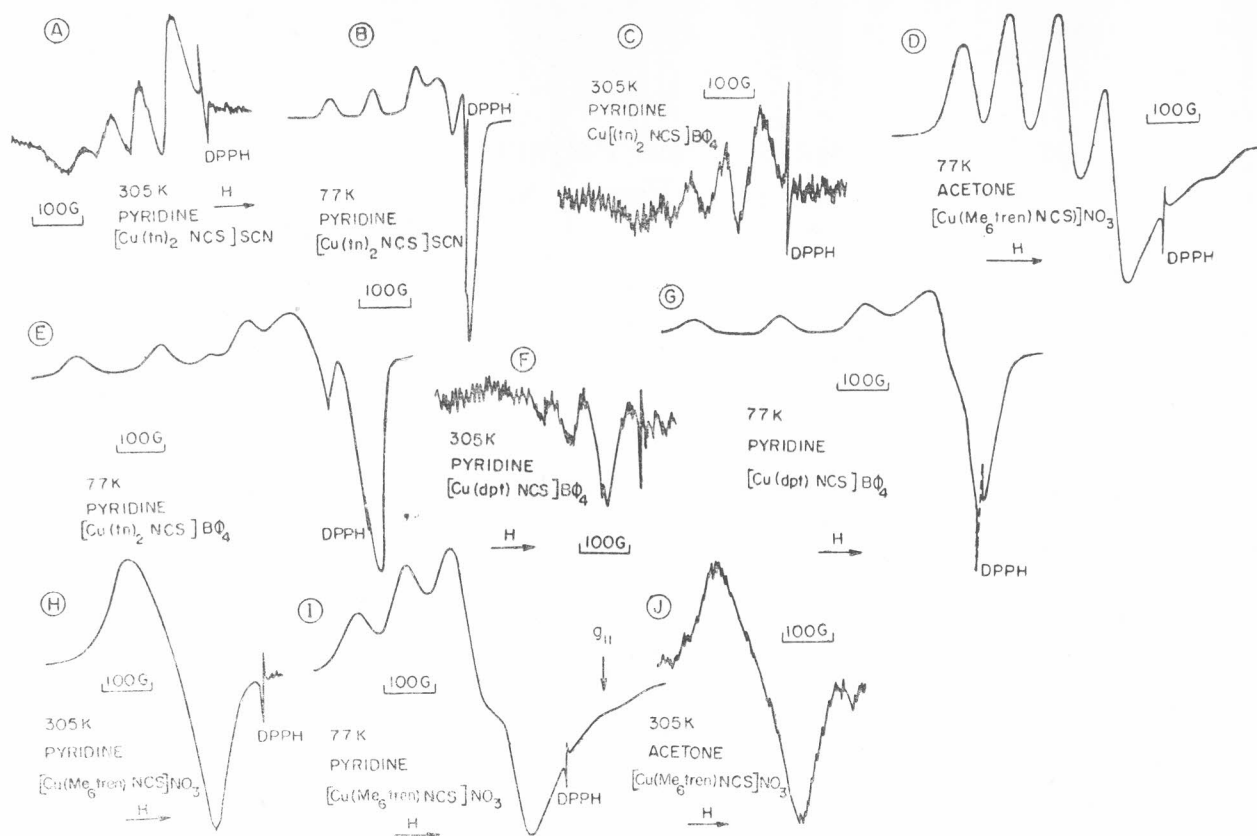


Fig. 1 — ESR spectra of (A,B) $[\text{Cu}(\text{tn})_2\text{SCN}]\text{SCN}$, (C,E) $[\text{Cu}(\text{tn})_2(\text{NCS})]\text{B}\phi_4$, (F,G) $[\text{Cu}(\text{dpt})\text{NCS}]\text{B}\phi_4$ in pyridine and (D,H,I,J) $[\text{Cu}(\text{Me}_6\text{tren})(\text{NCS})]\text{NO}_3$ in pyridine and acetone both at room (305K) and liquid nitrogen temperatures

from the frozen solution spectra using the procedure of Sands⁹ and others¹⁰. The value of g_{\perp} and A_{\perp} are obtained from the average g [$\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3$] and A [$\langle A \rangle = (A_{\parallel} + 2A_{\perp})/3$] values obtained from solutions at room temperature. The g and A values of these complexes are given in Table 1. As is evident from the g ($g_{\parallel} > g_{\perp} > 2.04$) values the electric field symmetry is tetragonal formed with either elongated octahedron or square pyramidal and hence the ground state correspond to either B_{1g} or B_{2g} . This indicates that the trigonal bipyramidal structure of $[\text{Cu}(\text{tn})_2\text{SCN}]^+$ in solid will change to square pyramidal structure in solution due to solvent interaction as predicted earlier by IR conductivity and optical data. The dpt complex also exhibits a similar behaviour.

In the case of $[\text{Cu}(\text{Me}_6\text{tren})(\text{NCS})]\text{NO}_3$ in pyridine and acetone solutions, the spectra are found to be entirely different from that of the other three complexes. Here lowfield side spectrum consists of four lines with higher intensity than the high field side spectrum where one weak line is recorded (Fig. 1). This type of spectrum can only be observed in the case of trigonal bipyramidal or compressed octahedron symmetry. In the case of the powders of $\text{Cu}(\text{II})$ doped bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)zinc(II)¹¹ this type of spectrum is recorded but the highfield weak line is well resolved unlike the present case. The optical absorption values (12500 and 14500 cm^{-1}) in the above complexes are same as those found in the present case. To make sure that the position

TABLE 1 — ESR, OPTICAL ABSORPTION AND BOND PARAMETERS OF COPPER(II) POLYAMINE COMPLEXES

| Complex | $\langle g \rangle$ | $\langle A \rangle \times 10^4$ cm^{-1} | g_{\parallel} | g_{\perp} | $A_{\parallel} \times 10^4$ cm^{-1} | $A_{\perp} \times 10^4$ cm^{-1} | $\Delta E_{xy} \times 10^{-3}$ cm^{-1} | $\Delta E_{xz} \times 10^{-3}$ cm^{-1} | α^2 | β^2 | β_1^2 |
|---|---------------------|---|-----------------|-------------|---|---|--|--|------------|-----------|-------------|
| $\text{Cu}(\text{tn})_2(\text{SCN})_2$ | | | | | | | | | | | |
| (a) Pyridine | 2.119 | 62.8 | 2.212 | 2.072 | 167.4 | 10.5 | 15.20 | 17.60 | 0.7125 | 1 | 0.8721 |
| $\text{Cu}(\text{tn})_2\text{NCS}.\text{B}\phi_4$ | | | | | | | | | | | |
| (a) Pyridine | 2.121 | 62.8 | 2.222 | 2.069 | 172.0 | 8.2 | 15.60 | 18.60 | 0.7283 | 0.997 | 0.8720 |
| $\text{Cu}(\text{Me}_6\text{tren})\text{NCSNO}_3$ | | | | | | | | | | | |
| (a) Pyridine | | | 1.924 | 2.190 | | 93.00 | 14.20 | 11.00 | | | |
| (b) Acetone | | | 1.924 | 2.190 | | 88.4 | 14.20 | 11.00 | | | |
| $\text{Cu}(\text{dpt})\text{NCS}.\text{B}\phi_4$ | | | | | | | | | | | |
| (a) Pyridine | 2.1204 | | 2.233 | 2.065 | 160.4 | | 15.80 | | 0.7465 | | 0.7381 |

of the weak line correspond to the g value, we have calculated the g_{\perp} value from the average g [$\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3$], obtained from the room temperature spectrum and the g_{\perp} value obtained from the frozen solution spectrum. The value obtained above tallies very well with the value obtained from the weak line position. The values of g_{\parallel} , g_{\perp} , A_{\perp} and optical absorption peaks obtained from acetone and pyridine are found to be nearly same indicating that the solvation of the complex in both the solvents is equal. One of the most important features of the ESR data of this Me₆tren complex is that the g_{\parallel} value is the smallest of all the values in Cu(II) complexes so far investigated.

The nature of the σ and π bonds are investigated in the case of (tn)₂ and dpt complexes where complete optical data (ΔE_{xy} and ΔE_{xz}) and ESR data (g_{\parallel} , A_{\parallel} , A_{\perp} and g_{\perp}) are available (Table 1). ΔE_{xy} and ΔE_{xz} are assigned to the optical absorption peaks observed in solutions as given in Table 1. In the case of other (tn)₂ complexes the peak at 14600 cm⁻¹ is used as the ΔE_{xy} (refs. 8 and 12). In our case the value is found to be slightly higher. Molecular orbital theory put forward by Maki and McGarvey¹³ is used to calculate and metal-ligand bond nature. In fact this theory is strictly applicable to square-planar complexes. But many workers applied this theory to complexes having other than square-planar structure^{9,14-16}, considering only the atoms in the principal plane for the sake of simplicity. The expressions of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} in terms of molecular orbital coefficients are given as follows^{8,13}:

$$g_{\parallel} = 2.0023 - 8\mu[\sigma\beta_1 - \frac{1}{2}\alpha'(1 - \beta_1^2)^{\frac{1}{2}}T(n)] \quad \dots(1)$$

$$g_{\perp} = 2.0023 - 2\mu\left[\alpha\beta - \frac{1}{\sqrt{2}}\alpha'(1 - \beta^2)^{\frac{1}{2}}T(n)\right] \quad \dots(2)$$

$$A_{\parallel} = P\left[-\left(\frac{4}{7} + K_0\right)a^2 + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) - 4\mu\alpha'(1 - \beta_1^2)^{\frac{1}{2}}T(n) - \frac{(3.2)^{1/2}}{7}\mu\alpha'(1 - \beta^2)^{\frac{1}{2}}T(n)\right] \quad \dots(3)$$

$$A_{\perp} = P\left[\left(\frac{2}{7} - K_0\right)a^2 + \frac{11}{14}(g_{\perp} - 2) - \frac{(11.2)^{\frac{1}{2}}}{14}\mu\alpha'(1 - \beta^2)^{\frac{1}{2}}T(n)\right] \quad \dots(4)$$

In the above expressions the constants have their usual meanings⁸. α^2 , β_1^2 and β^2 are measures of in-plane σ , in-plane π and out-of-plane π -bonds respectively. In the case of dpt since complete

optical data are not available α^2 is calculated using the simplified expression¹⁷ (5)

$$\alpha^2 = -\frac{A_{\parallel}}{P} + (g_{\parallel} - 2.0) + \frac{3}{7}(g_{\perp} - 2.0) + 0.04 \quad \dots(5)$$

Using this value of α^2 in g_{\parallel} expression, the value of β_1^2 is calculated. The bond parameters (α^2 , β_1^2 and β^2) thus calculated are given in Table 1. From these bond parameters the conclusions drawn are: (i) A considerable in-plane π -bonding is observed similar to the other polyamine Cu(II) complexes⁸ disproving once again the statement that the aliphatic amines are incapable of π -bonding; (ii) there is no out-of-plane π -bonding in (tn)₂ complexes; and (iii) the σ -bonding in all the cases is same and moderately strong. This is of the same order as that observed in other polyamine Cu(II) complexes^{1,8}.

We could not estimate the bond nature in Me₆tren complex as the complete optical and ESR data are not available.

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