

Electron Paramagnetic Resonance Study of 2-Diethylamino ethanolato-Trifluoroacetato Copper (II)-Tetramer

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Abstract. The EPR study of 2-Dimethylamino-ethanolato-trifluoroacetato Copper (II)-Tetramer (DTCT) has been carried out. The theory of Cu^{2+} ion has been discussed. The EPR spectra of DTCT in Powder and glassy states have also been given. The spin Hamiltonian parameters of Cu^{2+} EPR spectra in DTCT at different solvents with varied concentrations are estimated in this paper.

1. Introduction

It has been of interest over many years to study the effects of halogeno substitution of the carboxylate ligand on structures transition metal complexes¹⁻⁴. Copper (II) acetate forms with 2- Dimethylamino ethanol a novel centrosymmetric nuclear structure whereas in other similar complexes a tetranuclear cubane like structure is found³⁻⁴. The compound 2-Dimethylaminoethanolato Trifluoroacetato Copper (II) tetramer (DTCT) is also found to have a tetranuclear cubane like structure in which the Cu and bridging ethanolato O atoms form Cu_4O_4 cubane type core⁴. In the core the short Cu-O (ethanolato) bonds form an 8-membered ring folded in a boat like conformation. Each Cu has a distorted octahedral environment with two ethanolato O atoms, a carboxyl O atom and an amino N atom forming the equatorial plane. A carboxyl O atom and an ethanolato O atom occupy the axial sites. The study of line shapes and line widths of the EPR spectra from the Paramagnetic samples diluted in diamagnetic solvents provides interesting informations regarding the paramagnetic species. Such studies have been extensively done in past and elaborate theories have been developed⁵⁻¹⁰. There have been a number of studies in past on EPR line widths in solution by Misra and coworkers¹¹⁻¹⁶.

2. Theory of EPR of Cu^{2+} Ion

The electronic state of the divalent copper ion, Cu^{2+} , is $[\text{Ar}]^{18} 3d^9$ and the unfilled d shell has odd number of electrons which consequently provide EPR signals. For convenience the cupric ion, Cu^{2+} is regarded as a single positive hole in the completely filled shell and becomes similar to d^1 ions. The energy level pattern of d^1 configuration would look inverted as compared to d^2 configuration. In an octahedral field the five fold degeneracy is partially lifted and the 2D term splits into lower doublet 2E_g spanned by $|d_{x^2-y^2}\rangle$ and $|d_{z^2}\rangle$ orbitals and an upper ${}^2T_{2g}$ triplet spanned by $|d_{xy}\rangle$, $|d_{yz}\rangle$ and

$|d_{zx}\rangle$ orbitals. The doublet does not split by spin-orbit coupling. It is expected therefore, that in octahedral environment Cu^{2+} is subjected to Jahn-Teller distortion to remove the degeneracy leading to a lowering of the ground state energy¹⁷⁻²⁰. A tetragonal distortion removes the degeneracy according to the following scheme²¹⁻²³.

$${}^2E_g \rightarrow {}^2A_{1g} + {}^2B_{1g}$$

$${}^2T_{2g} \rightarrow {}^2B_{2g} + {}^2E_g$$

The ground state would therefore be either ${}^2A_{1g}$ or ${}^2B_{1g}$ spin doublet to give EPR spectrum. If the Cu^{2+} ion lies in an elongated tetragonal distortion, the ground state would be ${}^2B_{1g}$ ($|d_{x^2-y^2}\rangle$), whereas in the case of compressed tetragonal distortion ${}^2A_{1g}$ ($|d_{z^2}\rangle$) becomes the ground state. The EPR is observed for the ground state and is characterised by the characteristic g values²², e.g. $g_{\perp} > g_{11} \approx 2$, ${}^2A_{1g}$, ${}^2A_{1g}$ and $g_{11} > g_{\perp} > 2$ for ${}^2B_{1g}$ usually hold²². For cupric ion in an axially elongated octahedral environment by McGarvey²⁴ and improved by Kivelson and Neumann²⁵. The EPR spectrum of Cu^{2+} in tetragonal (axial) symmetry is discussed by the following Hamiltonian.

$$\begin{aligned} H = & g_{11} \beta B_z S_z + g_{\perp} \beta (B_x S_x + B_y S_y) + A_{11} S_z I_z \\ (2.1) \quad & + A_{\perp} (S_x I_x + S_y I_y) + Q [I_z^2 - \frac{1}{3} I(I+1)] \end{aligned}$$

where $S=1/2$ and $I=3/2$ are the electronic and nuclear spins respectively. The resonance field values for \vec{B} parallel to Z-axis, i.e. $\theta = 0^\circ$ and \vec{B} perpendicular to z-axis i.e. $\theta = 90^\circ$ are given by low²⁶ and are reproduced here for Cu^{2+} ion for $\theta = 0^\circ$

$$(2.2) \quad B_{(m)} = B_0 - A_{11} - \frac{A^2}{2B_0} [I(I+1) - m^2]$$

and for $\theta = 90^\circ$

$$(2.3) \quad B_{(m)} = B_0 - A_{\perp} m - \frac{(A_{11}^2 + A_{\perp}^2)}{4B_0} [I(I+1) - m^2]$$

where $B_{(m)}$ is the resonance field for the $m \leftrightarrow m$, hf transition; $I = 3/2$; $m = 3/2, 1/2, -1/2$ and $-3/2$ for Cu^{2+} ion and

$$(2.4) \quad B_0 = \frac{h\nu}{\beta g_{\perp} A_{\perp}}$$

where ν is the frequency (Resonant), g_{\perp} and A_{\perp} are the g -value (at $\theta = 0$), hyperfine parameter value (at $\theta = 90^\circ$) respectively. Q is the quadrupole interaction parameter which being small has not been considered here.

3. Experimental

The Polycrystalline form of the title compound DTCT was obtained by evaporation of an ethanol solution containing Cu (II) trifluoroacetate and 2-dimethylamino-ethanol in molar ratio 1:1 as described by Ahlgren²⁻⁴ et al. EPR spectra of solutions in different solvents were recorded using flat liquid sample cell. The title compound was dissolved in solvent viz. Pyridine (Py), ethanol, Dimethyl Sulfoxide (DMSO), 50:50 mixture of ethanol and 2-dimethylaminoethanol (2-DMAE) to prepare the solution concentration 10^{-3} mol/litre. To make the glass of the Cu^{2+} complex the title compound was mixed thoroughly in the glass forming (60:40) glycerine: water mixture. To record EPR spectra at LNT samples were filled in 4 mm outer diameter quartz sample tubes and immersed into liquid nitrogen in a cold finger quartz dewar. DPPH is used as a standard g -marker ($g_{\text{DPPH}} = 2.0036 \pm 0.0002$).

4. Results and Discussion

The EPR spectra of polycrystalline DTCT (finely powdered sample) is shown in fig. 1. The details of h.f. structure get suppressed to great extent due to dipolar broadening on higher gains the h.f. peaks on lower magnetic field side becomes discernible (Fig. 1). The

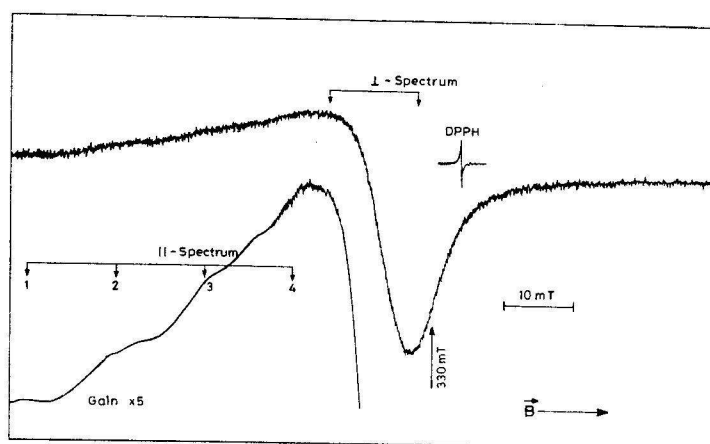


Fig. 1. X-band EPR spectrum of DTCT in polycrystalline state of RT, To see the h_f peaks of II-spectrum the gain was increased 5 fold.

parallel ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$) parts of the powder EPR spectrum are identified and analysed using the expressions given in equations (2.2) and (2.3) to get the values of g_{11} , g_{\perp} , A_{11} and A_{\perp} [The so called spin Hamiltonian Parameters (SHP)]. The parameters are given in Table 1.

Table 1. Spin Hamiltonian Parameters from samples of DTCT in Powder and Glassy state.

Sample	g-values		A-values	
	g_{\perp}	g_{11}	A_{\perp}	A_{11}
1. Powder	2.077 ± 0.005	2.278 ± 0.005	42 ± 5	125 ± 5
2. Glass	2.080 ± 0.005	2.372 ± 0.005	17 ± 5	143 ± 5
Gly : water (60:40)				
3. Frozen Solution in Py. at LNT	2.055 ± 0.005	2.343 ± 0.005	35 ± 5	123 ± 5
4. Frozen Solution in DMSO at LNT	2.070 ± 0.005	2.289 ± 0.005	25 ± 5	78 ± 5
5. Frozen Solution in Ethanol+ 2DMAE at LNT	2.050 ± 0.005	2.240 ± 0.005	—	180 ± 5

The EPR spectra of some frozen glassy samples in various solvents recorded at LNT are shown in Figs. 2-5. The SHP obtained from these spectra are collated in Table 1

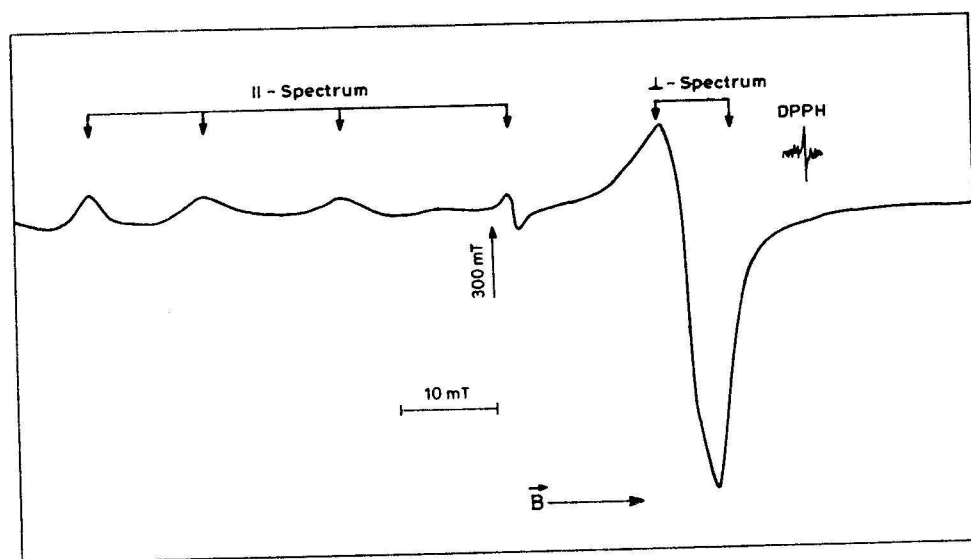


Fig. 2. X-band EPR spectrum of DTCT in glassy state at LNT.

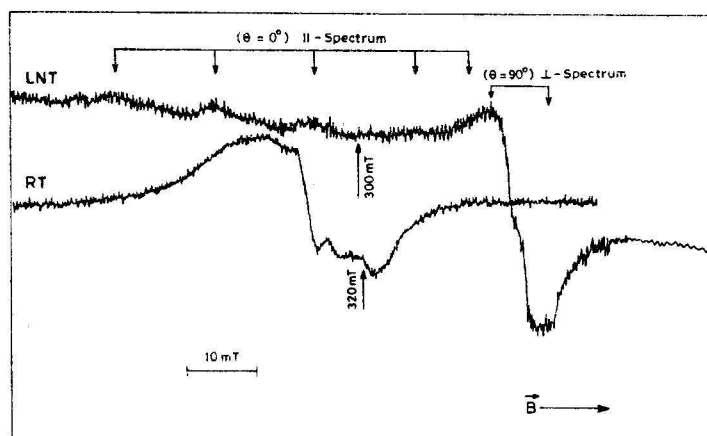


Fig. 3. X-band spectrum of 10^{-3} mol/litre solution of DTCT in DMSO at RT and at LNT.

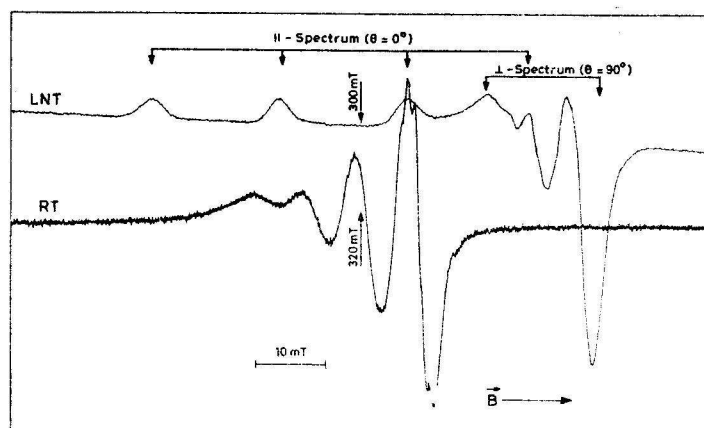


Fig. 4. X-band EPR spectra of DTCT 10^{-3} mol/litre solution in ethanol+2 DMAE 50:50 at RT and LNT.

alongwith the other similar data. The g -values indicate that $g_{11} > g_{\perp} > 2$. This fact indicates that the ground state of the Cu^{2+} ion in the present case is ${}^2B_{1g} (|dx^2 - y^2\rangle)$ hence Cu^{2+} ion is surrounded by an elongated octahedron of ligands. This fact becomes more evident in Pyridine solvent where SHF structure also becomes evident in the EPR spectra on some hf peaks (Fig. 5). The EPR spectra of the compound (DTCT) in solutions

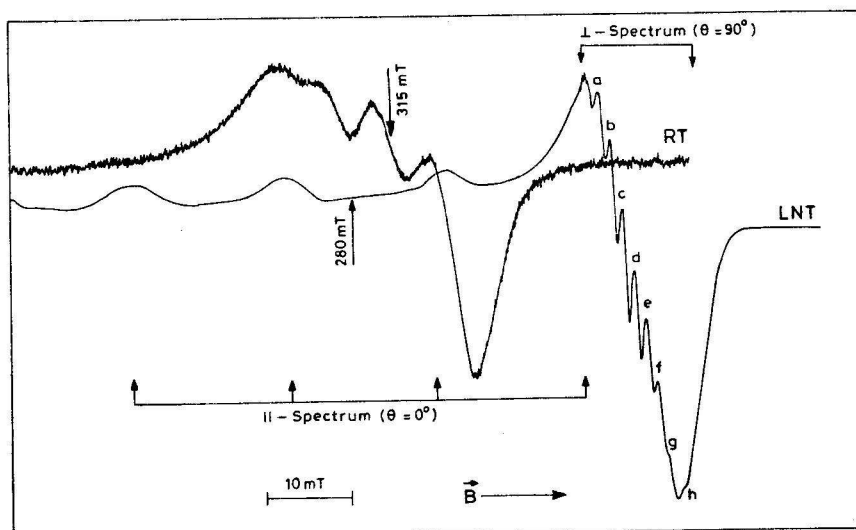


Fig. 5. X band EPR spectra of 10^{-3} mol/litre solution of DTCT in Py solvent at RT and LNT. SHF is seen in \perp -spectrum at LNT.

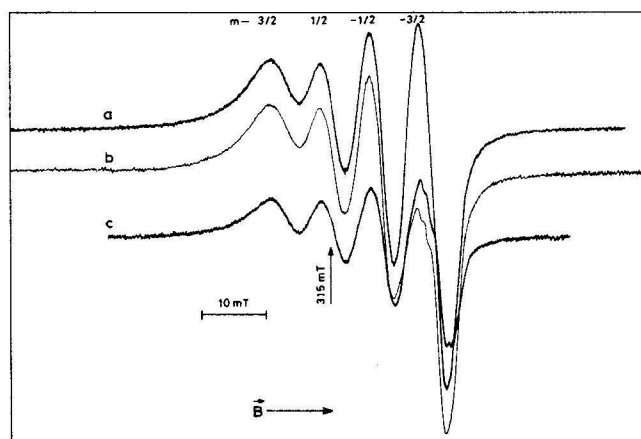


Fig. 6. RT EPR spectra of DTCT solution in ethanol 2 DMAE mixture (a) 10^{-2} mol/litre (b) 5×10^{-3} mol/litre and (c) 10^{-3} mol/litre.

in various solvents and concentrations are shown in Figs. 3-8. The m -dependence of hf in solutions is given below in modified form

$$(4.1) \quad \Delta H_{(m)} = a_0 + a_1 m + a_2 m^2 + a_3 m^3$$

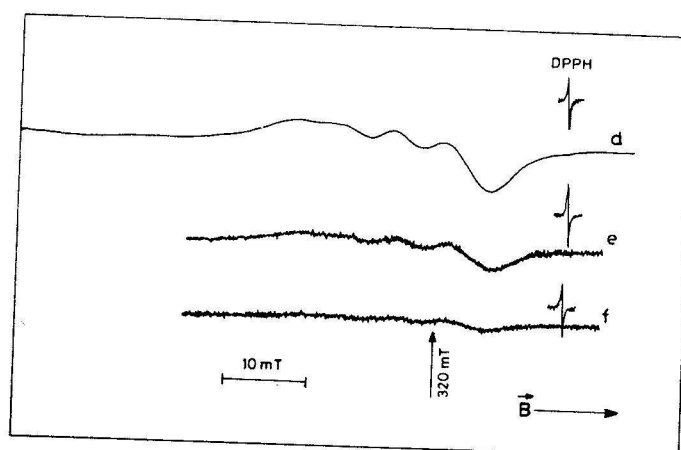


Fig. 7. RT EPR spectra of DTCT solution in ethanol-2DMAE mixture (d) 5×10^{-4} mol/litre (e) 10^{-4} mol/litre and (f) 5×10^{-5} mol/litre.

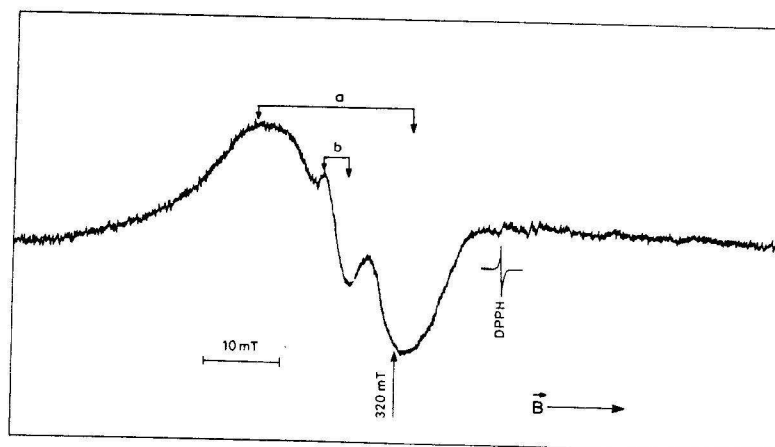


Fig. 8. X-band EPR spectrum of 10^{-3} mol/litre solution of DTCT in ethanol at RT.

The EPR spectra are described by an isotropic spin Hamiltonian of the following form²⁷:

$$(4.2) \quad H_{eff} = g_{eff} \beta B \vec{S} + A_{eff} \vec{I} \cdot \vec{S}$$

and the corresponding resonance fields are given by²⁷

$$(4.3) \quad B_{(m)} = B_0 - A_{eff} m - (A_{eff}^2 / 2B_0) [I(I+1) - m^2]$$

The values of g_{eff} and A_{eff} obtained from the analysis of solution spectra using equation (4.3) are given in Table-2. The linewidth parameters of equation (4.1) are obtained by comparing the experimental linewidths with the calculated linewidths using best fit parameter. The experimental linewidth ΔH_{expt} and the calculated value ΔH_{cal} are also given in Table-3 alongwith the best fit linewidth parameters. It can be seen from Figs 3 and 8 that in 10^{-3} mol/litre solution in DMSO and ethanol at RT the hf structure is averaged out almost completely and the spectrum comprises a broad line at $g_{eff} \approx 2.2$. However one narrow signal (marked b in Fig. 8) is also additionally seen which may probably originate due to some free radical being produced in the solution. However the smearing of hf structure is not seen in solution spectra in Fig. 7 upto the dilution 5×10^{-3} mol/litre in (ethanol + 2 DMAE) 50:50 mixture. In Fig. 4, the EPR spectrum of the heated solution in (ethanol+2DMAE) 50:50 mixture at 10^{-3} mol/litre is shown at RT and LNT. It is seen that at LNT the hf peaks are very clear in \parallel -spectrum and the difference at LNT and RT spectra is quite discernible. This difference arises to the solution state at RT being converted to a glassy state into the frozen solution at LNT; on this case also the LNT spectrum supports the axial symmetry of the copper complex.

Table 2. Average values of g and A_{eff} Parameters for Cu^{2+} obtained from solution EPR spectra of DTCT at RT.

Solvent	Concentration (mol/litre)	g_{eff}	A_{eff} (G)
1. Ethanol + 2DMAE	10^{-2}	2.11 ± 0.02	73
2. "	5×10^{-3}	2.11 ± 0.02	73
3. "	10^{-3}	2.11 ± 0.02	77
4. "	5×10^{-4}	2.11 ± 0.02	78
5. Ethanol + 2DMAE (Heated)	5×10^{-4}	2.11 ± 0.02	78
6. Pyridine	10^{-3}	2.14 ± 0.02	63
7. DMSO	10^{-3}	2.26 ± 0.02	—
8. Ethanol	10^{-3}	2.14 ± 0.02	—

Table 3. Experimental and calculated hf linewidths of Cu^{2+} EPR spectra of DTCT in Ethanol + 2DMAE (mixture solution, 50:50). The fitted Parameters are also given.

Concentration (mol/litre)	m	ΔH_{exp} (G)	ΔH_{cal} (G)	a_0 (G)	a_1 (G)	a_2 (G)	a_3 (G)
10^{-2}	3/2	45	45				
	1/2	40	40	36.87	5.41	2.5	-1.66
	-1/2	35	34.2				
	-3/2	40	40				

5×10^{-3}	3/2	45	45	36.87	5.41	2.5	-1.66
	1/2	40	40				
	-1/2	35	34				
	-3/2	40	40				
10^{-3}	3/2	40	42.8	33.25	0.947	3	0.421
	1/2	35	34.5				
	-3/2	33	34				
	-1/2	40	37.2				
5×10^{-4}	3/2	40	40	32.94	-2.04	4.25	0.170
	1/2	35	33				
	-3/2	35	34				
	-1/2	42	40.5				

5. Conclusion

The EPR spectra of DTCT in solution and Glassy States clearly indicate that the copper is in Cu^{2+} state and is surrounded by an elongated octahedron of ligands. The ground state of Cu^{2+} ion is $^2B_{1g} (|d_x^2 - y^2\rangle)$. The lineshape and linewidth in solution spectra are explained by the well known theory developed earlier^{5,6,8,9}. Solvents are affecting the immediate environment of Cu^{2+} in the complex in solutions as mentioned by some changes in SHP and EPR spectra in different solutions.

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