

Electron paramagnetic resonance study of free radicals in γ -irradiated single crystal of tris(glycine) calcium(II) dibromide

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Abstract. Tris(glycine) calcium(II) dibromide single crystal has been irradiated with a γ -source to produce free radicals and the irradiated sample has been subjected to EPR studies. The observed spectra reveal that an NH_4 radical is formed by rupturing glycine molecule due to irradiation. The unpaired electron is localized on the C–N bond. The proton hyperfine interaction on the unpaired spin shows orthorhombic symmetry and the spectroscopic splitting factor remains isotropic.

Keywords. Electron paramagnetic resonance; organic radical; spin Hamiltonian; tris(glycine) calcium dibromide.

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1. Introduction

Irradiation by means of x-rays or γ -rays in crystals creates lattice defects. The study of such defects and its surroundings is of great interest in electron paramagnetic resonance (EPR) investigations. EPR studies on artificially created defects in the aminoacids viz glycine (Weiner and Koski 1963; Ghosh and Whiffen 1959; Sinclair 1971; Collins and Whiffen 1966; Box *et al* 1966) and glycine hydrochloride (Box *et al* 1969) are well known. Recently a review of EPR, ENDOR and ELDOR studies on biologically significant complexes (Wells 1983) has been reported. We report the results of our measurements on γ -irradiated tris(glycine) calcium(II) dibromide (TGCB).

2. Crystal structure

TGCB has the chemical formula $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{CaBr}_2$ and is an addition compound of glycine and calcium bromide. It crystallizes in an orthorhombic unit cell of dimensions

$$a = 9.15 \text{ \AA}, \quad b = 14.84 \text{ \AA} \quad \text{and} \quad c = 20.31 \text{ \AA}.$$

There are eight formula units in the unit cell in the space group $\text{Pbc}2_1$. Six different glycine molecules exist as zwitter ions, $\text{NH}_3^+\text{CH}_2\text{COO}^-$, since the two C–O distances in each glycine molecule are nearly the same and three hydrogen bonds are around each

nitrogen atom (Mohana Rao and Natarajan 1980). All glycine molecules possess the same bond distances but the bond angles differ slightly from each molecule. The O—O—C—C α groups are planar and terminal nitrogen atoms deviate from the mean plane by 0.25, 0.34, 0.11, 0.17, 0.04 and 0.16 Å and the dihedral angles, between O—O—C—C α and C—C α —N plane are 9.2, 16.0, 5.3, 6.0, 2.2 and 5.6°.

3. Experimental

TGCB crystals were grown by slow evaporation technique at room temperature with their stoichiometric constituents. Well-developed crystals were irradiated for about 30 hr using a γ -source ^{60}Co to a dose of 1 Mrad at room temperature. Soon after irradiation, EPR measurements were carried out at the Regional Sophisticated Instrumentation Centre (RSIC), Indian Institute of Technology (IIT), Madras in three mutually perpendicular planes using E-4 Varian EPR spectrometer operating at 100 kHz field modulation. γ -irradiation for at least 25 hr was found to be necessary for observing the EPR spectra. The spectra were recorded for every 10° rotation about crystal *a*-, *b*- and *c*-axes at room temperature.

4. Results

For an arbitrary orientation a group of five EPR transition lines (quintet) is observed and each of these lines in turn splits into three prominent components (triplets). The quintet line intensity ratios are 1:4:6:4:1. When the magnetic field is parallel to *a*-axis the quintet is well resolved and the successive line separation of triplets is about 4 gauss. The separation between successive lines of quintet is nearly 20 gauss. When the crystal is oriented along *b*- or *c*-axis the quintet has a small spread and also the triplets overlap. Consequently the line position measurements could be made with an error between 2 and 5 gauss. When *a*-, *b*- and *c*-axes of crystal are along the magnetic field *H*, the EPR spectra were recorded and are as shown in figures 1, 2 and 3 respectively. The variations of the average line separation of the quintet in the *ac*, *ab* and *bc* planes are shown in figures 4a, b and c respectively. Since the line separation of the triplet could not be measured accurately, we assume an average separation of 5 gauss. The spin Hamiltonian parameter A_p (quintet hyperfine separation) is fitted to the relation (Narayana *et al* 1976).

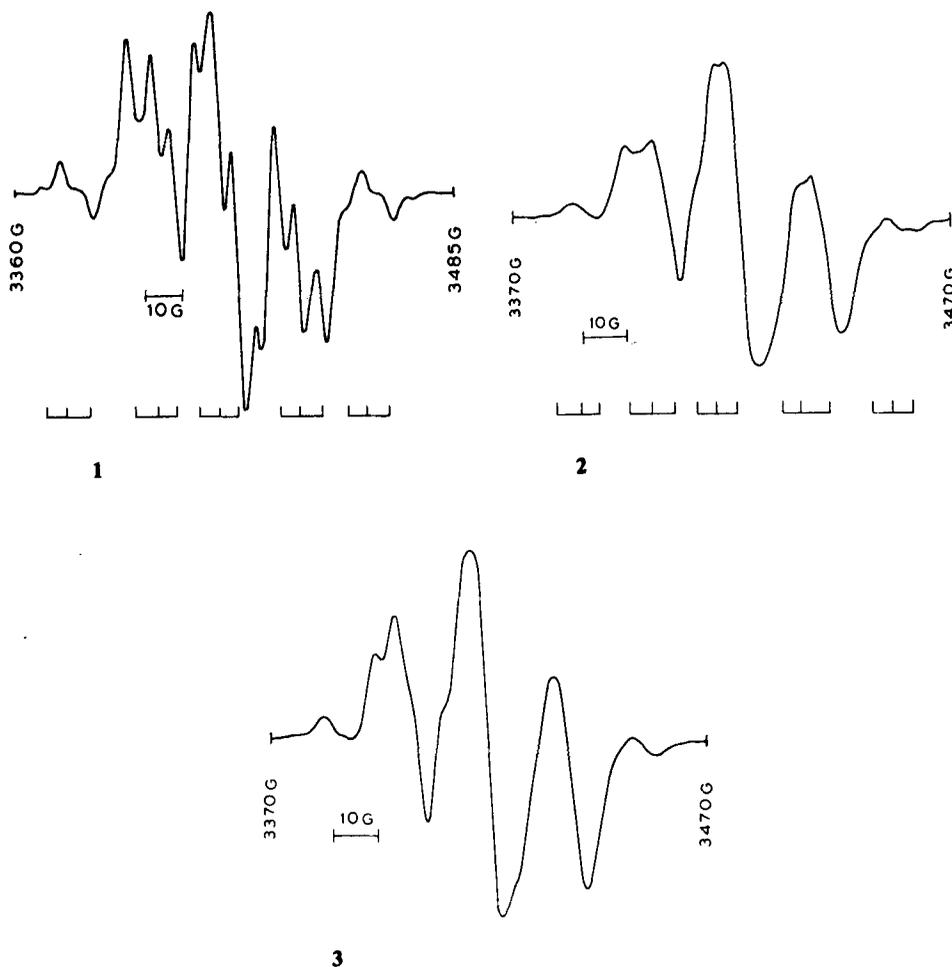
$$(gA_p)^2\theta = g_{\text{iso}}^2 A_{\text{max}}^2 \cos^2 \theta + g_{\text{iso}}^2 A_{\text{min}}^2 \sin^2 \theta, \quad (1)$$

where A_{max} and A_{min} correspond to the maximum and minimum line separations in the adjacent components of the quintet respectively, in a given plane of rotation. g_{iso} denotes isotropic *g* tensor.

The observed spectra could be described by a spin Hamiltonian

$$\mathcal{H} = g_{\text{iso}}\beta\bar{H}\cdot\bar{S} + \bar{S}\cdot A_p\cdot\bar{I}_p + \bar{S}\cdot A_n\cdot\bar{I}_n. \quad (2)$$

The first term in (2) is the interaction between external magnetic field and electron spin. The second and third terms describe the hyperfine interaction due to protons and nitrogen respectively. The principal A_p values determined using Schonland's method

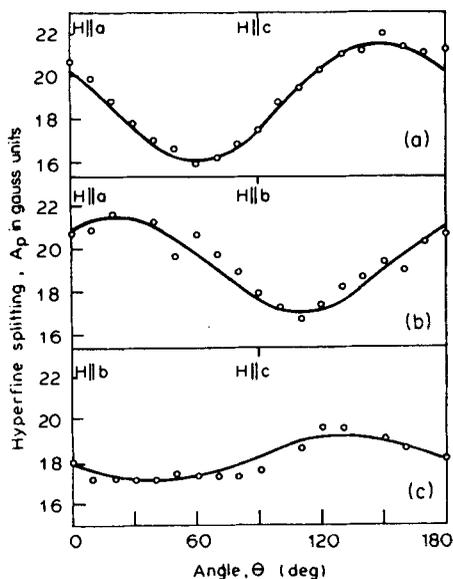


Figures 1, 2 and 3. EPR spectrum of tris(glycine) calcium(II) dibromide γ -irradiated single crystal when aligned with crystallographic a -, b - and c -axes respectively along the external magnetic field at room temperature.

(Schonland 1959) are presented in table 1. The principal A_n values could not be determined due to the fact that exact line positions of the triplets could not be measured in many orientations. The principal A_p values show orthorhombic symmetry with slight deviation from axial symmetry.

5. Discussion

In the a -axis spectrum (figure 1) from the appearance of a quintet pattern with the intensity ratios 1:4:6:4:1, we can conclude that an unpaired electron is being influenced by a paramagnetic species of nuclear spin $I = 2$. Each quintet component is further split into a triplet due to further interaction with a paramagnetic nucleus $I = 1$. In γ -irradiated TGCB, the existence of quintet EPR transitions and the splitting of each



Figures 4a, b, c. Angular variation of quintet hyperfine separation arising from the interaction of protons with free electron of the glycine molecule in *ac*, *ab* and *bc* planes. Solid line indicates theoretical values and open circles indicate experimental values.

Table 1. Spin Hamiltonian parameters of NH_4 radical in γ -irradiated TGCB crystal.

	Principal hyperfine constant A_p in units of gauss	Direction cosines with respect to crystallographic <i>a</i> -, <i>b</i> - and <i>c</i> -axes frame		
		<i>l</i>	<i>m</i>	<i>n</i>
A_x	22 ± 1	0.7827	-0.2573	-0.5091
A_y	17 ± 1	0.4505	0.8538	0.2609
A_z	16 ± 1	0.4294	-0.4301	0.6659
Plane	<i>ab</i>	<i>bc</i>	<i>ca</i>	
<i>g</i>	1.980 ± 0.005	1.979 ± 0.005	1.980 ± 0.005	

component of quintet into a triplet are in accordance with the presence of four protons ($I = 2$) and nitrogen ($I = 1$) in the glycine molecule.

γ -irradiation ruptured glycine molecule in TGCB and consequently the bonding is altered in such a way that the unpaired electron is coupled equivalently by four protons. Three of them are amine protons and the remaining being the α proton. Zeeman field lifts the spin degeneracy of the unpaired spin into $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$ states. Each state of spin density successively interacts with four equivalent protons in splitting levels with the population ratios 1:1, 1:2:1, 1:3:3:1 and 1:4:6:4:1. Each of these final levels is coupled by nitrogen to have equal intense triplet structure. Transitions are

observed according to the selection rules $\Delta M_s = \pm 1$ and $\Delta m_l = 0$. This fact leads to the conclusion that the radical formed in TGCB is NH_4 . The slight unequal intensity and unequal spacings of the triplet lines observed may be due to non-uniform distribution of electron spin density over the radical.

Weiner and Koski (1963) studied the EPR spectra of X-irradiated glycine and they have assigned two radicals viz $H_\sigma\text{NH}_3$ and $\dot{\text{C}}\text{H}-\text{COO}^-$. The $H_\sigma\text{NH}_3$ radical is due to dissimilar protons as H_σ or H_n (i.e.) one of the amine protons has different N-H distance than the other two. Then the odd electron density would be predominantly in a σ -orbital, which is a linear combination of H_σ 1s orbital and N 3s orbital. In TGCB, the quintet pattern suggests that the spin density of the unpaired electron of the glycine molecule resides on the C-N σ orbital and the four protons are coupled equivalently by this spin density. The frequency of libration of the four hydrogen bonds is sufficiently rapid at room temperature and they act in an equivalent manner on the spin resonance spectrum (Weiner and Koski 1963). The radical formed in TGCB is the same as enunciated by Weiner and Koski except the difference that the four protons equivalently interact instead of being dissimilar. This is confirmed from the 1:4:6:4:1 intensity ratios in the quintet pattern. A comparative study is made with the earlier results of Weiner and Koski (1963) and Ghosh and Whiffen (1959) and the results are shown in table 2. Due to the complexity of the spectrum in TGCB the other radicals which are believed to exist could not be separated and hence are not reported here with the exception of NH_4 radical.

In the present system there are six glycine molecules in the asymmetric part which are crystallographically inequivalent. By generating other glycine molecules, there will be 24 glycine molecules. The direction cosines l , m and n of the C-N bonds with respect to a -, b - and c -axes are presented in table 3. From table 3 it is clear that three pairs are

Table 2. Comparison of hyperfine coupling constants (in gauss units).

Radical	Nucleus				Reference
	H_c	H_n	N	H_A	
$\text{NH}_3-\dot{\text{C}}\text{H}-\text{COO}^-$	26.8	18.9	3.5	—	Ghosh and Whiffen (1959)
$H_\sigma\text{NH}_3$	31.8	16.4	2.9	—	Weiner and Koski (1963)
NH_4	—	—	5.0	22.0	Present work

Table 3. Direction cosines of C-N orientations of glycine molecule in the a -, b - and c -axes frame.

	l	m	n
N(11)-C(21)	0.5027	-0.8158	-0.2857
N(12)-C(22)	-0.4382	0.8155	0.3904
N(13)-C(23)	-0.9842	0.0694	0.1628
N(14)-C(24)	-0.9786	-0.0794	-0.1900
N(15)-C(25)	0.3431	0.8252	0.4487
N(16)-C(26)	-0.3733	-0.8046	-0.4619

nearly magnetically equivalent. N(11)–C(21) and N(12)–C(22) pair, N(13)–C(23) and N(14)–C(24) pair and N(15)–C(25) and N(16)–C(26) pair are assumed to be nearly magnetically equivalent. Since the *z*-axis of the NH₄ radical is believed to lie along C–N bond direction, we may expect effectively 12 magnetically inequivalent NH₄ radicals. Hence EPR results obtained in table 1 are due to the averaged effect of all NH₄ radicals.

6. Conclusion

γ -irradiated TGCB crystals possess predominantly NH₄ radical. The four protons equally influence the unpaired electron spin density which resides on the C–N bond. The unpaired electron is influenced by the three protons from the amine group and the fourth proton being the α proton. Such a combination of interaction on the unpaired electron density gives rise to quintet separation and each component is further split into a triplet.

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