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Synthesis and Mossbauer Spectroscopy: Iron(III) Compexes of Bis–Benzimidazole Based Bidentate Ligands

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Abstract: Iron is especially important in the life processes as it is directly involved in the transport and storage of oxygen, electron transport, the metabolism of H_2 by dehydrogenase and several other vital metabolic functions.In this paper we shall study the synthesis and Mossbauer of iron(III) Compexes of Bis–Benzimidazole Based Bidentate Ligands.

Key Words:-synthesis and Mossbauer,iron(III)

1 .INTRODUCTION

Iron is especially important in the life processes as it is directly involved in the transport and storage of oxygen, electron transport, the metabolism of H_2 by dehydrogenase and several other vital metabolic functions.

It is safe to say that with a few possible exceptions in the bacterial world, there would be no life without iron. Generally, the importance of iron in various life processes comes about because of the ability of iron to exist in two stable oxidation states, ferrous (Fe^{2+}) and ferric (Fe^{3+}). These have the d^6 and d^5 electronic configuration respectively and thus can exist in both the high spin and low spin states. Most of the iron species involved in the uptake, transport and storage of iron in animals contain high spin Fe^{3+}, though the iron may be complexed initially as Fe^{2+}. Absorption of dietary iron across the gastrointestinal tract may also involve Fe^{2+} species(1), especially given that ascorbic acid influences iron absorption markedly(1,2).

The Fe^{3+}/Fe^{2+} redox potential varies over a wide range depending upon the nature of the ligand. Anionic oxygen ligands, such as carboxylates and phosphates,stabilize Fe^{3+} and therefore form complexes with low redox potentials. The Fe^{3+}/Fe^{2+} reduction potential often quoted for aqueous systems is 770 mV, but this only refers to acid solutions. As the pH is raised, so that H_2O bound to iron ionizes to OH^-, the redox potential drops sharply(3). The oxidation–reduction potentials of Fe which occur in various metabolic function can vary over a wide range depending upon the ligands attached to the iron. Nature has been very clever in utilizing molecules to

fulfill various needs and it is amazing how frequently iron is of central importance.

The low solubility of iron is the chief hurdle to its biological uptake. Many micro–organisms overcome this by secreting into the external medium small chelators, known as siderophores, that bind iron and are then reabsorbed by the organism as an iron complex. After its uptake the complex is broken down to release the iron. This breakdown may involve chemical degradation of the siderophore ligand, or simple release of iron, perhaps caused by its reduction to Fe^{2+}. A key feature of uptake is that iron must be able to cross the duodenum membrane to enter the mucosal cells. This means that most absorbed iron will be bound to small ligands, with the resulting complexes not carrying a high charge. Once absorbed, the iron enters the iron storage protein, ferritin, or is passed out of the mucosal cells into the blood, where it is carried by the iron transport protein, transferring, to tissues requiring iron[(4)].

Iron transport and storage in animals are tightly regulated. Ferritin is an abundant store in tissues involved in hemoglobin breakdown (e.g. liver and spleen)[(5)] and transferring or related proteins are available in most body fluids to sequester free iron[(4)].

Many different spectroscopic technique have been employed in the study of biological materials. These methods include optical absorption, infrared, electron spin resonance (ESR), nuclear magnetic resonance (NMR) and Mossbauer spectroscopy. The spectroscopic methods helps to understand how the iron is converted from mineral to protein and once in the protein what is the specialized role played by the iron in the function of that protein. Mossbauer and ESR spectroscopy helps to know the electronic and molecular structure of these proteins. Mossbauer techniques has seen its greatest development so that an accurate description of the chemical states and their energies, the symmetries of the crystalline or molecular environment and the covalent sharing of the valence electrons. In Mossbauer spectroscopy of ^{57}Fe, the radiation is specific for the 57 Fe which eliminates the complicatioin caused by the presence of other atoms. Most elements do not have a suitable isotope available for Mossbauer spectroscopy. Because iron is of such paramount importance in the molecules of life, it is indeed fortunate that ^{57}Fe exhibits such a good Mossbauer resonance.

Ferrichrome A. It is one of the most studied iron transport proteins. It is found in the smut fungus ustilagosphaerogena and has a structure similar to several molecules which are growth factors for several microorganisms. The molecule consists of a ferric ion bound by three bidentatehydroxamic acid residues as established by X–ray crystallography[(6)], Electron spin resonance experiments[(7)] on ferrichrome show a strong resonance observed at g = 4.3.

Deferoxamine. It is a growth factor for several micro–organism in which three hydroxamic acid residues bind ferric iron[(8)]. The iron complexing ability of this substance is used in cases of severe iron poisoning to chelate excess iron and is available for chemical use. The ferric complex is red brown and has a magnetic susceptibility, μ_{eff} = 5.86 B.M. at room temperature. A complete Mossbauer study of the ^{57}Fe

complexes by deferoxamine has been done[9] at low temperature in small applied fields and are typical of high spin ferric ion with rhombic distortion with qudrupole splitting 0.77 mm s^{-1}.

MycobactinP.Mycobactins are growth factors for most species of mycobacteria[10] and their production by the mycobacterium is stimulated by iron deficiency in the growth medium. The mycobactins consists of two hydroxamic acid residues which bind the ferric ion as well as a third bidentate ligand with a nitrogen and an oxygen at the iron site. The crystal structure of mycobactin–P has been determined[11]. Mossbauer experiments[12] have been done on the frozen alcohol solution and the data were fit using the spin Hamiltonian. However, subsequent ESR experiments[13] have shown a rather narrow resonance at g = 4.3.

Enterobactin. It is derived from certain enteric bacteria such as Escherichia coli in which the iron is bound by three bidentate catechol groups. There are three "charged" oxygens which bind the iron. Enterobactin is described[14] as the prototype and is produced by enteric bacteria when placed in an iron deficient medium. Enterobectin has a high affinity for iron. ESR experiments[15] indicate the characteristic g = 4.3, resonance found in the other high spin ferric compounds. Mossbauer experiments show unusually well resolved paramagnetic hyperfine structure(16).

Transferrins: The transferrins are iron chelating agent found in the various fluids of vertebrates including humans[17]. They are powerful chelators. They have two iron binding sites per molecule.

Each of the natural iron binding compounds above has a very strong affinity for ferric iron, relatively weak attraction for ferrous iron. The study of the natural iron binding compounds has brought forth several new and interesting aspects concerning the electronic states of the ferric ion and has stimulated some new thinking with regard to the ligand fields acting on the metal ion. Thus there is current interest in the synthesis of iron(III) coordination compounds with benzimidazole based ligands, with an aim to correlate some of their spectral properties with iron sites in native enzymes.

2. PREPARATION OF METAL COMPLEXES:-

(i) $[Fe(L)Cl_3].nH_2O$ (where L = SAMB, GAMB)

The ligand SAMB (580 mg, 0.002 mol) and GAMB 608 mg, 0.002 mol) were separately dissolved in methanol (25 ml). A solution of $FeCl_3.6H_2O$ (270 mg, 0.001 mol) in methanol (10 ml) was added to the respective ligand solution. The solution turned dark brown, and was stirred at room temperature. After 1 hour stirring, brown coloured precipitate separated out. The solution was left stirring for an additional 2 hours. The precipitate was centrifuged and washed with methanol. The product obtained was redissolved in DMF: MeOH mixture (2:1) and was kept in the refrigerator for a day when a brown coloured product was collected in each case and dried in vauum over P_2O_5.

(ii) $[Fe(L)_2(NO_3)_2]$ $(NO_3).nH_2O$ (where L = SAMB, GAMB)

The ligand SAMB (580 mg, 0.002 mol) and GAMB (608 ml, 0.002 mol) were separately dissolved in methanol

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(25 ml), $[Fe(NO_3)_3].9H_2O$ (424 mg, 0.001mol) was also taken in methanol (10 ml). Both the clear ligand solutions were mixed with iron(III) nitrate solution separately resulting in a brown coloured solution. Reaction mixture was stirred for about 8 hours. The volume was reduced on rotator evaporator, when a brown coloured product separated out. It was centrifuge and washed with methanol. The product obtained was redissolved in DMF:methanol mixture (2:1) and was kept in the refrigerator overnight, when a brown coloured product was obtained in each case, which was dried in vacuum over P_2O_5.

(iii) $[Fe(L)(HCOO)_3].nH_2O$ (where L = SAMB, GAMB)

The ligand SAMB (580 mg, 0.002 mol) and GAMB (608 mg, 0.002 mol) were separately dissolved in methanol (25 ml). $Fe(HCOO)_3$ (approx. 0.001 mol) was prepared in situ. and was added to the respective ligand solutions. The solution turned brown. It was then stirred at room temperature. After some time a dark brown coloured precipitate separated out in each case. It was centrifuged and washed with methanol. The product obtained was redissolved in DMF:methanol (2:1) mixture and was left in the refrigerator for a day. A dark brown coloured product was obtained. It was dried in vacuum over P_2O_5. Elemental analysis of all these iron(III) complexes is reported in Table-1.

Table-1: Microanalytical Data of Iron(III) Complexes

S. No.	Complex	% of Carbon Obsc. (Calcd.)	% of Hydrogen Obsc. (Calcd.)	% of Nitrogen Obsc. (Calcd.)	% of Iron Obsc. (Calcd.)
1.	$[Fe(SAMB)Cl_3].2H_2O$	44.13 (44.23)	4.36 (4.50)	11.37 (11.46)	11.35 (11.43)
2.	$[Fe(GAMB)Cl_3].2H_2O$	45.25 (45.38)	4.65 (4.77)	11.0 (11.14)	11.0 (11.11)
3.	$[Fe(SAMB)_2(NO_3)_2](NO_3).3H_2O$	49.22 (49.32)	4.67 (4.79)	17.47 (17.58)	6.26 (6.37)
4.	$[Fe(GAMB)_2(NO_3)_2](NO_3).3H_2O$	50.32 (50.45)	4.92 (5.08)	16.90 (17.03)	6.04 (6.17)
5.	$[Fe(SAMB)(HCOO)_3].2H_2O$	48.60 (48.75)	4.70 (4.83)	10.72 (10.83)	10.70 (10.80)
6.	$[Fe(GAMB)(HCOO)_3].2H_2O$	49.62 (49.73)	4.91 (5.08)	10.42 (10.54)	10.37 (10.52)

SAMB–($C_{18}H_{18}N_4$); GAMB– ($C_{19}H_{20}N_4$)

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3. RESULTS AND DISCUSSION:-

I. MOSSBAUER SPECTROSCOPY:-

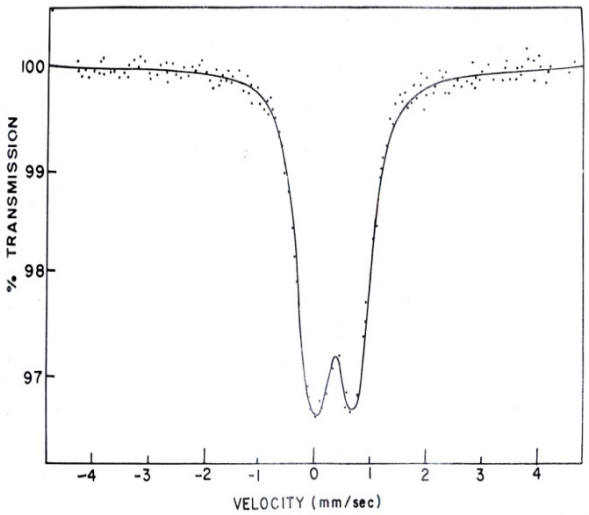

Fig.4.1(A): ^{57}Fe Mössbauer spectrum of $[Fe(GAMB)Cl_3]$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
GAMB = $C_{19}H_{20}N_4$

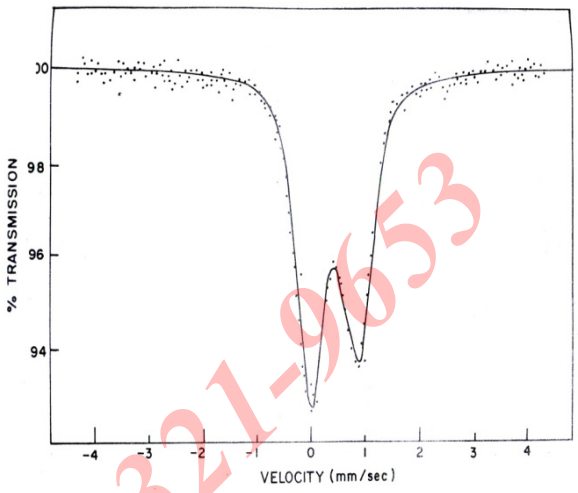

Fig.4.1(C): ^{57}Fe Mössbauer spectrum of $[Fe(GAMB)(HCOO)_3]$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
GAMB = $C_{19}H_{20}N_4$

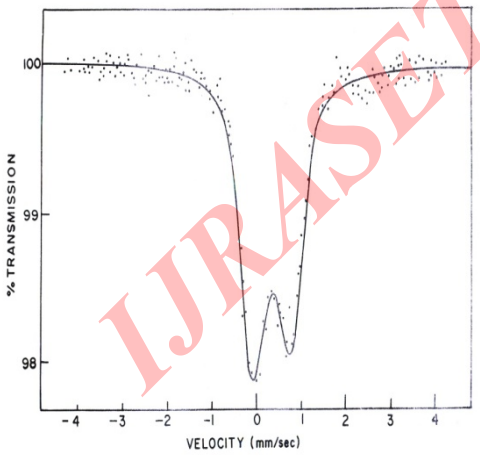

Fig.4.1(B): ^{57}Fe Mössbauer spectrum of $[Fe(GAMB)_2(NO_3)_2](NO_3)$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
GAMB = $C_{19}H_{20}N_4$

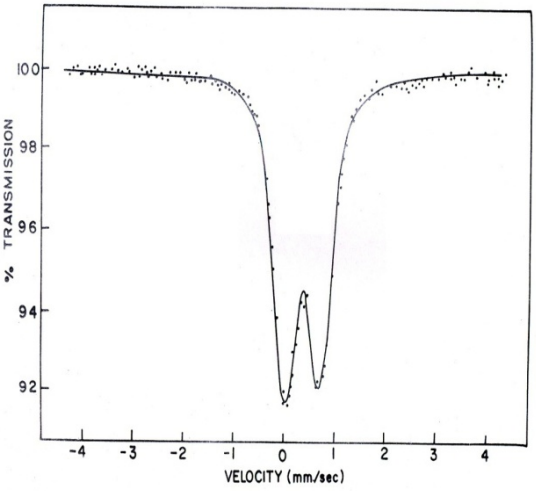

Fig.4.1(D): ^{57}Fe Mössbauer spectrum of $[Fe(SAMB)Cl_3]$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
SAMB = $C_{18}H_{18}N_4$

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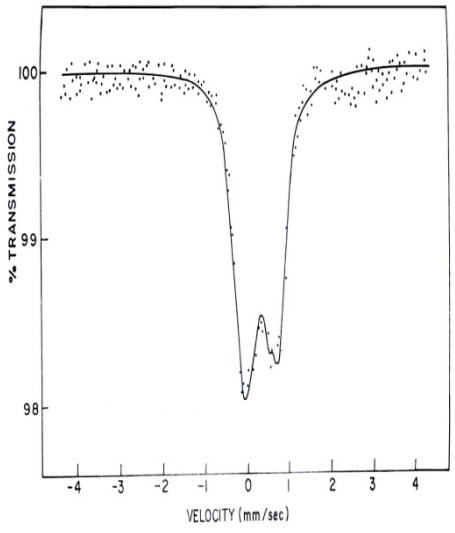

Fig.4.1(E): ^{57}Fe Mössbauer spectrum of $[Fe(SAMB)_2(NO_3)_2](NO_3)$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
SAMB = $C_{18}H_{18}N_4$

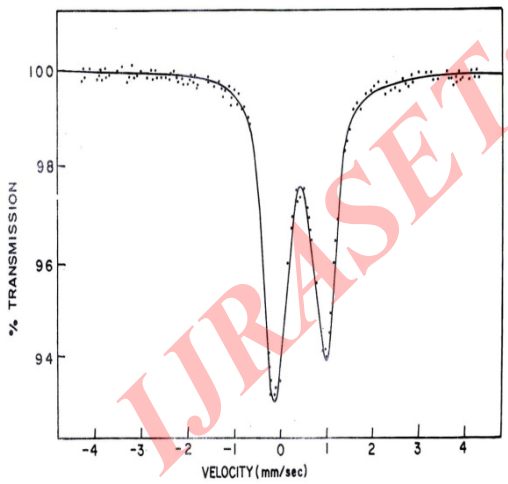

Fig.4.1(F): ^{57}Fe Mössbauer spectrum of $[Fe(SAMB)(HCOO)_3]$ complex at room temperature. The solid line represents computer fitting of the observed data (open circles) to a single doublet.
SAMB = $C_{18}H_{18}N_4$

Mossbauer spectra of all the Fe(III) complexes of the present series have been obtained by using Mossbauer source mounted on a constant acceleration spectrometer (Fig. 4.1:A–F). The velocity scale was calibrated by using a foil of natural α–Fe at room temperature, and all isomer shift measurements are referred to the centre of the α–Fe spectrum. Experimental spectra were fitted to a number lorentzian lines by using a least–squares computer program. Spectra were fitted with two lines which were allowed to vary independently. The values for isomer shift and quadrupole splitting were obtained by matching the lines into a doublet.

The values of isomer shift for all the complexes are consistent with the formulation of iron atom as high spin ferric ion and well within the range observed for related high spin ferric complexes.[18]

Several studies have attempted to establish electronic and structural relationships for a wide variety of five coordinate iron(III) compounds as a function of the two basic Mossbauer parameters, the isomer shift (δ) and the quadrupole splitting (ΔEQ).

The magnitude of the isomer shift depends on the total S–electron density at the resonant iron nucleus, which is related to the degree of covalency of the bonds. The increase in the s–electron density is attributed to increased π–back bonding from the iron atom to the ligand, that is compensated by a synergistic flow of σ density to the iron. The increase in the covalency is accompanied by an increase in the s–electron density on the central atom and some times by decrease in

d–electron density, both changes result in the increase in electron density at the metal nucleus. In iron compounds the isomer shift decreases with an increase in the electron density at the nucleus. The more covalent complexes have lower isomer shift. For the present series of Fe(III) complexes the values of isomer shift (δ) lie in the range of 0.32–0.44 nm s^{-1}, (Table -2) with respect to natural iron, typically observed for other high spin iron(III) complexes[19]. These values of isomer shift lies close to that of lactoferrin[20] (0.39 mm s^{-1}) and transferrin (0.38mm s^{-1}) proteins also. For the complexes where the iron(III) ligand bonding is more ionic an isomer shift of ca 0.5 mm s^{-1} with respect to iron metal is observed. Thus the lower values of isomer shift indicates substantial covalency for Fe(III) ligand bond in our iron(III) complexes.

The quadrupole splitting of the resonance lines arises from the electric field gradient at the nucleus, as a consequence of asymmetry in the electronic environment.

Table-2: Isomeric Shift (δ) and Quadrupole Splitting (ΔEQ) Data of Fe(III) Complexes

S.No.	Complex	Isomeric shift (δ) (mm/sec)	Quadrupole Splitting (ΔEQ) (mm/sec)
1.	$[Fe(SAMB)Cl_3]$	0.368	0.69
2.	$[Fe(SAMB)_2(NO_3)_2](NO_3)$	0.362	0.77
3.	$[Fe(SAMB)(HCOO)_3]$	0.436	0.85
4.	$[Fe(GAMB)Cl_3]$	0.358	0.65
5.	$[Fe(GAMB)_2(NO_3)_2](NO_3)$	0.328	0.73
6.	$[Fe(GAMB)(HCOO)_3]$	0.443	1.05

SAMB–($C_{18}H_{18}N_4$); GAMB– ($C_{19}H_{20}N_4$)

The most valuable information concerning bond properties, anisotropy, electron population of molecular orbitals and local structure may be extracted from the quadrupole splitting. Therefore, in principle, the ΔEQ values are useful for elucidating the geometry of the complexes and the values assist in examining the σ–donor and π–acceptor properties of the ligand. The quadrupole splitting decreases with increase in the symmetry of the central iron atom. In the present series of Fe(III) complexes the formate complexes shows quite a large value for the quadrupole splitting reflecting an unsymmetrical field around the ferric ion. Upon comparing the quadrupole splitting data for chloro, nitrato and format complexes, the following order is observed.

Chloro complexes <nitrato complexes < format complexes which suggests that format complexes are most distorted.

The values of quadrupole splitting are comparable to that of $Fe(L_1)_3.6H_2O$ (0.92 mm s^{-1}) where L_1 is nicotinylhydroxamic acid and Fe(EHGS)(1.60mms^{-1})where EHGS=N–2–((o–hydroxyphenyl)glycino)ethyl salicylidomimine. Similar values are obtained in the case of structurally characterized, rhombically distorted iron(III) complexes as well as in cases of some iron tyrosinate proteins.

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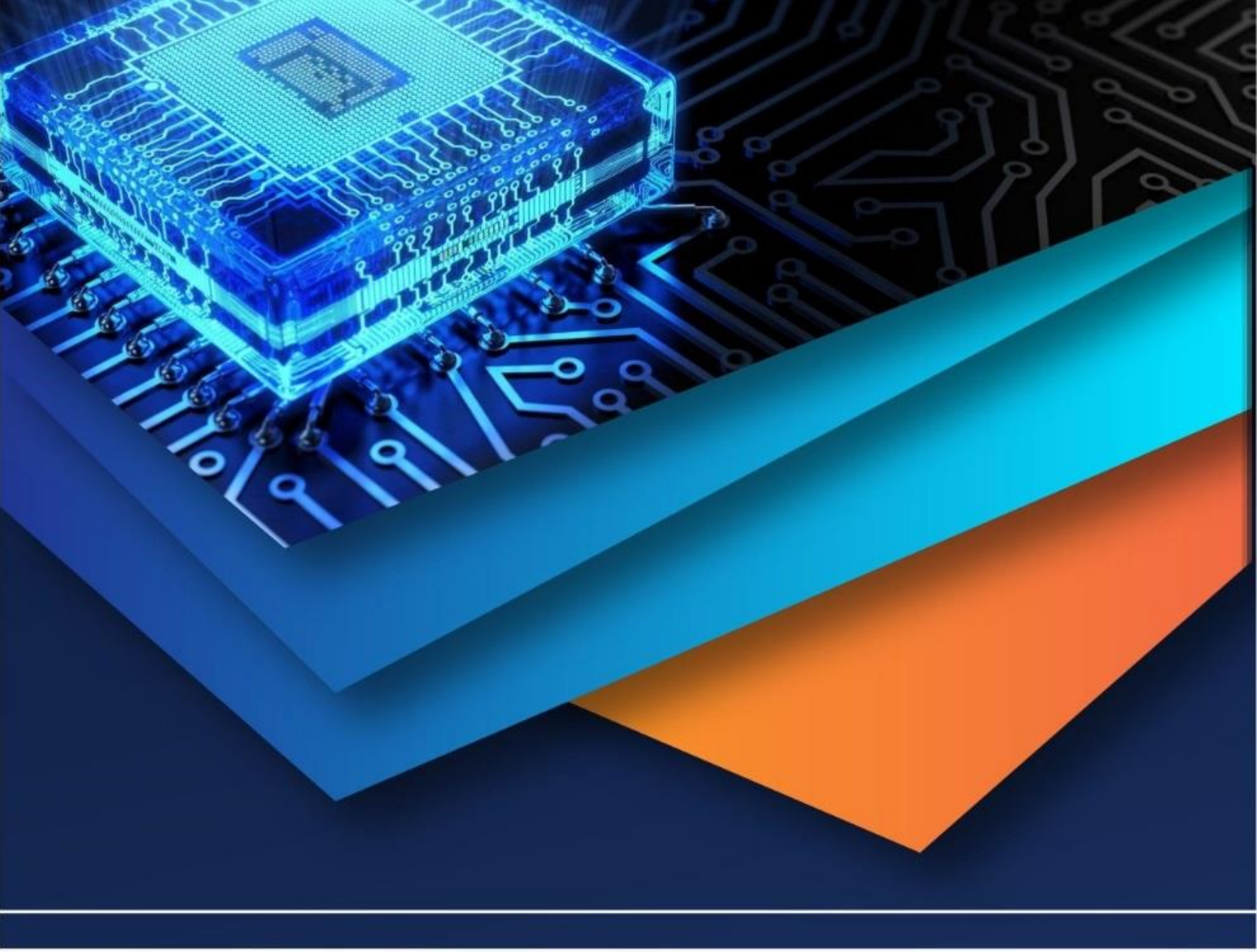

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