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Studies on Metallic Complexes of [(E)-4-{(1-(2-hydroxyphenyl)-ethylidine amino}- 1, 2, 4-triazolidine, 3, 5-dithione]

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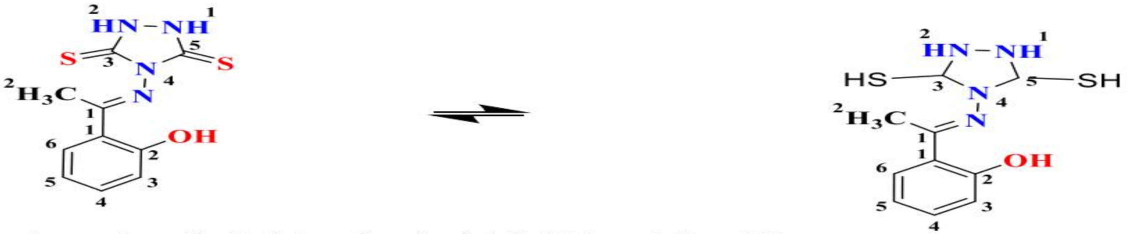
I. INTRODUCTION

Triazole Schiff bases play an important role as ligands in coordination chemistry1 and demonstrate substantial pharmacological and biological activities 2 . Specifically 1, 2, 4-triazole and its derivatives exhibit properties of antibacterial 3, antioxidant 4, anticonvulsant5, antifungal6, antiviral7, and antiinflammatory8 agents. Metal complexes of 1,2,4- triazole Schiff bases are used as biocides in controlling many harmful species of fungi that cause infectious diseases in plants and living organisms. Metals complexes of triazole derivatives are also used in stimulating plants growth9 . Based on the above, we pursued synthesis of substituted imino-1,2,4-triazole and its metal complexes.



(*E*)-4-((1-(2-hydroxyphenyl)ethylidene)amino)-1,2,4-triazolidine-3,5-dithione

Thione **Thiol**

(E) -4-{(1-(2-hydroxyphenyl)-ethylidine amino}-1,2,4-triazolidine,3,5-dithione is multidentate chelating ligand and can exist as thione, thiol tautomer's as shown below.

The ligand (LH2) containing mercapto group(>C=S) exists in thione tautomer in acidic medium(Ph≤6) but in basic medium it can get tautomerise to thiol form(>C-SH).The ligand has donor sites oxygen, nitrogen and sulphur as well and it is expected that it can form strong complexes with class 'a' and class' b' metals ions both. In present chapter I report the complexes of Cr(III),Fe(II),Iron(III),Mn(II),Ni(II),Cobalt(II),Zn(II) and Cd(II)

II. EXPERIMENT

A. Chromium (III) Complex [CrL(LH)]H2O

About 0.01 gram mole of hydrated chromium (III) chloride[Cr(H2O)4Cl2]Cl.H2O was dissolved in aqueous methanol and treated with 0.021 gram mole of ligand (LH2) dissolved in 30 ml hot methanol.

The mixed solution was refluxed on steam bath for half an hour by raising the pH of solution by adding a few drop triethylamine. The brownish yellow complex of chromium (III) separated gradually.

The product was cooled and filtered on small Buckner funnel and was washed several time with aqueous methanol. The complex was dried in a desiccator and product was analysed. The analytical result of complex is recorded in Table A.

B. Preparation of $[Fe(LH)_2]2H_2O$

About 0.01 gram mole of Mohr's salt $(NH_4)_2FeSO_4.7H_2O$ was dissolved in aqueous methanol and treated with 0.021 gram mole of ligand (LH_2) dissolved in 30 ml hot methanol. The mixed solution was refluxed on steam bath for half an hour by raising the pH of solution by adding a few drop triethylamine. The brownish yellow complex of Iron(II) separated gradually. The product was cooled and filtered on small Buckner funnel and was washed several time with aqueous methanol. The complex was dried in a desiccator and product was analysed. The analytical result of complex is recorded in Table A

C. [Mn(LH)2]2H2O

About 0.01 gram mole of hydrated Manganese (II) chloride [MnCl2].7H2O was dissolved in aqueous methanol and treated with 0.021 gram mole of ligand (LH2) dissolved in 30 ml hot methanol. The mixed solution was refluxed on steam bath for half an hour by raising the pH of solution by adding a few drop triethylamine. The dark brown precipitate of complex separated gradually. The product was cooled and filtered on small Buckner funnel and was washed several time with aqueous methanol. The complex was dried in a desiccator and product was analysed. The analytical result of complex is recorded in Table A

Table - A
Analytical Results And Colour Of The Complex

S. No.	**Complex**	**% Element: Found/ (Calc .)**						**μ_{eff} at 30-31^{0}C in B.M**
		Colour	**M**	**C**	H	**S**	**N**	
1	**$Cr(C_{10}H_9N_4OS_2)(C_{10}H_8N_4OS_2)$ H_2O**	**Grey Silver**	**8.6** **(7.5)**	**40.06** **(39.7)**	**2.8** **(2.4)**	**24.3** **(23.5)**	**18.6** **(17.8)**	**3.72**
2	**$[Mn(C_{10}H_9N_4OS_2)_2]2H_2O$**	**Grey**	**8.8** **(7.7)**	**38.64** **(37.5)**	**2.8** **(2.3)**	**20.6** **(19.8)**	**18.4** **(16.6)**	**5.91**
3	**$Fe(C_{10}H_9N_4OS_2)_2]$ $2H_2O$**	**Brown**	**9.0** **(8.1)**	**38.58** **(36.8)**	**2.8** **(2.4)**	**20.6** **(20.3)**	**18.0** **(17.9)**	**4.83**

Table — B
Solubility and Electrical Conductance Data (31o C)

Complex	**Qualitative value in solvents**				**Molar conductance value**	
	Water	**Methanol**	**Benzene**	**DMF**	**Ohm $^{-1}$mol^{-1} cm^2{DMF)**	
$[CrL(LH)_2]H_2O$	INS	SI S	SI S	FS	12	
$[Mn(LH)2]2H2O$	INS	SI S	SIS	FS	6	
$[Fe(LH)2]2H2O$	INS	SI S	INS	FS	8	

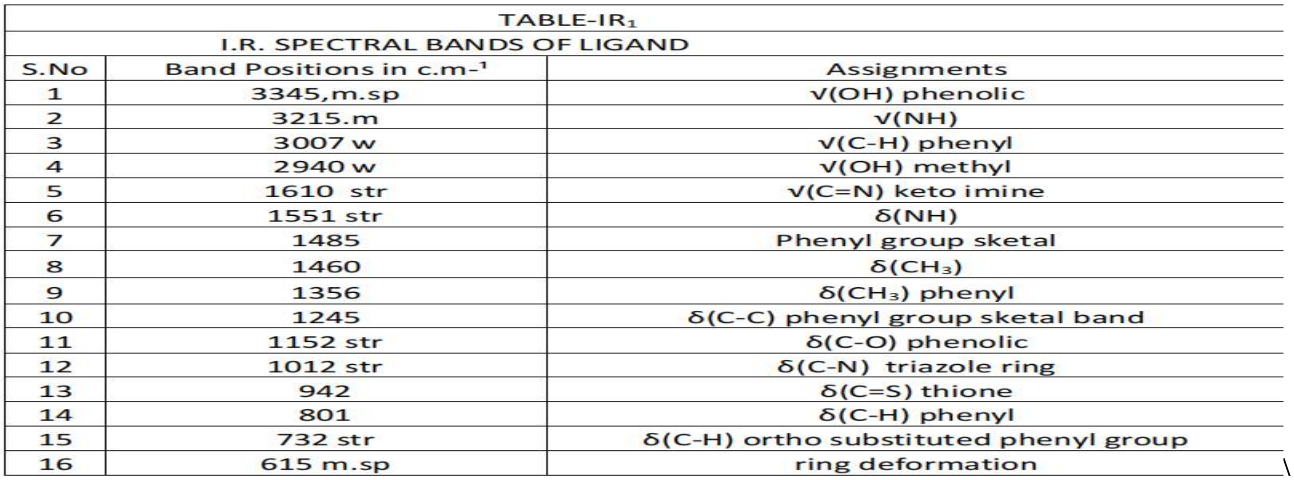


TABLE-IR$_1$		
I.R. SPECTRAL BANDS OF LIGAND		
S.No	Band Positions in c.m^{-1}	Assignments
1	3345,m.sp	ν(OH) phenolic
2	3215.m	ν(NH)
3	3007 w	ν(C-H) phenyl
4	2940 w	ν(OH) methyl
5	1610 str	ν(C=N) keto imine
6	1551 str	δ(NH)
7	1485	Phenyl group sketal
8	1460	δ(CH_3)
9	1356	δ(CH_3) phenyl
10	1245	δ(C-C) phenyl group sketal band
11	1152 str	δ(C-O) phenolic
12	1012 str	δ(C-N) triazole ring
13	942	δ(C=S) thione
14	801	δ(C-H) phenyl
15	732 str	δ(C-H) ortho substituted phenyl group
16	615 m.sp	ring deformation

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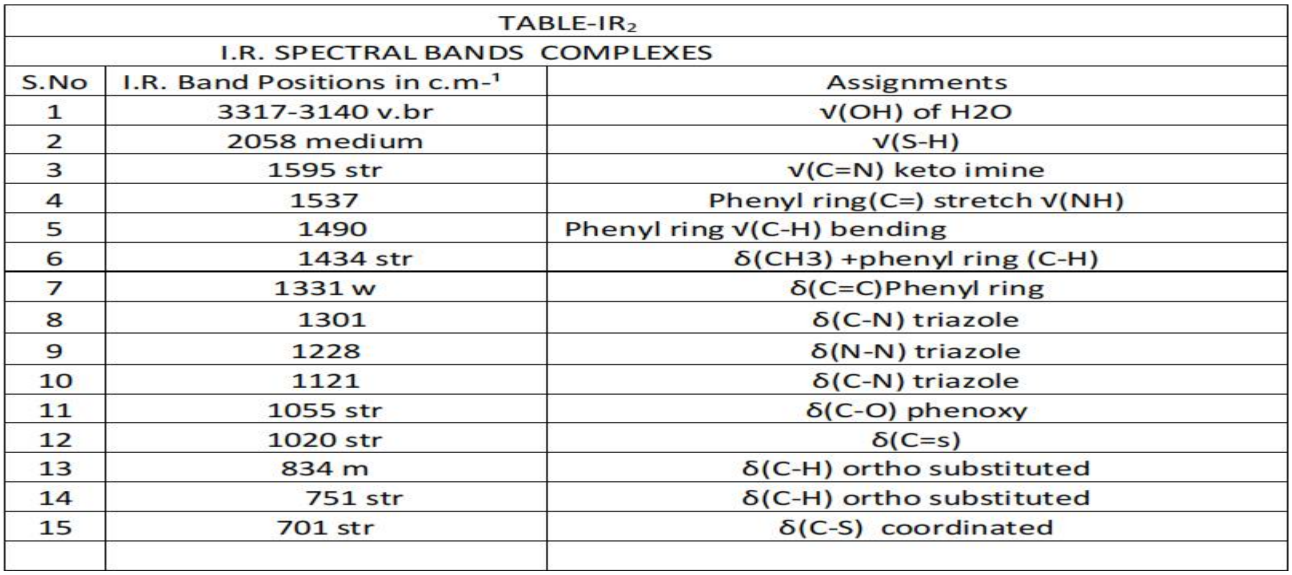


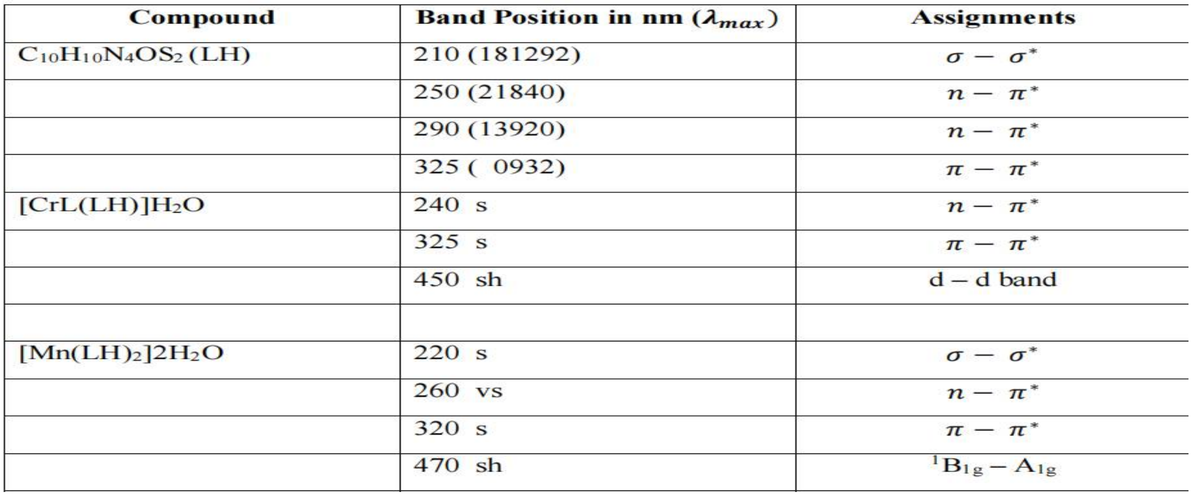
TABLE-IR_2

I.R. SPECTRAL BANDS COMPLEXES

S.No	I.R. Band Positions in c.m-¹	Assignments
1	3317-3140 v.br	ν(OH) of H2O
2	2058 medium	ν(S-H)
3	1595 str	ν(C=N) keto imine
4	1537	Phenyl ring(C=) stretch ν(NH)
5	1490	Phenyl ring ν(C-H) bending
6	1434 str	δ(CH3) +phenyl ring (C-H)
7	1331 w	δ(C=C)Phenyl ring
8	1301	δ(C-N) triazole
9	1228	δ(N-N) triazole
10	1121	δ(C-N) triazole
11	1055 str	δ(C-O) phenoxy
12	1020 str	δ(C=s)
13	834 m	δ(C-H) ortho substituted
14	751 str	δ(C-H) ortho substituted
15	701 str	δ(C-S) coordinated

Table — C

Electronic Absorption Band Positions Of Ligand And Their Compliexes



Compound	Band Position in nm (λ_{max})	Assignment
$C_{10}H_{10}N_4OS_2$ (LH)	210 (181292)	$\sigma - \sigma^*$
	250 (21840)	$n - \pi^*$
	290 (13920)	$n - \pi^*$
	325 (0932)	$\pi - \pi^*$
[CrL(LH)]H_2O	240 s	$n - \pi^*$
	325 s	$\pi - \pi^*$
	450 sh	d – d band
$[Mn(LH)_2]2H_2O$	220 s	$\sigma - \sigma^*$
	260 vs	$n - \pi^*$
	320 s	$\pi - \pi^*$
	470 sh	${}^1B_{1g} - A_{1g}$

III. RESULTS AND DISCUSSION

The donor molecule [(E) -4-{(1-(2-hydroxyphenyl)-ethylidine amino}-1,2,4-triazolidine,3,5-dithione]
[H2L] is multidentate N,O and S donor ligand and form bis chelated complex of composition
[CrL(LH2)]H2O, [Fe L(H2L)]H2O and [M(HL)2]2H2O.(M=Mn2+,CO2+,Fe2+,Cu2+,Ni2+ and Zn2+) solid state. The complexes are stable in air and dissolved partially in ethanol, methanol and acetone. These complexes are almost insoluble in water and dissolve appreciably in dimethylformamide and dimethylsulphoxide as well. The molar conductivity of complexes were determined qualitatively. The molar conductance value of the complexes in DMF show negligible electric conductance (in the range 12-20 Ohm –1mol–1 cm2 Table-A) suggesting that the complexes are non-ionic and inner complexes. The complexes are fairly stable in water but on heating in air they lose water molecule below 90-1000 c, indicating that H2O present in complexes are uncoordinated zone. The I.R spectra of complexes supports the presence of water molecule in complexes displaying very broad and strong I.R. band near 3340-3145c.m-1 . The magnetic susceptibility of complexes were determined at room temperature by Guoy method using Hg[CO(HCS)4] as standard. As expected Zn(II) complexes Zn(HL)2.2H2O having 3d10 electronic system is diamagnetic while others are paramagnetic. The chromium(III) complex [CrL(LH2).H2O] room temperature magnetic moment value 3.69 B.M, suggesting oxidation number +3 for chromium. The ions magnetic moments value of Cr(III) than spin orbit complexing effect μobs=μso(1-4λ). The λ value for Cr(III) is -329 c.m-1 which lower the magnetic value of Cr(III) complex than expected value for

spin contribution. The ground state energy term of Cr(III) is 4A2g which queenchs the orbital contribution also for magnetic moment of Co(II) is 5.10B.M. at 30-310 c which suggest octahedral geometry of complexes. The observed magnetic moment value 5.10 B.M corresponds to both spin and orbital contribution.

μL+S=

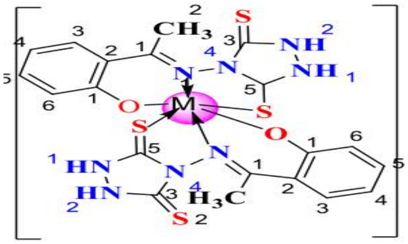
The magnetic moment value for manganese(II) complex [Mn(HL)2]2H2O has been found to be 5.91 B.M which supported oxidation state Mn 2+ (ground state term6S0).The magnetic moment value of Cu(II) complex 1.87 B,M and that of Ni(II) complex (3.41) at room temperature also occur in expected range of octahedral environment of ligand molecule donor atoms around metal ions.

A. I.R. of the Complex

The I.R. spectra of all most all complexes display a broad and strong band at 3320-3140 c.m-1 attributed to √(OH) frequency of water molecule present in complexes. A medium to weak broad band present in complexes located at 2058-2056 c.m-1 is tentatively assigned to √ (C-H) vibration of ligand located at 1615 c.m-1 is shifted to lower frequency by 15-22 c.m-1 and observed at 1595 c.m-1 in copper(II) complexes.

The (N-H) bending band of ligand molecule located at 1557 c.m-1 is slightly shifted to lower frequency in complexes and observed at 1537 c.m-1 . The phenyl ring skeletal vibration in complexes is observed near 1490 ±5 and 1331±5 c.m-1 . The (N-N),(C-N) and (C-C) stretching bands present in ligand is also retained in this complex, molecule and can be attributed to I.R. bands located at 1301,1228 and 1121 c.m-1 .The coordinated phenolic group √(C-O) vibration has been found to present at 1055 c.m-1

The thioamide √(C=S) stretch is observed at 1021 c.m-1 . The I.R. band located at 834 and 751 c.m-1 in Cu(II) complex. Cu(LH)22H2O has been assigned to out of plane bending (C-H) unit of ortho substituted phenyl group. The I.R. spectrum band at 701 c.m-1 is assigned to ring deformation vibration. The I.R. spectrum of complexes have been not been recorded in far I.R. region.(650-150) c.m-1 and therefore nothing can be said to regarding M-L (M-N,M-O or M-S) stretching bands.



(M=Cr^{3+} ,Fe^{3+})

B. Structure Of Complexes

Nickel(II) forms complexes of coordination number four, five and six. The four coordinated complexes are either tetrahedral with sp3 hybrid bonding or square planar with dsp2 bonding. The planar complexes are almost diamagnetic, but theoretically paramagnetic; planar complexes are also possible. 11

Tetrahedral Ni(II) complexes are paramagnetic and their room temperature magnetic moment values are usually higher than the spin only value, expected for two unpaired electrons (2.83 BM)12, however, In some cases lower magnetic moment values have been reported 13-14. The high magnetic moment values of complexes are due to orbital contribution and are the functions of temperature. It is well known that the high magnetic moment also depend upon the detail symmetry of the ligand field present, as well as on the delocalisation of electron In the ligand molecule15. Five coordinated complexes are either diamagnetic square pyramidal or paramagnetic trigonal bipyramidal with sp3 d hybridisation and their magnetic moment values are similar to four coordinated tetrahedral nickel(II) complexes.16-17 . Six coordinated octahedral complexes are always paramagnetic, but the possibility of diamagnetic complexes can not be rulled out. In an octahedral field, the lowest lying singlet state is 3A2g. It is separated from the two triply degenerate levels 3T2g and 3T1g by large energy intervals, that cages the nickel (II) ion to behave as if it is in a state for which the orbital contribution is negligible and therefore, the octahedral nickel(II) complexes display magnetic moment values allmost equal to 2.83x $(1 - 10\ 4\lambda\ Dq)$ i.e., about 10 % higher than the spin only value. In this case, the magnetic moment value is independent of temperature and symmetry of the ligand field. In most of the complexes, the room temperature magnetic moment values of the octahedral nickel(II) complexes are observed between 2.90 — 3.4 BM18. Besides regular tetrahedral, planar and octahedral complexes, a large number of nickel (II) complexes have been reported in which they exist in equilibrium with two different structural species the same crystal or sometimes as the mixture of two different geometrical isomer in the varying proportions. Thus, a large number of nickel(II) complexes display anomalous magnetic moment values.

Kilborn etal. reported anomalous magnetic moment value of [Ni(C10H9N4S2O)].2H2O and concluded that the lower magnetic moment value is due to the presence of both planar and tetrahedral species in equal proportions. A large number of nickel(II) complexes displyiag magnetic moment values between 0.5 —2.8 BM have been reported 20-27 in which the lower μeff values of the complexes; have been attributed to the presence of tetrahedral, trigonal Bipyramidal or octahedral species in square planar nickel(I1) complexes28-29 . Dave etal. have also reported a number of nickel(II) complexes with C10H10N4OS2(LH) displaying anomalous magnetic moment values (3.00 - 3.41 BM) for complexes[Ni(C10H9N4S2O)].2H2O suggested that the solid complexes are equilibrium mixture of planar and tetrahedral species. They have also suggested that the lowering of the magnetic moment values in nickel (II) complexes is due to a partial population of a spin triplet state close to the idealised ground state 1A13 for D4 symmetry.

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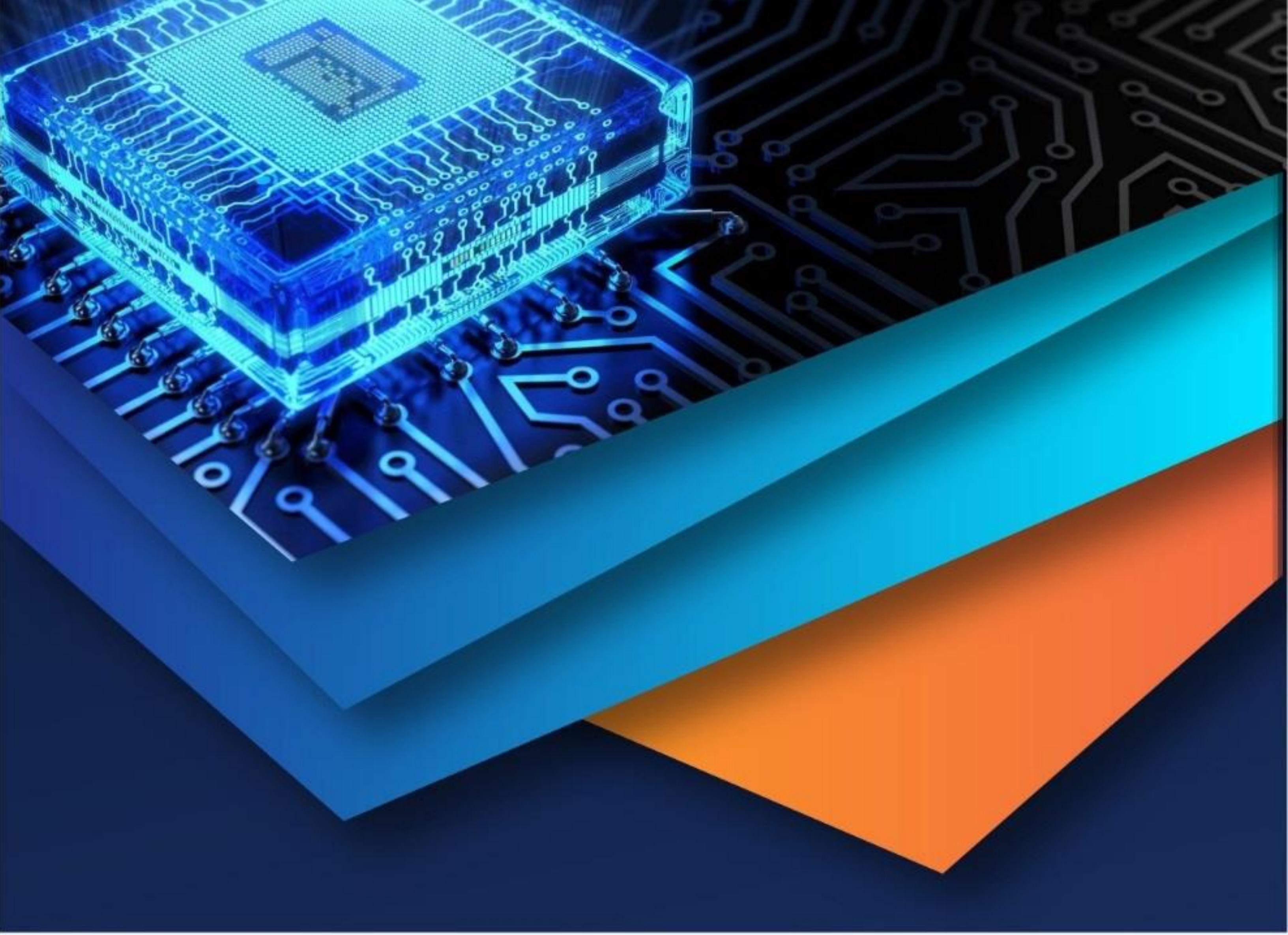

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