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A Review on Some Trinuclear Copper Complexes

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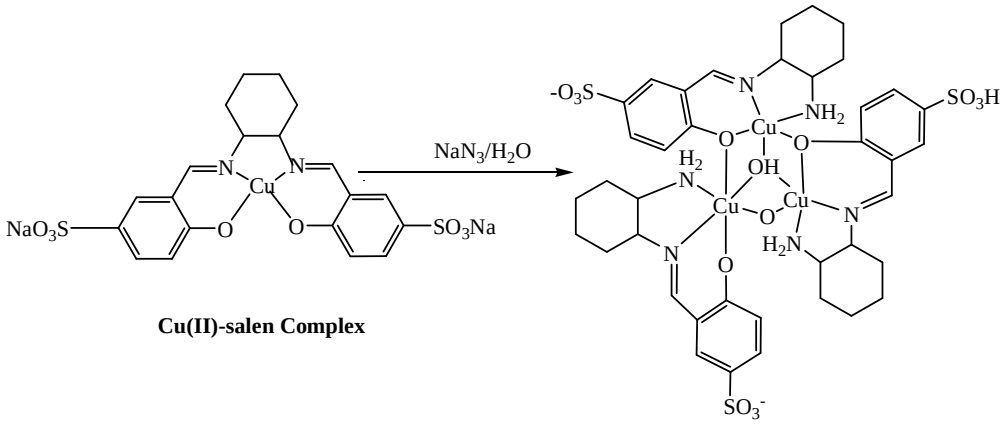
Abstract: This article describes synthesis, characterization and properties of some trinucler copper complexes.

I. INTRODUCTION

In the last two decades, much attention has been paid to supramolecular coordination chemistry because of the potential applications in catalysis,[1] small molecule capture or separation,[2] photoluminescence,[3] imaging,[4] biology,[5] and electronics.[6] In exploring the novel materials with demanding functional aspects, the self-assembly process for the formation of trinuclear metal complexes becomes crucial. In this context, trinuclear copper(II) complexes are the essential functional units in a number of multicopper blue oxidases,[7] such as laccase and ascorbate oxidases. These enzymes catalyze the four-electron reduction of dioxygen to water with concomitant one-electron oxidation of various substrates such as ascorbate, polyphenols and aromatic polyamines.[8] So, the preparation of low molecular weight trinuclear copper(II) complexes having a triangular arrangement of copper(II) ions are important towards the investigation of these complexes for mimicking the behaviour of natural products. Different trinuclear copper(II) complexes with or without [$Cu_3(\mu_3$-OH)] core are reported in the literature.[9-11] Additionally, there is an increasing interest in studying the cyclic trinuclear copper(II) complexes because they can be geometrically frustrated systems which offer the opportunity to examine magnetic exchange models such as spin frustration, spin delocalization, or antisymmetric exchange.[12-14]

II. RESULTS AND DISCUSSION

Zhang and co-workers[15] have reported a μ_3-hydroxo trinuclear copper(II) complex, $[Cu_3(\mu_3\text{-OH})(L^{2a})_2(HL^{2a})]\cdot 5H_2O\cdot EtOH$ (**1**) [$(HL^{2a})^-$ = *N*-(5-sulfonatosalicylidene)-1,2-diaminocyclohexane] with core structure closely resembling the central moiety in multicopper oxidase. They have observed that during the study of a copper(II)-salen complex of *N*,*N*-bis(5-sulfonatosalicylidene)-1,2-diaminocyclohexane $(H_2L^{1a})^{2-}$ catalyzing the three-component (sodium azide, epoxide and non-activated terminal alkyne) 1,3-Huisgen cycloaddition recations, the trinuclear copper(II) cluster 1 is produced. The formation of this μ_3-OH bridged trinuclear copper(II) cluster from copper(II)-salen complex is shown in Fig.1.



Cu(II)-salen Complex

Fig.1 Formation of $[Cu_3(\mu_3\text{-OH})(L^{1a})_2(HL^{1a})]\cdot 5H_2O\cdot EtOH$ (1) from copper(II)- salen complex.

Gautier-Luneau et. al.[16] have reported a trinuclear copper(II) complex, $Na_3[Cu_3(mal)_3(H_2O)]\cdot 8H_2O$ (**2**) which is isolated by evaporating an aqueous solution containing $Cu(OAc)_2\cdot H_2O$, malic acid ($HO_2CCH_2CHOHCO_2H$) and NaOH (Fig. 2). Single crystal X-ray structure analysis of complex **2** discloses that three copper centers are connected by alkoxo bridges and form an almost isosceles triangle with Cu---Cu separations of 3.076(1), 3.504(1) and 3.513(1) Å. The overall low temperature magnetic behaviour corresponds to an antiferromagnetically coupled triangular system. The EPR spectrum (g = 2; 10.18 T) is characteristic of a spin state $S = {}^1/_2$ with a rhombic anisotropy of [g] which indicates that the electronic spin density is delocalised on three copper atoms.

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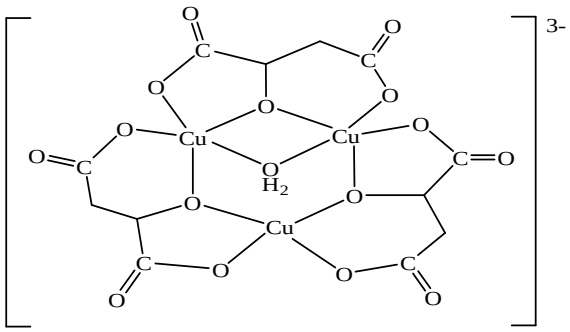


Fig. 2 Structure of $Na_3[Cu_3(mal)_3(H_2O)]\cdot 8H_2O$ (2).

A trinuclear copper(II) complex, $[Cu_3(L^{3a})Cl_6]$ (**3**) (Fig.3) comprising a terpyridine ligand (**L^{3a}**) functionalized with bis(2-pyridylmethyl)amine has been designed and synthesized by Vilar

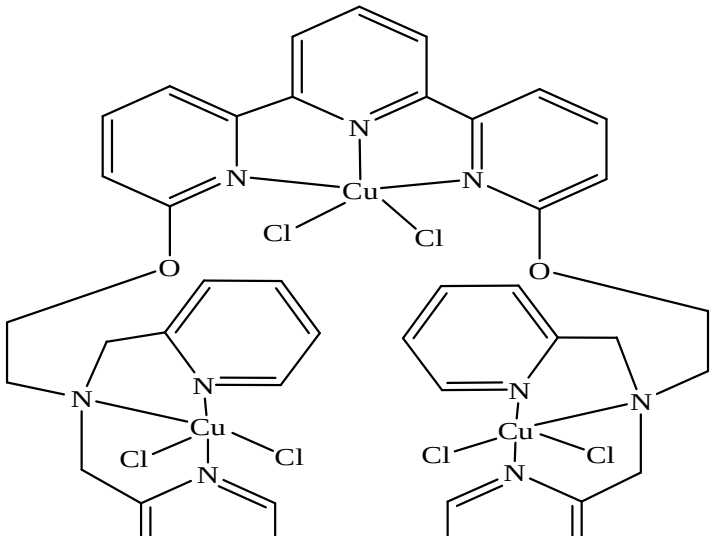


Fig. 3 Structure of $[Cu_3(L^{3a})Cl_6]$ (3).

and co-workers[17] as DNA nucleases and cytotoxic agents. Complex 3 shows its DNA cleavage activity in absence of any external coreductant. This complex exhibits high cytotoxicity against a wide panel of cell lines (tumoral U2OS, SH-SY5Y, cisplatin-resistant MOLT-4, and normal HEK 293T and GM05757) without tumor selectivity. The presence of this complex in both the cytoplasm and the nucleus is evaluated by cellular uptake studies. Immunoblotting analysis and DNA-flow cytometric studies establish the ability of complex 3 to induce cellular DNA damage, confirming the link between *in vitro* DNA cleavage ability and cellular toxicity.

Wu and co-workers[18] have reported a new family of trinuclear copper(II) complexes with $[Cu_3L^{4a}]$ motif synthesized in situ by using a polydentate ligand, *N′*^{2},*N′*$^{2'}$-bis(2-hydroxybenzoyl)biphenyl-2,2′-dicarbohydrazide (H_6L^{4a}) (Fig.4) in the presence of hexamethylenetetramine (hmta), morpholine (Hmor) and pyridine (py). They have successfully isolated five different assemblies, $[Cu_3L^{4a}(DMF)_{2.5}(hmta)]\cdot 3H_2O$ (4), $[Cu_3L^{4a}(DMA)(H_2O)(Hmor)]$ (5), $[Cu_3L^{4a}(py)_2]\cdot DMF$ (6), $[Cu_3L^{4a}(DMF)(H_2O)]\cdot 2DMF$ (7) and $[Cu_3L^{4a}(DMA)(H_2O)]\cdot 0.5DMA$ (8) in which the $[Cu_3L^{4a}]$ units are connected with each other to form one-dimensional chains *via* bridging of *N*-containing exogenous ligands or sharing an oxygen atom of $(L^{4a})^{6-}$. Thermo gravimetric and magnetic measurements are carried out for complexes 6 and 8. Low temperature magnetic susceptibility measurements indicate the antiferromagnetic properties of both complexes 6 and 8.

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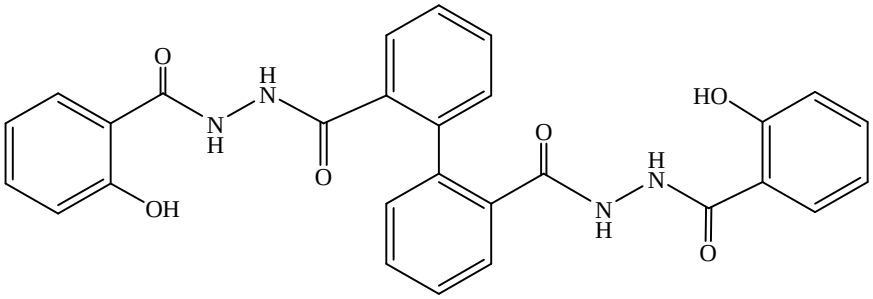
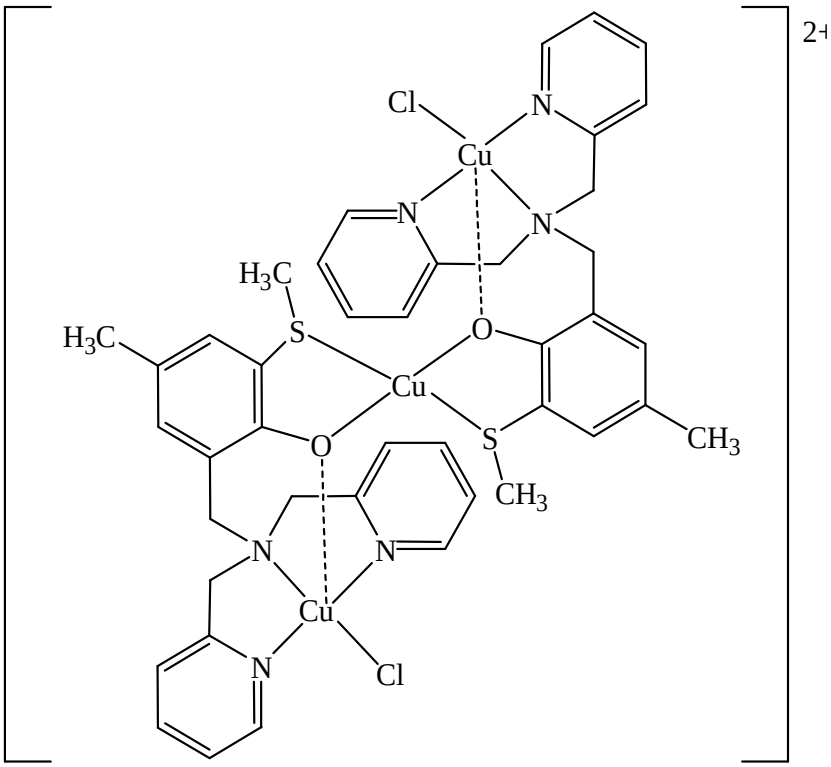


Fig. 4 Structure of the ligand H_6L^{4a}.

A multidentate ligand 2-[(bis(2-pyridylmethyl)amino)methyl]-4-methyl-6-(methylthio)phenol (HL^{5a}) is used to synthesize a trinuclear copper(II) complex, $\{[CuL^{5a}Cl]_2Cu\}(PF_6)_2\cdot H_2O$ (9) by Manzur *et. al.*[19] As shown in Fig.5, two of the monometallic units are coordinated to the central copper(II) ion by means of the sulphur from the -SCH_3 group and a bridging phenoxo oxygen atom of $(L^{5a})^-$ ligand. Density functional calculation for complex 9 indicates a ferromagnetic exchange between first neighbour interaction with *J* value of +11.7



cm^{-1}. Furthermore, an antiferromagnetic exchange for **9** has been observed for the second neighbour interaction with *J* value of -0.05 cm^{-1}.

wo hydroxo-bridged trinuclear copper(II) complexes, $[Cu_3(\mu_3\text{-}OH)(L^{6a})_3](ClO_4)_2\cdot 1.5H_2O$ (10) and $[Cu_3(\mu_3\text{-}OH)(L^{7a})_3](ClO_4)_2\cdot 0.5H_2O$ (11) (Fig. 6) with partial cubane (Cu_3O_4) core, where HL^{6a} = 2-[(2-Dimethylamino-ethylimino)-methyl]-phenol and HL^{7a} = 4-(2-Dimethylamino-ethylimino)-pentan-2-one have been reported in the literature by Bian *et. al.*[20] The X-ray crystal structure analyses reveal that both the two complexes comprise three

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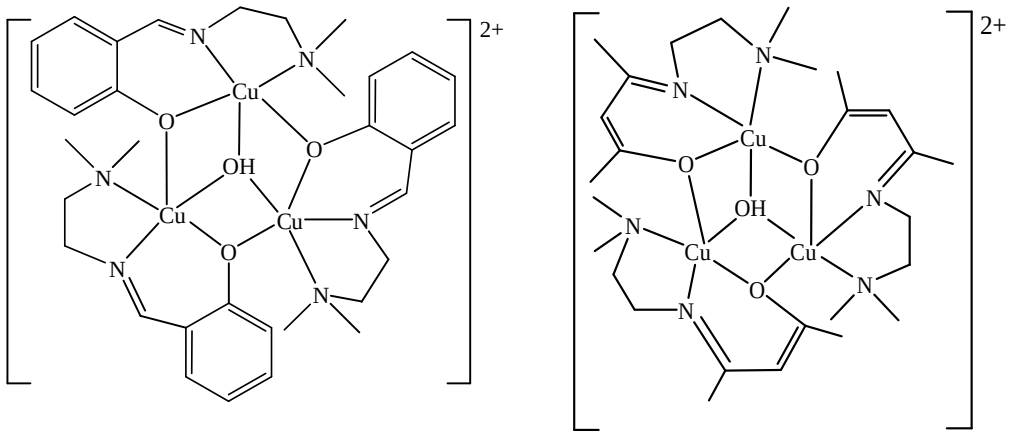


Fig. 6 Structures of $[Cu_3(\mu_3\text{-}OH)(L^{6a})_3](ClO_4)_2\cdot 1.5H_2O$ (10) and $[Cu_3(\mu_3\text{-}OH)(L^{7a})_3](ClO_4)_2\cdot 0.5H_2O$ (11).

$[Cu(L^{6a})]$ or $[Cu(L^{7a})]$ subunits, respectively, which are interconnected through two types of oxygen bridges provided by the oxygen atoms of the ligands and the central μ_3-OH group. As indicated by low temperature magnetic susceptibility data, complex **10** shows antiferromagnetic interactions among the copper centers with J = -2.40 cm^{-1} and g = 2.038, while complex **11** displays ferromagnetic interactions among the copper centers with J = +7.83 cm^{-1} and g = 2.02.

Xing and co-workers[21] have synthesized a new copper(II) complex of formula $Na_2[Cu_3(L^{8a})_4]\cdot 2H_2O\cdot 2CH_3OH$ (12) (H_2L^{8a} = 5-phenyl pyrazole-3-carboxylic acid) (Fig. 7) and characterized by single crystal X-ray crystallography. Crystal structure analysis of 12 indicates that this complex is a trinuclear species consisting of one anionic cluster and two sodium ions. Within the anionic cluster, two types of coordination modes are observed around the copper centers: the central copper is coordinated to four nitrogen atoms of four $(L^{8a})^{2-}$ ligands yielding a distorted tetrahedral (CuN_4) geometry, while each of the two terminal coppers is coordinated to two oxygen and two nitrogen atoms of $(L^{8a})^{2-}$ forming a slightly distorted square planar (CuN_2O_2) geometry. Copper and sodium atoms are connected by bridging carboxylate of the ligand, whereas copper atoms are connected with each other by pyrazole nitrogens of the ligands. Additionally, a three-dimensional network is also formed through linking among the copper and sodium atoms by carboxylate oxygens.

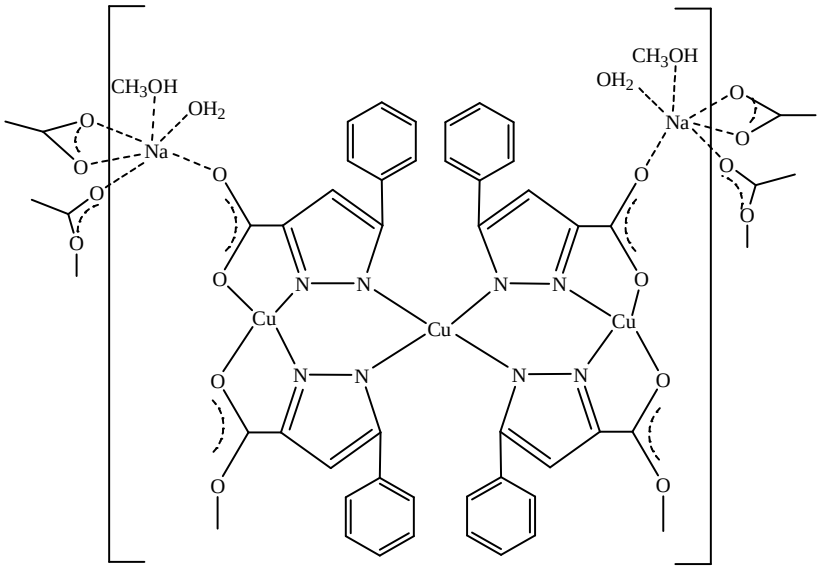


Fig. 7 Structure of $Na_2[Cu_3(L^{8a})_4]\cdot 2H_2O\cdot 2CH_3OH$ (12).

Recently, Plass and co-workers[22] have reported the synthesis, crystal structure and magnetic property of a trinuclear copper(II) complex, $[Cu_3(L^{9a})(bpy)_3](ClO_4)\cdot 3DMF$ (13), where H_5L^{9a} = tris(2-hydroxybenzylidene) triaminoguanidine and bpy = 2,2′-bipyridine. The synthetic scheme of complex 13 is presented in Fig. 8. The X-ray crystal structure shows that the complex cation

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looks like a hemisphere, with the equatorial coordination planes of copper centers nearly coplanar to the ligand backbone at a dihedral angle of 14° between the planes. The solid state supramolecular structure is basically governed by two distinct motifs of π-π interactions. The temperature dependence magnetic susceptibility measurements show that the triaminoguanidine ligand mediates very strong antiferromagnetic interactions among the copper centers with *J* value of -324 cm^{-1}.

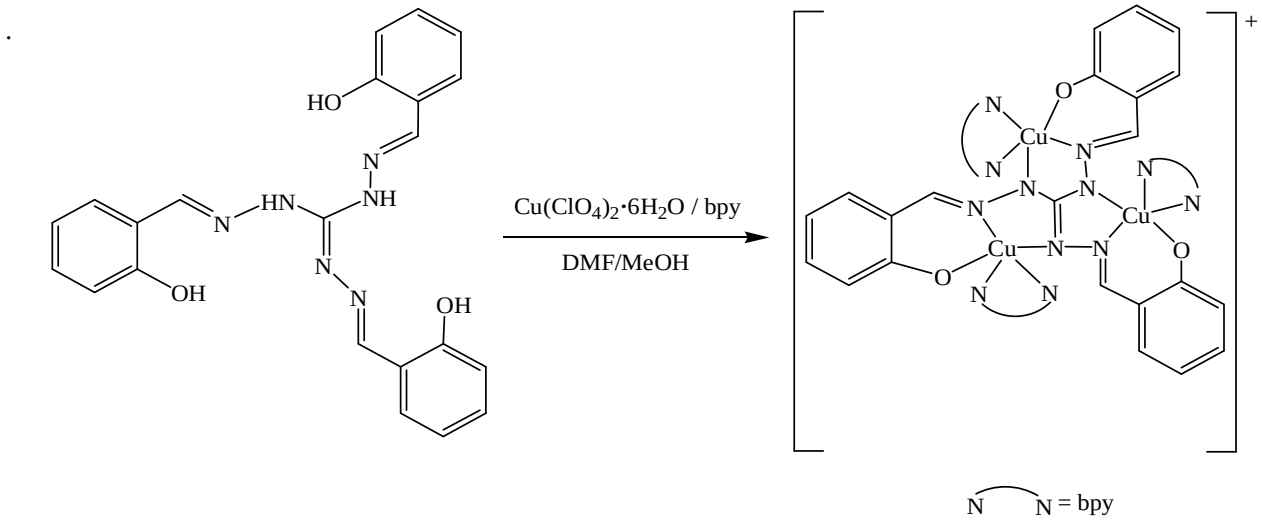


Fig. 8 Synthetic scheme of $[Cu_3(L^{9a})(bpy)_3](ClO_4)\cdot 3DMF$ (13).

In 2004, Chakravarty and co-workers[23] have reported a new angular trinuclear copper(II) complex, $[Cu_3L^{10a}L^{11a}(1\text{-MeIm})(H_2O)](ClO_4)$ (14) (Fig. 9) as a model for the active site of multicopper oxidases, where H_3L^{10a} and H_2L^{11a} are penta- and tetradentate Schiff base ligands. This complex is prepared as a perchlorate salt from a reaction of $[CuL^{11a}]$ and $[Cu_2L^{10a}(\mu\text{-Br})]$ in the presence of 1-methylimidazole (1-MeIm). The Cu---Cu distance of ~3.3 Å in the angular unit is 0.4 Å shorter than those found in the active site of oxidized form of ascorbate oxidase. Low temperature magnetic susceptibility data for **14** in the temperature range of 300-18 K show an overall antiferromagnetic behaviour of the complex. For this Cu_3 complex, the magnetic moment values of 3.07 and 2.18 μ_B at 300 and 18 K, respectively, are observed. This complex is also modelled structurally for the trinuclear active site of blue copper oxidases.

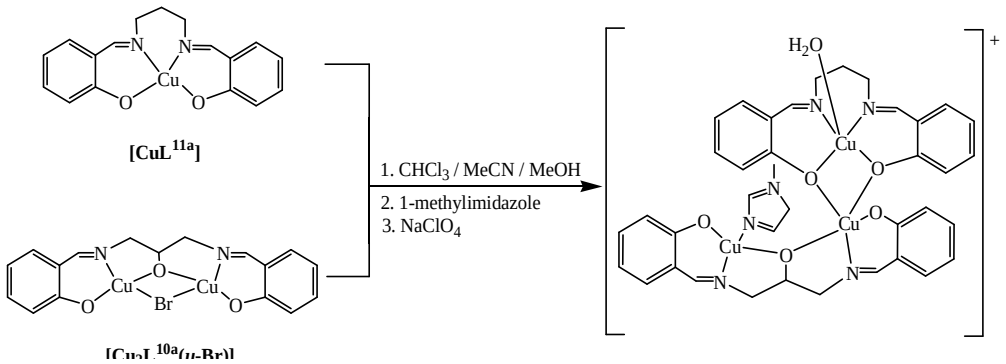


Fig. 9 Synthetic route of $[Cu_3L^{10a}L^{11a}(1\text{-MeIm})(H_2O)](ClO_4)$ (14).

III. CONCLUSIONS

Multi-copper complexes have become a promising class of coordination compounds in which variation of the metal salts, ligands, counter ions or experimental conditions lead to a variety of structural motifs. The in-depth study on *in vitro* models of quantitative assay for developing target specific drug design based on structure-activity relationship has also become a prevalent theme in the biological processes. The findings of the current study will contribute towards designing the new polynuclear transition metal complexes as potential binding agents to different biological macromolecules and subsequent metal-based pharmaceuticals.

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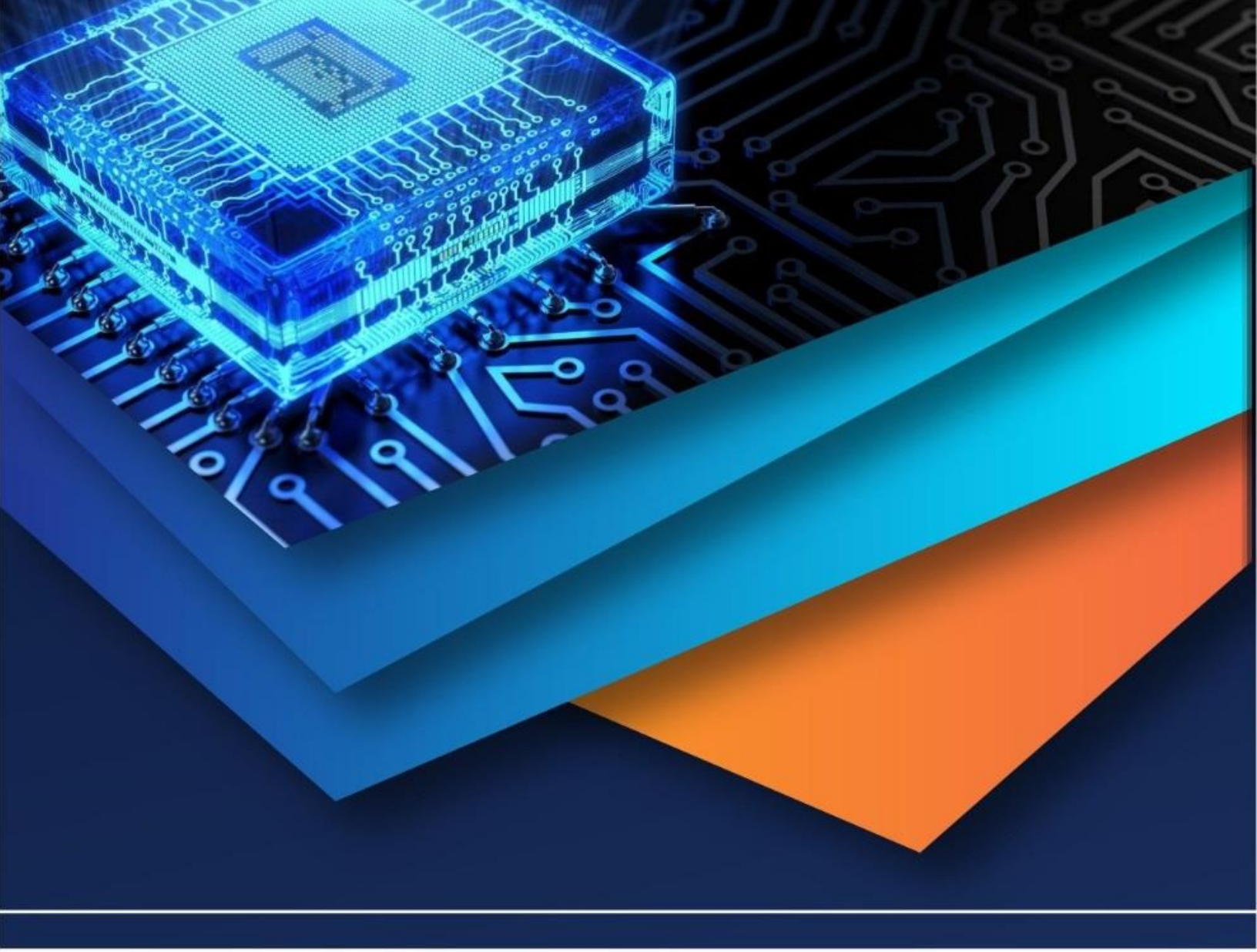
IV. ACKNOWLEDGEMENTS

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