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REVIEW

Synergetic and Cooperative Effects in Multimetallic Macrocyclic Complexes for Biological, Catalytic and Magnetic Activity

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The advancement of direct synthetic approaches toward the controllable synthesis of multimetallic complexes turns into an earlier and significant undertaking before the inside and out investigations of novel properties and functions of multimetallic complexes. As an elective methodologies for the synthesis of multimetallic complexes have incorporated the utilization of large macrocycles with more than one binding site and furthermore the connecting of macrocycles through interfacing units. This review highlights the arising patterns in the synthesis and uses of multimetallic macrocyclic complexes, including bi- and tri-metallic gatherings just as bigger obvious metal clusters and polymeric species.

Keywords: Multimetallic complexes, Robson macrocycles, Antimicrobial activity, Single molecule magnetic behaviour, Catalysis.

INTRODUCTION

Researchers have always been inspired by nature to mimic natural phenomenon to understand how they work and to construct extremely complex biosystems from simple precursors [1]. The idea of multimetallic has also come from nature that provides a broad scope of metalloenzymes having more than one metal moiety. To accomplish efficient catalytic activity metal moieties interact in a cooperative fashion in these metalloenzymes [2]. For instance, to catalyze the transformation of urea to carbon dioxide and ammonia two nickel(II) centres interact in a cooperative fashion in natural metalloenzymes urease (Fig. 1) [3]. Moreover, another natural catalyst anaerobic carbon monoxide dehydrogenase can drive reversibly the change of CO_2 into CO [4]. The main component of [NiFe]-carbon monoxide dehydrogenase in anaerobic microscopic organisms is the supposed C-group, where [3Fe-4S]-cluster is bound to a Ni-Fe constituent (Fig. 2). Ni^{2+} possesses officially the 4th corner of an ordinary [4Fe-4S]-group, while a pendant Fe moiety is in the nearness and exclusively attached to the [3Fe-4S]-cluster by a bridging sulfide ligand. Tetrahedral coordination circle of the pendant Fe is occupied by cystein and histidine ligands. Incorporating more than one metal unit into a similar covalent system prompts extraordinary expected advantages, particularly assuming the functions of the various metals are interdependent [5]. Design and synthesis of multimetallic complexes with multimetal centers has become a fascinating area of contemporary research in the field of inorganic and bioinorganic chemistry [6,7]. The reason for synthesizing the multimetallic complexes are multifarious but most important is their application in activating substrates arising from complementary property and synergistic reactivity of differing metal atoms. The interest lies on possible applications of these complexes in numerous fields like heterogeneous catalysis [8], molecular devices [9], magnetic switches [10] and their ability to exhibit metallic and superconducting behaviour [11]. Due to these reasons, the synthesis of multimetallic complexes has become an important branch in synthetic coordination chemistry. Rather than monometallic framework (Fig. 3a), multimetallic frameworks should be contained something like three chemical moieties to show cooperativity. The substrate gets initiated by coordinated or successive action of two successful moieties in a cooperative chemical reaction. The active functional moieties might possibly be fundamental for a comparative molecule. Cooperativity in multimetallic frameworks can be assumed to happen when the mutual effect arising from the coordinated

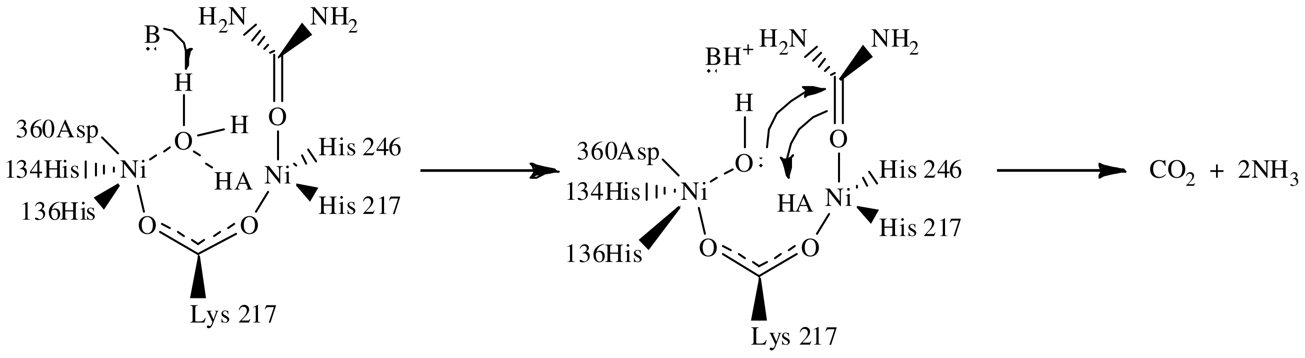

Fig. 1. Conversion of urea to CO_2 and NH_3 by urease enzyme

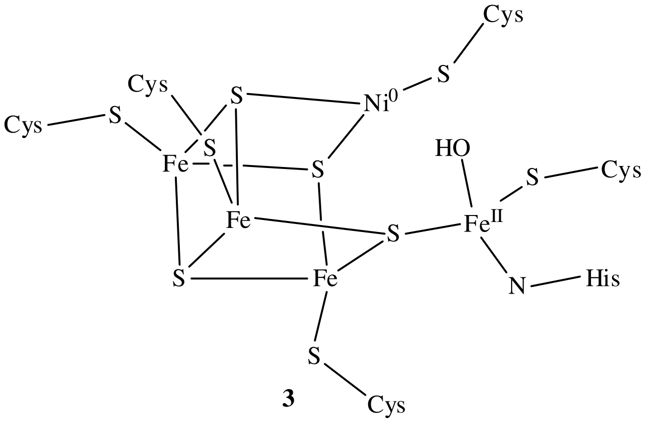

Fig. 2. Enzymatic centers of carbon monoxide dehydrogenase in reduced form

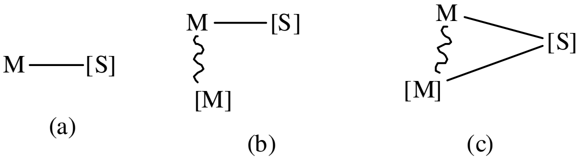

Fig. 3. Various collaborations lead to cooperativity in multimetallic frameworks

effort of the substrate with the multimetallic structure is more prominent than the joined particular effects of their relating mononuclear complexes. This cooperative effect of multimetallic centers is significant for high catalytic activities [12-17]. Both electronic and ligand impacts might be answerable for the noticed explicit reactivity of multimetallic complexes. The subsequent metal can either interface straight forwardly with the substrate (C) or just with the other metal moiety (B), for instance through electronic correspondence or adjustment of intermediates. Restricting of the substrate to one metal impacts the communication of this metal to the next metal moiety. On the other hand, the subsequent metal can likewise be considered a ligand on the primary metal, which impacts the stereoelectronic collaborations of the main metal with the substrate in contrast with the mononuclear complex. A more delicate case emerges when the substrate ties at least two metal centers simultaneously (Fig. 3c). In this specific interaction the overall investment of ligand *versus* electronic impacts relies upon the idea of the singular framework [18].

Synthetic approaches towards multimetallic complexes: Multimetallic complexes give a variety of fascinating designs, remarkable properties and functions [19-23]. Synergistic and agreeable associations among the metal ions collected in the confined little space of the multimetallic frameworks are answerable for such advanced functions [24]. In any case, there is an issue to segregate the multimetal complexes in exceptional returns particularly on account of metal group buildings containing at least three metal ions. To defeat this issue new methodologies and techniques have produced for the agreeable high return synthesis of the multimetallic complexes dependent on a supramolecular approach in a helpful manner [25]. Macrocyclic ligands have been widely adjusted to perceive single metal particles with more selectiveness and great liking dependent on the size match rule. The subsequent metal macrocycle complexes play a major aspect in imitating the role of regular metal ion carriers and understanding and replicating the reactant movement of metalloenzymes. On account of the known macrocyclic impact, macrocyclic ligands show an improved active and thermodynamic stability in correlation with their open chain analogs. By goodness of such extraordinary coordination properties of macrocyclic ligands, it is normal that bigger macrocycles with various coordination destinations could go about as an external platform to coordinate the arrangement of multiatom species inside, for example, multimetallic clusters. Accordingly, the use of polydentate macrocyclic ligands might give an advantageous instrument to acquire multimetallic groups in a reproducible manner [26].

Previously, multimetallic complexes were frequently synthesized by the experimentation technique for mixing metal ions in with organic ligands, bringing about erratic mixtures. However, presently, there are two current methodologies used to synthesize multimetallic complexes. The first is utilization of macrocycle forerunners to frame discrete group complexes in a one-pot technique. The subsequent macrocycle encased an array inside its pit, prompting some size particularity and primary controller. By this technique just buildings, which are size viable with the macrocycle are created. This technique forestalls the development of exceptionally large clusters. These complexes are for the most part steady, held together by chelation from the macrocycle. Though this methodology can be specific, bothersome results, for example, multimetallic macrocycle buildings of different bulks or non-macrocyclic array are regularly acquired. One more way to deal with synthesis of multimetallic buildings is the utilization of preformed macrocycles as formats. This methodology is more significant on the grounds that the products are in all actuality unsurprising, reproducible and stable to additional ligand replacement and their functions (for example solvency) can be altered by changing the fringe substituents of the macrocyclic ligand while keeping the center multimetallic cluster flawless. Hence, the utilization of macrocycles to develop multi-metallic complexes provides potential for reproducing the construction, properties and function of the buildings, opening up new freedoms for essential examinations and uses [27]. Then again, metal-organic structures give one more viable way to deal with make a refined coordination space. Metal-organic systems are 3D lattices made out of metal particles and connecting natural ligands, having high porosity, a huge surface region, high adsorption limit and great thermal steadiness [28-34]. Macrocyclic multimetallic buildings enjoy promising benefits, for example, (i) synergetic impacts dependent on the metal–metal or metal–ligand participation, (ii) varieties of (blended) metal components, (iii) great reactivity, selectivity and vigor coming about because of macrocyclic constructions and (iv) limitless mixes of metals and ligands. The helpful impact of different metal centers is significant for high synergist execution [18,35-40]. Helpful catalysis might start from at least two metal particles in closeness. The presence of various metals is significant for magnificent reactant exercises. Macrocyclic ligands with numerous chelating destinations ought to be all around intended to efficiently present diverse metal components. One another important characteristic of multi-metallic macrocyclic complexes is vigour that might arise from the complex and tight gathering of metal particles and ligands with different coordination locales. Inspite of the fact that macrocyclic complexes can be produced by planning macrocyclic ligands, the self-gathering of metal particles and ligands might be upheld by more confounded and inconspicuous metal-ligand and ligand-ligand interactions. Mixing of metal particles and ligands some of the time brings about uncommon vigor. In view of underlying variety, macrocyclic multimetallic complexes show an assortment of physical properties [41,42]. In the area of host-guest chemistry, they can go about as host atoms for the multipoint acknowledgment of guest particles [43,44].

Robson macrocycles (RMCs): A beginning of multimetallic macrocyclic complexes: In mid-seventies, Robson *et al.* [45] detailed diphenoxo-connected homodinuclear bivalent complexes of first row transition metal particles obtained from a tetraiminodiphenolate macrocyclic ligand (Fig. 4), which is the [2 + 2] buildup result of 4-methyl-2,6-diformyl phenol and 1,3-diaminopropane [46]. These macrocyclic ligands were arranged in such a manner that these following the method of template synthesis, in which dialdehyde and diamine are permitted to gather within the sight of a metal particle. For instance, a [2+2] Robson dinuclear macrocycle buildings, 8-M_2 (**Scheme-I**) acquired by the reaction between 4-methyl-2,6-diformyl phenol and 1,3-diaminopropane within the sight of different metal particles, for example, Ni^{2+} or Cu^{2+} [46]. Schiff base macrocyclic structures containing a N_4O_2 *bis*-anionic center are known Robson macrocycles (RMCs), which dependent on two phenolate and four imine functionalities. In a large portion of those revealed metal complexes, the aldehydic part is 4-methyl-2,6-diformyl phenol. By single-crystal X-ray diffraction studies, it is affirmed that each N_2O_2 restricting pockets inside macrocycle **8** (**Scheme-I**) was involved by a metal particle. These metal moieties were connected by bridging phenoxo ligands, bringing about short M....M distances. RMCs are secluded structures and their functions can be adjusted effectively by substituting their structure blocks. For instance, by substituting 2-hydroxy-1,3-diaminopropane (**9**) in place of 1,3-diaminopropane, one can frame either a [2+2] or [3+3] macrocycle utilizing a metal layout (**Scheme-II**). Among [2+2]

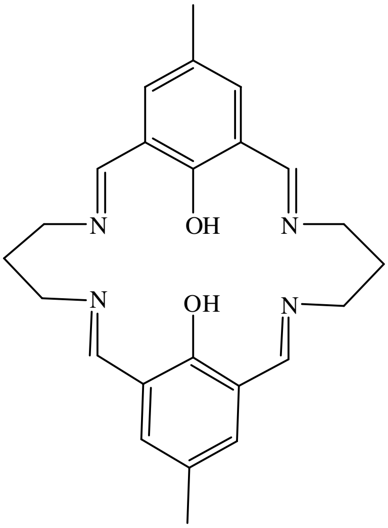

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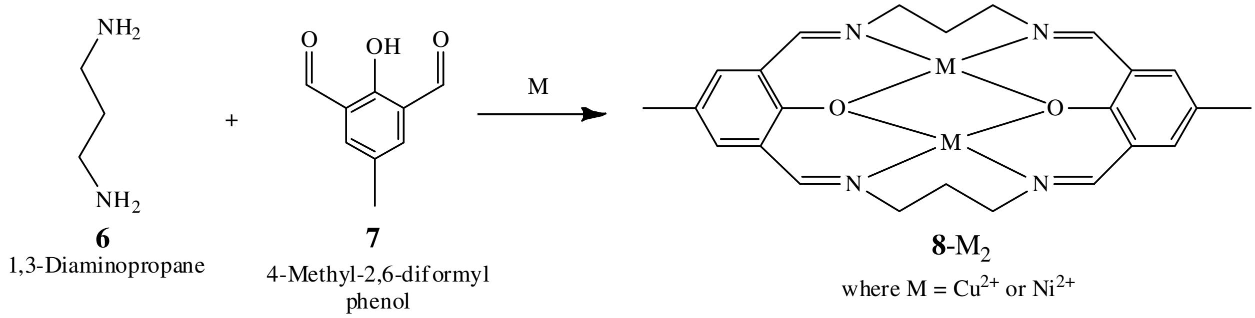
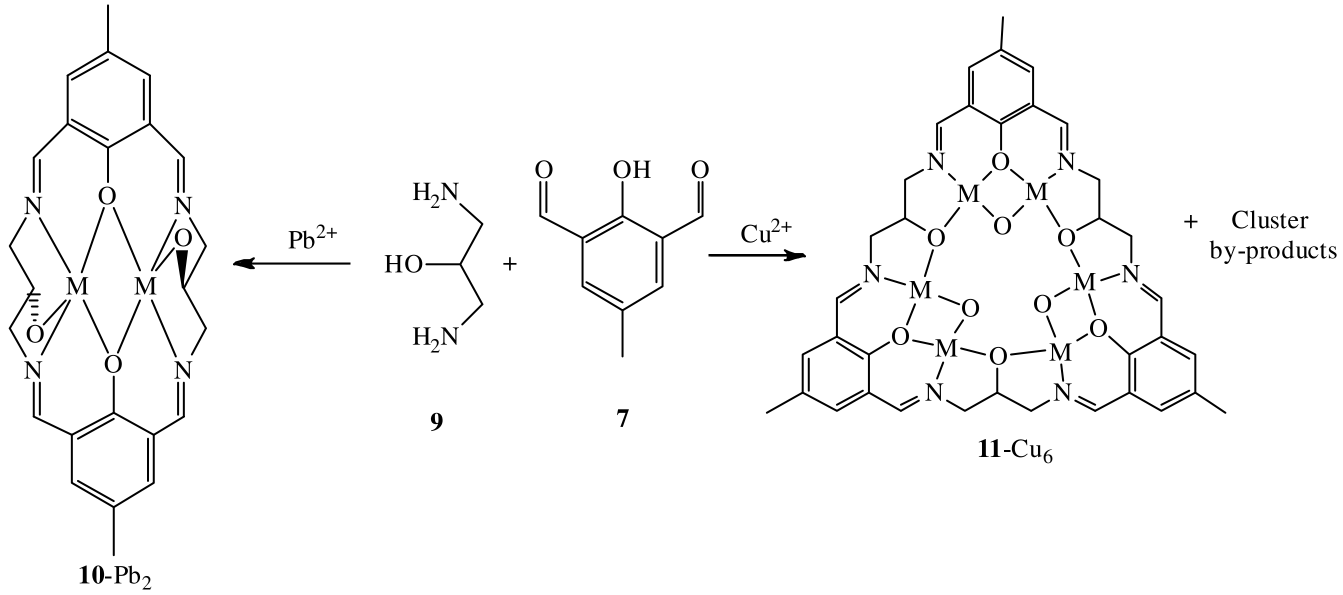
Fig. 4. Structure of tetraiminodiphenolate macrocyclic ligand



Scheme-I: Reaction of 1,3-diaminopropane with 4-methyl-2,6-diformyl-phenol to form 8-M_2



Scheme-II: Reaction of 2-hydroxy-1,3-diaminopropane (**9**) with **7** to form 10-Pb$_2$ or 11-Cu$_6$

or [3+3] macrocycles which is significant product, it relies upon the size of metal particle.

Assuming the size of metal particle is large like Pb^{2+}, a [2+2] macrocycle is significant product [47]. Assuming the size of metal is little similar to Cu^{2+}, a [3+3] macrocycle is shaped [48]. A large portion of the metal complexes from Robson macrocycles have been produced by an interaction that includes the metal-templated synthesis of the macrocycle. Then again, the synthesis of metal complexes following the course of straight combination, *i.e.* the reaction of metal particles with a pre-disengaged RMC, has been substantially few detailed. As a matter of fact, it was hard to pursue this course up to a specific phase of improvement due to the trouble in disengaging RMCs by the immediate buildup of 2,6-diformylphenols and diaminoalkanes, because of the uncontrolled oligomerization process in such reactions. Notwithstanding, the issue has been overwhelmed by taking on a proton-templated way to deal with disconnect salts of the diprotonated macrocycles [49]. Nag *et al.* [50] revealed the union of immersed tetraaminodiphenol analogs of Robson type macrocycles and used those to integrate various homo/heteronuclear metal buildings. Ultimately, it was perceived that these tetraimino/aminodiphenol macrocyclic ligands give an astounding stage to explore helpful metal–metal interactions in magnetic exchange, double exchange, redox properties, synergist exercises and biomimetic reactivities.

Application of macrocyclic ligands and their multimetallic complexes: Macrocyclic ligands and their metal complexes were found to have broad applications in different areas and are acquiring consideration in view of their wide scope of appropriateness as antimicrobial, antifungal or anticancer agents, their catalytic action [51-71], their job as redox reaction mediator and as polymerization catalyst. These complexes can imitate the dynamic site of metalloenzymes [72], find uses in molecular sensing [73-75], separation [76-81] and ionic/proton conductivity [82-84] and can also be utilized in biochemical activity [85] and drug delivery [86,87]. On the other hand, due to high porosity and vacant inner space, they can store [88-91] and purify a gas [78-71].

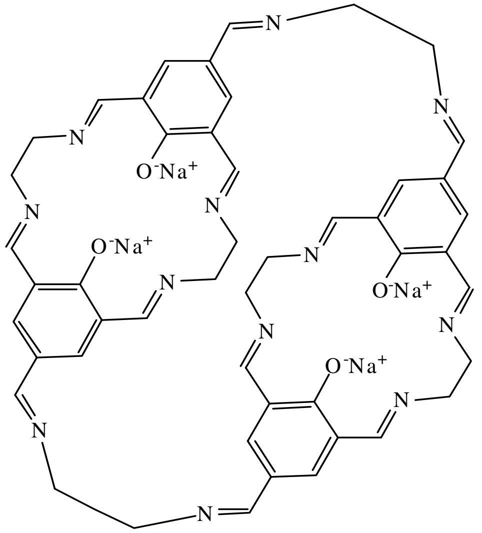
Ligands and complexes for antimicrobial activity: Biological activity of manganese(II), copper(II), nickel(II), cobalt(II) and zinc(II) metal complexes of macrocyclic multidentate Schiff-base ligand Na$_4$L have been reported (Fig. 5). These complexes alongside the ligand have been evaluated for antibacterial activity utilizing three bacterial strain specifically *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The complexes have shown more noteworthy antimicrobial activity than the comparing ligand for initial two bacterial strains. However, metal complexes don't show any consequences for the activity of third bacterial strain [92].

Ligand [H$_4$L] and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) (Fig. 6) have been tested for antimicrobial activity against chose fungi and bacteria utilizing well diffusion strategy. These metal complexes show considerable inhibitory action against bacteria and fungi strains [93].

Also, the biological activity of manganese(II), cobalt(II), nickel(II) and zinc(II) macrocyclic multimetallic complexes of the kinds [MLX$_2$Sn(CH$_3$)$_2$] and [CuLSn(CH$_3$)$_2$]X$_2$ (M = Mn(II), Co(II), Ni(II) and Zn(II); X = Cl$^-$ or NO$_3^-$) have been reported (Fig. 7). These metal complexes were checked for their antifungal activity against few fungal strains, in particular *Aspergillus fumigatus* and *Trichoderma harzianum*. The complexes show moderate antifungal activity against previously mentioned fungal strains [94].

Ligands and complexes for DNA binding and anticancer activity: Macrocyclic ligands and their multimetallic complexes have been found to show anticancer activity and also have been studied DNA binding activities.

DNA binding investigations of a new macrocyclic binuclear nickel(II) complexes (**Scheme-III**) by utilizing the mononuclear complex [NiL] (**19**) with different diamines have been reported. It was found that the aromatic diimine containing



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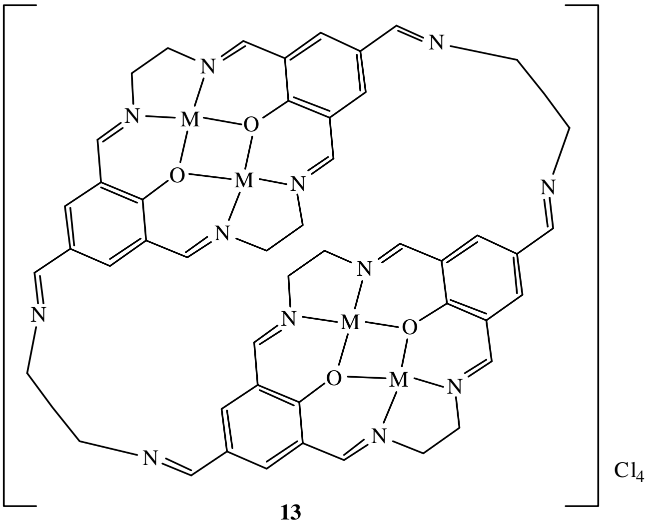
Ligand Na_4L



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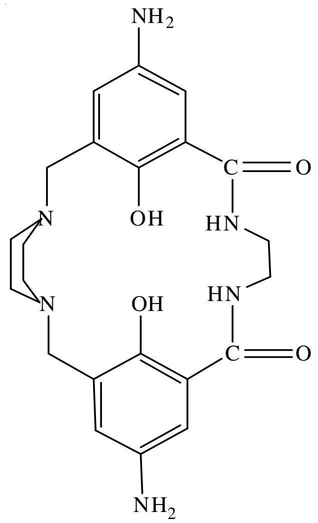
Where M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)

Fig. 5. Macrocyclic multidentate Schiff-base ligand Na_4L and it's metal complexes exhibiting antimicrobial activity



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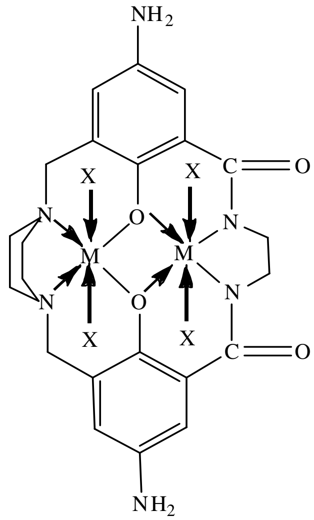
H_4L



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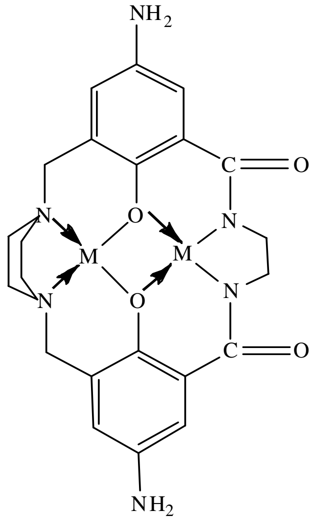
$M_2L.2H_2O$

Where; M = Mn(II), Co(II) and Ni(II)
X = H_2O



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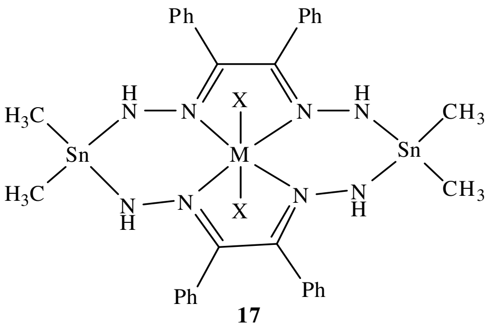
M_2L

Where; M = Cu(II) and Zn(II)

Fig. 6. Ligand H_4L and it's metal complexes exhibiting antimicrobial activity



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Where M = Mn(II), Co(II), Ni(II) and Zn(II)

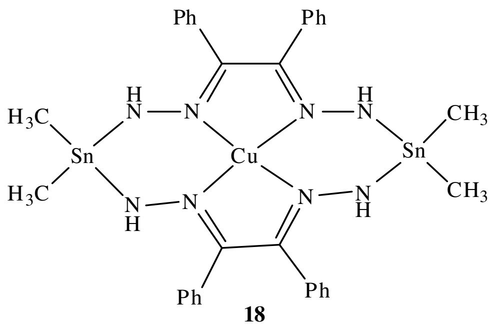

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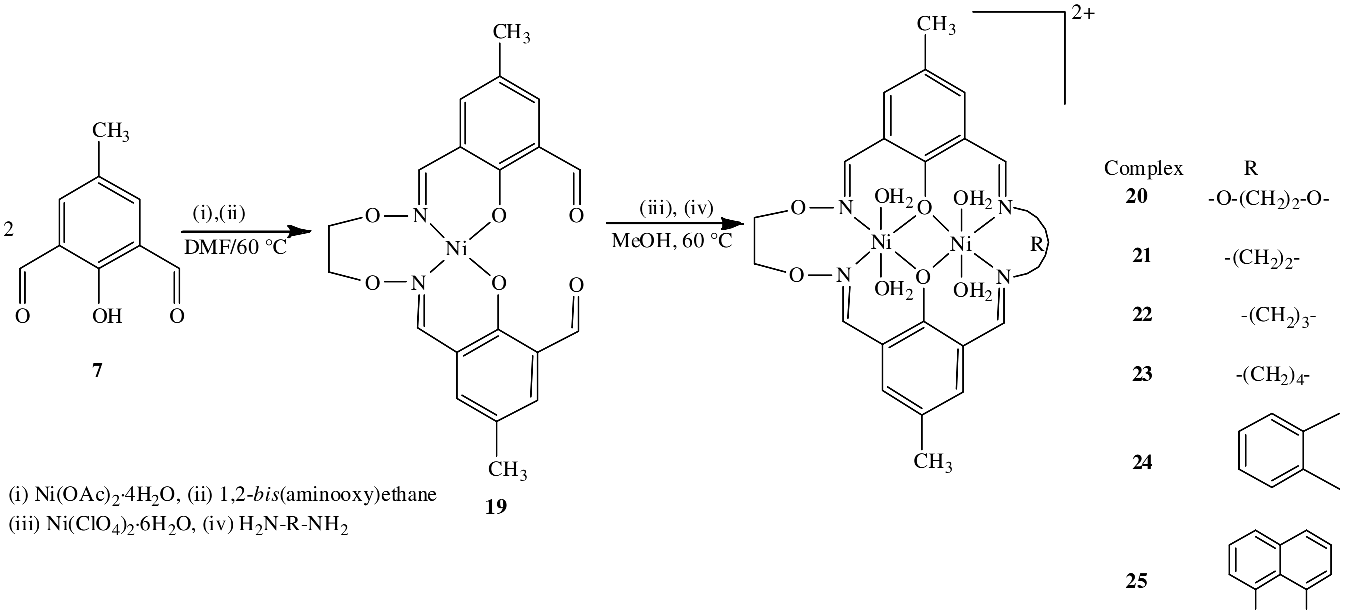
Fig. 7. Multimetallic macrocyclic complexes exhibiting antifungal activity



Scheme-III: Synthesis of dinuclear Ni(II) complexes

Ni(II) complex **25** show preferred binding propensity with DNA over aliphatic diimine containing Ni(II) analogs **20** and **22**. All the metal complexes can sever the DNA through hydrolytically, because a traditional extremist scrounger, for example, DMSO, was totally ineffectual in the cleavage action [95].

Anticancer activity of symmetrical macrocyclic dizinc(II) complex synthesized by utilizing ligand (L_1) and unsymmetrical macrocyclic dizinc(II) complexes synthesized by ligand [ZnL] (**28-32**) have been reported (**Scheme-IV**). Ligand L_1, dizinc(II) buildings **29**, **31** and **33** showed cytotoxicity in human hepatoma HepG2 cancer cells. The outcomes showed that complex **33**, a dizinc(II) complex with strong antiproliferative action, can actuate caspase-subordinate apoptosis in human cancer cells. Cytotoxicity of the buildings was additionally affirmed by the lactate dehydrogenase chemical level in HepG2 cell lysate and content media [96].

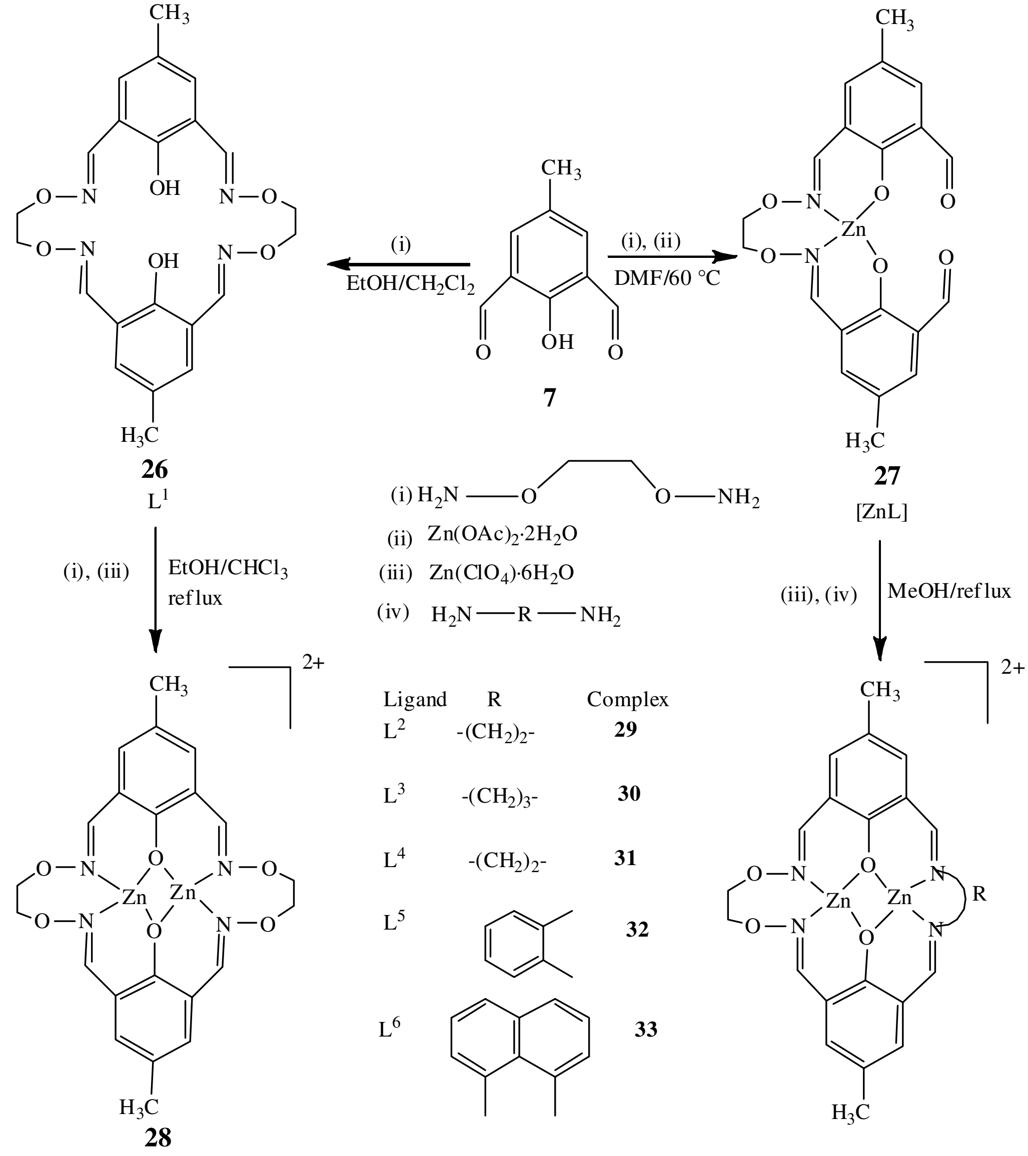
Ligands and complexes for catalytic applications: The significant role of a catalyst is to speed up rate of reaction, empowering them to continue under the most positive thermodynamic conditions and at lower temperatures and pressure.

CO_2 fixation: CO_2 is an inexhaustible unrefined substance for the creation of significant worth added synthetic compounds and various significant synergist responses have been created [97-104]. Various multimetallic macrocyclic buildings showing high catalytic activity for copolymerization of epoxide and CO_2 to form polycarbonates have been reported [105-112]. William *et al.* [113-115] revealed macrocyclic multimetallic complexes showing high catalytic activity for the copolymerization of cyclohexene oxide (CHO) and CO_2 utilizing a Robson macrocycle. Since CO_2 is plentiful, reasonable and an ozone harming substance, researchers have been keen on using CO_2 as a reagent. Complexes **34** showed equivalent reactivity to the best catalyst accessible at that point, while working at much a lower reaction pressure of 1 atm. and yielding moderately monodisperse polymers. Dinuclear cobalt complexes **35** and **36** displayed equivalent reactant action at 1 atm. CO_2 pressure. Complex **35** with a mixed valence Co(II)/Co(III) center showed multiple times higher TOF at 100 °C than complex **34**. At higher CO_2 pressure, both **35** and **36** showed a lot of higher reactant action. Notwithstanding, these frameworks are not restricted to utilize absolutely one kind of metal (Fig. 8).

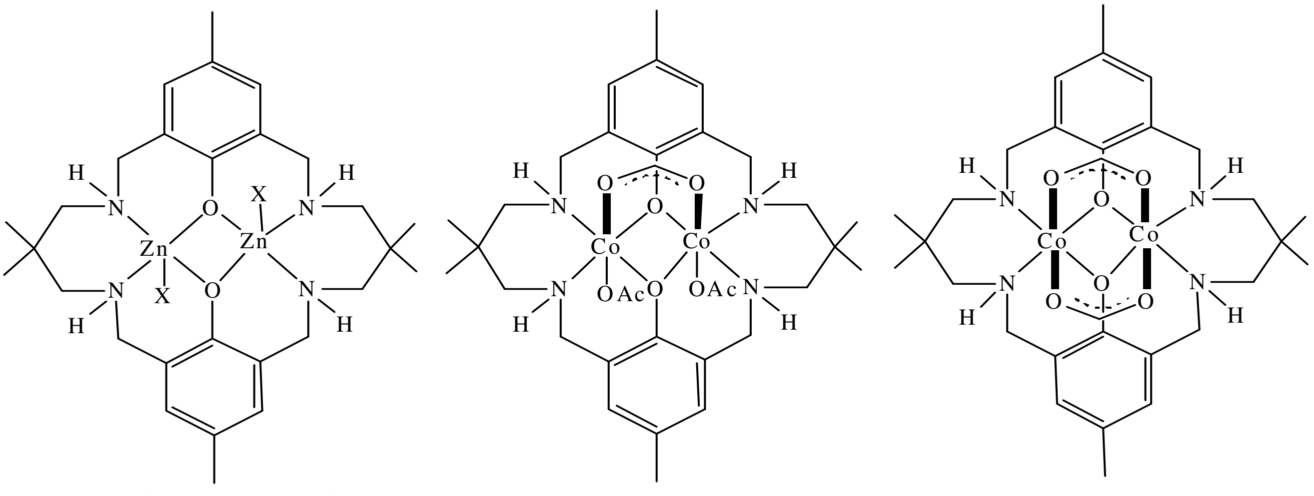
Macrocyclic heterodinuclear Mg/Zn complex **37** [113], complex **38** [114] and Ti/Zn complex **39** also have been reported [115] which show significant catalytic activity. Critically, mixed metal catalyst **41** was strikingly more compelling than either homodinuclear Zn complex **34**. The catalytic activity of heterodinuclear complex **38** was multiple times higher than that of a 1:1 combination of homodinuclear Zn. Obviously, the justification behind improved catalytic activity of heterodinuclear Mg/Zn buildings **37** and **38** is the synergistic impact of the two distinctive metal particles (Fig. 9).

Moreover, chiral dinuclear cobalt complexes **40** and **41** in the kinetic resolution of propylene oxide (PO) with CO_2 using phenyltrimethylammoniumtribromide as a nucleophilic co-catalyst have been reported [116]. Complex **40** showed higher enantioselectivity than complex **41** (Fig. 10).

Hydrolysis of phosphate esters: Phosphate esters in living things play a significant biological role. Robotic examinations on the hydrolytic cleavage of the P-O bond are a significant space of exploration. Various symmetrical and unsymmetrical macrocyclic bimetallic complexes to research the hydrolysis of phosphate diesters and monoesters have been accounted for [117,118]. Dinuclear Zn hydrates can exist in six potential structures among which *trans*-$[Zn_2L(OH)(H_2O)]^+$ structure **42** was viewed as the most dynamic catalyst for the hydrolysis of phosphodiester *bis*(4-nitrophenyl)phosphate (**Scheme-V**) [62]. Two Zn(II) particles agreeably work with the nucleophilic assault of the metal-bound OH^-, settling the anionic change state. Unthinking examinations on the hydrolytic cleavage of



Scheme-IV: Synthesis of symmetrical and unsymmetrical dizinc(II) macrocyclic complexes **28-33**



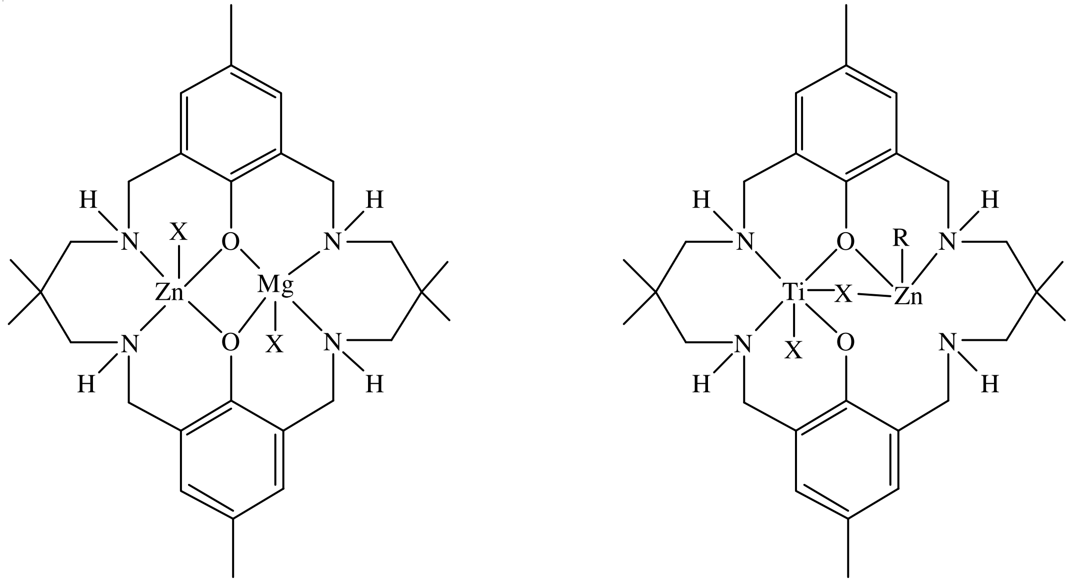
Where X = OAc, Cl

34

35

36

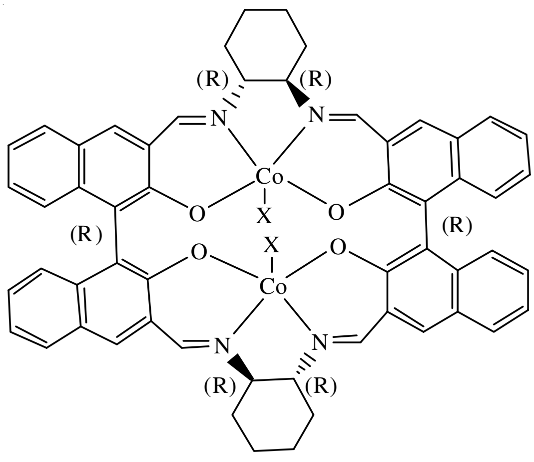
Fig. 8. Macrocyclic homodinuclear complexes exhibiting copolymerization of CO_2 and CHO



37; X = OAc
38; X = Br

Where X = O^iPr; R = Et
39

Fig. 9. Macrocyclic heterodinuclear complexes



X = OAc
40- (R, R, R, R, R, R); **41**- (S, R, R, S, R, R)

Fig. 10. Macrocyclic dinuclear complexes **40** and **41** involved in kinetic resolution of epoxide

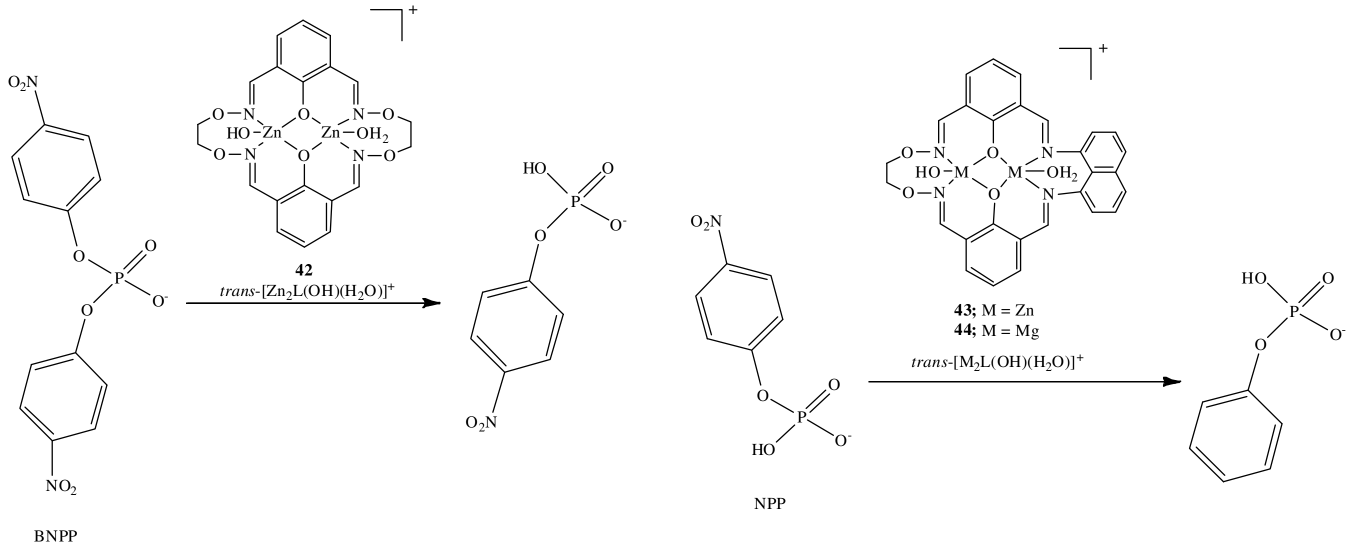
phosphate monoester 4-nitrophenyl phosphate (NPP) were completed by utilizing unsymmetrical binuclear catalysts **43** and **44** [63]. Zn catalyst **43** followed a vigorously ideal pathway including a deliberate bimolecular nucleophilic addition substituent reaction, while Mg catalyst **44** followed a stepwise bimolecular nucleophilic addition substituent reaction.

To study the hydrolytic cleavage of NPP and DNA, a series of macrocyclic dinuclear Ni complexes (**46-50**) and Zn complexes (**51-55**) (Fig. 11) have been accounted for [93,94]. Curiously, symmetrical Ni complex **46** showed higher catalytic activity for the cleavage of NPP than unsymmetrical complexes **47-52**. In the hydrolytic cleavage of DNA, macrocyclic Zn complexes displayed higher catalytic activity than Ni analogs, which was ascribed to the more Lewis acidic Zn(II) particle able to do firmly restricting the phosphate gathering of DNA. The phosphate gathering of DNA is initiated in a helpful way by the two Zn(II) particles, where the Zn(II) bound OH^- groups assaults the P atom to break one of the P–O bond of the DNA. Among the unsymmetrical Zn complexes, the best DNA cleavage action was noticed for complex **55**.

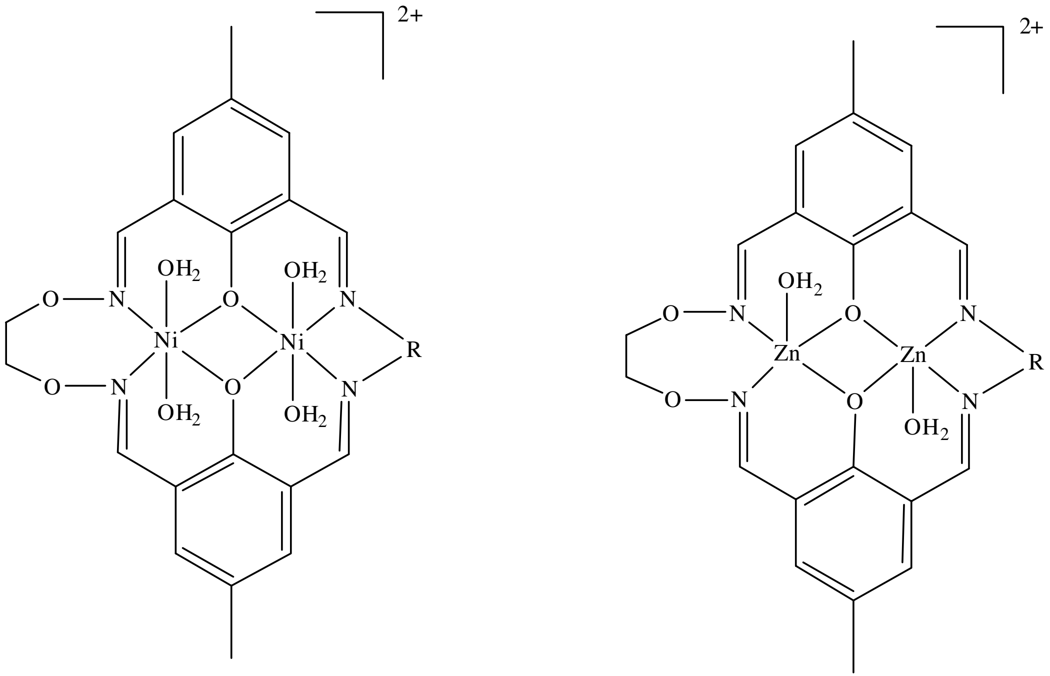
Moreover, dinuclear zinc(II) complex of macrocyclic [30]aneN_6O_4-ligand have been accounted for as an catalyst for hydrolysis of phosphate esters [119]. This dinuclear zinc(II) complex **57** is approximately 10 times more active contrasted with the comparing mononuclear complex **56** (Fig. 12). In complex **57**, two zinc(II) centers stay in nearness, prompting expanded helpful activity contrasted with complex **56** [120]. Countless reports exhibiting helpful catalysis utilizing bimetallic zinc(II) complexes dependent on various ligand framework and spacer units [121].

Ring opening polymerization: A dinuclear complex dependent on a *bis*(anilido)tetraimine macrocycle showing great action in the ROP of r-LA within the sight of 1 equiv./Zn of ^{i}PrOH in THF (Fig. 13, **58**) [122] have been accounted for by Williams, Brooker *et al.* [123], a similar gathering additionally explored this sort of frameworks, incorporating the clear cut isopropoxy and hexamethyldisilazane (HMDS)-analogs of **58** (**59-60** and **61-62**, separately). All mixtures demonstrated incredibly active, taking into account total lactide transformation inside 2 min at room temperature.

Mixed Zn/Co heterobimetallic complexes upheld by [2+2] Schiff base macrocycles (**63** and **64**, Fig. 13) [124] have been accounted for. These complexes demonstrated effective action in the ROP of ε-CL and δ-VL at 130 ºC within the sight of BnOH as co-activator. The comparing homodinuclear complexes were viewed as inactive or ineffectively dynamic in the ROP of ε-CL and δ-VL, individually, proposing the event of helpful impacts between the Co-and Zn centers in the mixed complexes **63** and **64**.



Scheme-V: Hydrolysis of phosphodiester BNPP and phosphate monoester NPP



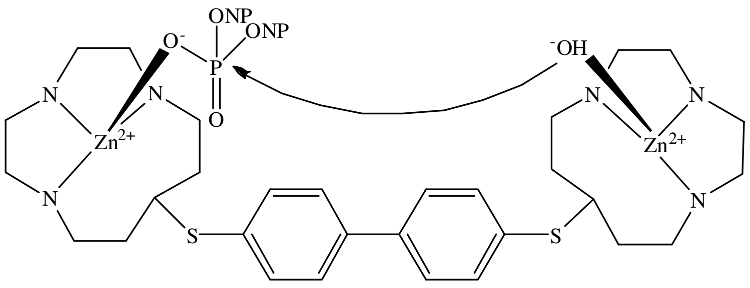
45; R = -O(CH_2)O-
46; R = -$(CH_2)_2$-
47; R = -$(CH_2)_3$-
48; R = -$(CH_2)_4$-
49; R = *o*-phenylene
50; R = 1,8-naphthylene

51; R = -$(CH_2)_2$-
52; R = -$(CH_2)_3$-
53; R = -$(CH_2)_4$-
54; R = *o*-phenylene
55; R = 1,8-naphthylene

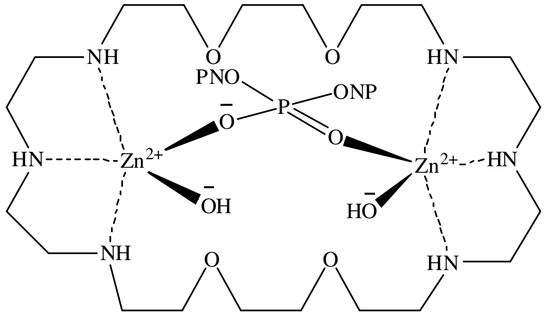
Fig. 11. Homodinuclear macrocyclic complexes

A series of heterobimetallic Co^{III}/M^{I} (where M belongs to first group) complexes bearing macrocyclic ligands (Fig. 14) have been reported. These complexes show high productivity and extraordinary yields of polypropylene carbonate (PPC) polyols in the ring-opening copolymerization reaction of CO_2 and propylene oxide [125]. The Co....K division measures 3.698 Å, which fall in the reach to show metal-metal collaboration in ring-opening intermediate and transition state [126]. Further instances of cooperativity in transition metal/alkali frameworks have as of late been accounted for by Garden and his co-workers [127].

Ligand and complexes for magnetic application: At the point when a reasonable mix of metal ions is utilized in the multimetal frameworks, the obtained heteronuclear complexes show exceptional magnetic properties. A multimetallic macrocyclic Schiff base complex Zn_3Er (complex **66**) has trademark

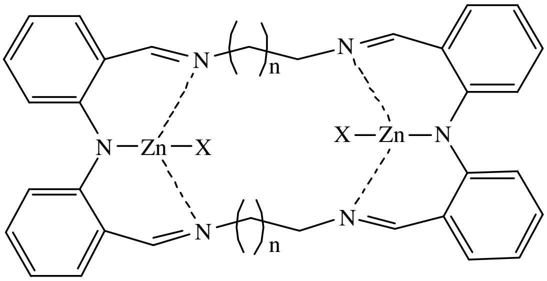


56

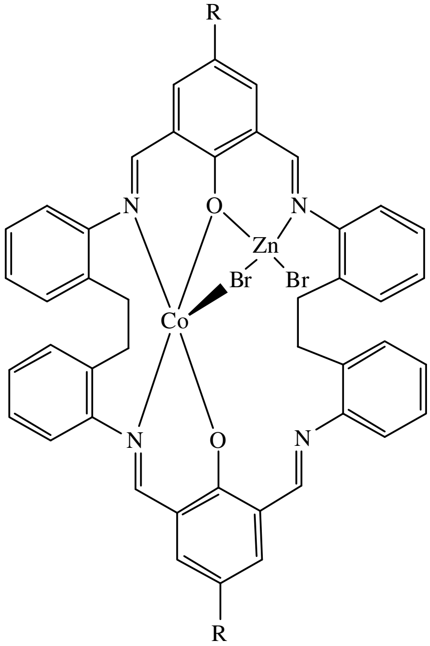


57

Fig. 12. Mononuclear and binuclear macrocyclic Zn(II) complexes

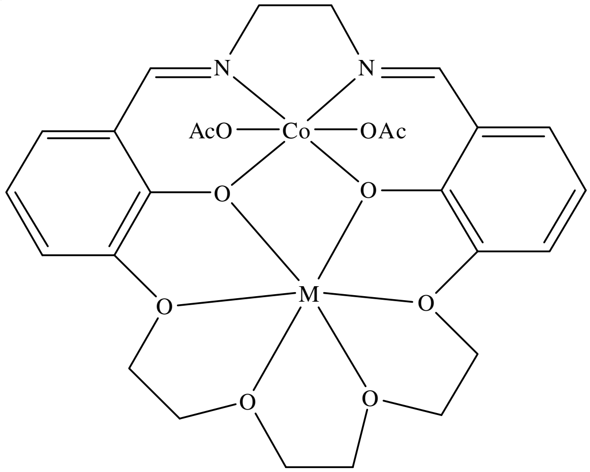


58 (n = 1, X = Et)
59 (n = 2, X = O^{i}Pr)
60 (n = 2, X = O^{i}Pr)
61 (n = 1, X = N(SiMe$_3$)$_2$)
62 (n = 2, X = N(SiMe$_3$)$_2$)



63 (R = Me)
64 (R = ^{t}Bu)

Fig. 13. Dinuclear complexes based on macrocyclic Schiff base ligand



where M = Na, K, Rb, Cs

65

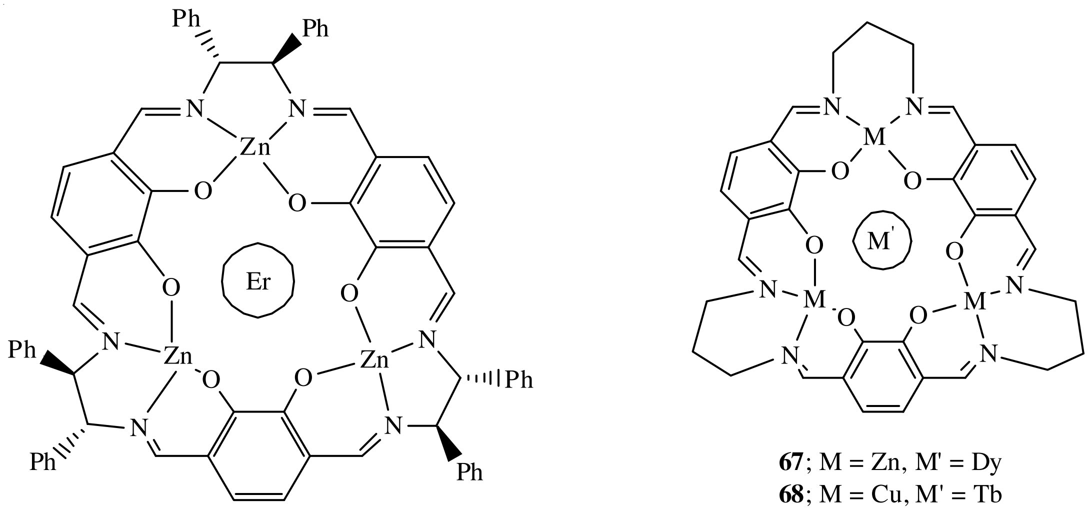
Fig. 14. Heterobimetallic complexes for ring opening polymerization

magnetic properties, *i.e.* single-molecule magnetic (SMM) behaviour (Fig. 15) [128]. Essentially, tetranuclear heterometallic complexes **67** and **68** were additionally ready to function as a SMM.

Magnetic behaviour of a series of homodinuclear β-diketone lanthanide(III) complexes, defined as [(Ln$_2$(acac)$_4$L1] [Ln^{3+} = Dy^{3+} (**71**), Tb^{3+} (**72**) and Gd^{3+} (**73**)] and [Ln$_2$(L1)(L2)$_2$] [Ln^{3+} = Dy^{3+} (**74**), Tb^{3+} (**75**) and Gd^{3+} (**76**)] have been reported (Fig. 16). Magnetic examinations uncover ferromagnetic association between Dy^{3+} and Tb^{3+} centers and zero-field slow relaxation of magnetization for Dy^{3+} complexes **71** and **74**. The relating magneto-structural connections of SMMs **71** and **74** were additionally examined by theoretical estimations and with experimental results [129].

Conclusion

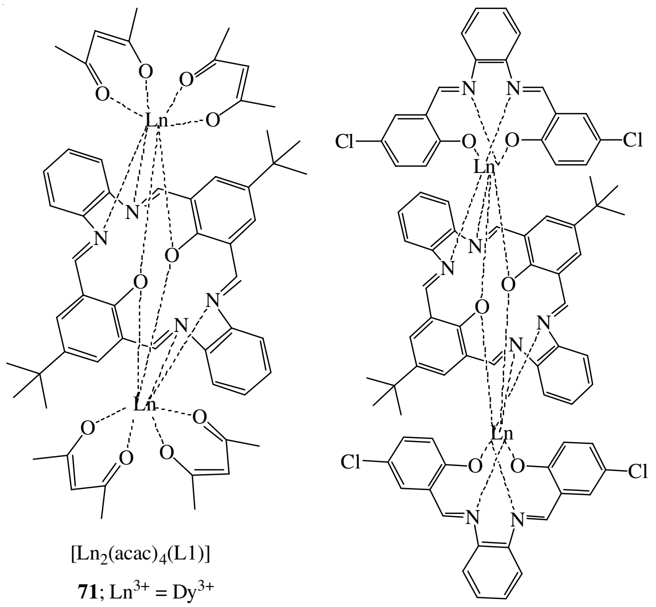
It is concluded that the gathering of the few metal ions in the confined space of the molecule brings about the synergistic and cooperative functions for magnetic, catalytic and biological



66

67; M = Zn, M' = Dy
68; M = Cu, M' = Tb

Fig. 15. Heteronuclear multimetallic macrocyclic complexes show single molecule magnetic behaviour



$[Ln_2(acac)_4(L1)]$
71; $Ln^{3+} = Dy^{3+}$
72; $Ln^{3+} = Tb^{3+}$
73; $Ln^{3+} = Gd^{3+}$

$[Ln_2(L1)(L2)_2]$
74; $Ln^{3+} = Dy^{3+}$
75; $Ln^{3+} = Tb^{3+}$
76; $Ln^{3+} = Gd^{3+}$

Fig. 16. Homodinuclear lanthanide macrocyclic complexes exhibiting magnetic properties

properties. The most intriguing late advances with regards to this field forecast a cornucopia of assorted revelations for quite a long time in the future. It is expected that further examination in this area will prompt new theoretical evident forward leaps in catalysis and give admittance to novel and economical materials that could upgrade the nature of regular day to day existence.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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