



A Brief Review On Homo-/Hetero-nuclear Coordination Compounds derived From Some Single Compartment Acyclic Schiff Base Ligands having N-, O-Donor Centres

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ABSTRACT

Tetradentate acyclic compartmental Schiff base ligand with N₂O₂ compartment afford suitable coordination environment for large variety of metal ions. This type of ligands can easily be synthesized by [2+1] condensation of a carbonyl compounds with a diamine. Several metal complexes have been reported from the single- and double-compartment acyclic Schiff base ligands which are the [2+1] condensation products of salicylaldehyde, 2-hydroxyacetophenone, 3-methoxysalicylaldehyde, 3-ethoxysalicylaldehyde and a diamine; The diamine counterpart in these ligands are ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1-methylethylenediamine, 2,2-dimethyl, 1,3-diaminopropane, *o*-phenylenediamine, *trans*-1,2-diaminocyclohexane, etc. Several review article has been published previously on compartmental Schiff base ligand compounds. This review article focused only the type and structures of Cu(II)/Ni(II)-second metal (s-, p-, d¹⁰-, 3d-, 4f-block metal) homo-/hetero- nuclear coordination compounds derived from single compartmental salicylaldehyde-diamine and acetophenone-diamine ligand systems.

Keywords: Single compartment acyclic Schiff base ligand, Coordination compound, Structure, Diamine, Salicylaldehyde, Acetophenone.

INTRODUCTION

In the design of metal–ligand complexes the choice of metal ions and the information encoded in the ligands are very important. There are many factors at the back for the choice of the ligand like its connectivity, dimensionality, size, shape, conformation, etc. The Salen-type Schiff base ligands can easily be synthesized¹⁻³ and can form complexes with almost all metal ions from

different parts of the periodic table to form homo- and hetero-nuclear complexes.¹⁴⁻⁹⁰ In recent years, great interest has been devoted to homo- and hetero-nuclear complexes derived from Schiff base ligands due to their magnetic⁴ and exciting structural properties. Schiff base ligands and their homo- and hetero-nuclear metal complexes have a range of applications including biological,^{5,6} analytical,⁷ industrial use as catalysts.^{8,9} the reaction of the single- and double-compartment acyclic Schiff base ligands



with a suitable metal salt produces a mononuclear compound in which the metal ion occupies the N(imine)₂O(phenoxo)₂ compartment.¹⁰⁻¹³ When several second metal ions (such as s-, p-, d-, f-block metal salt) from different parts of the periodic table are treated with the Cu(II)/Ni(II) mononuclear compounds the Cu(II)/Ni(II)-second metal homo-/hetero- nuclear complexes are produced. However various types of copper(II)/nickel(II)-second metal (s-, p-, d-, f- block metal) complexes¹⁴⁻⁹⁰ were reported previously from single compartmental salen-type Schiff base ligand which include dinuclear,^{20,21,24,25-33,47-50,80-84} trinuclear,^{22,23,36-42,52-55,85-87} tetranuclear,¹⁶ pentanuclear,¹⁴ hexanuclear,¹⁵ dimer of dinuclear,^{21,32,44-46,50,56-59,81} dinuclear based polymer,^{34,35,46,51} trinuclear based polymer,^{18,46,70} octanuclear,⁷¹ dinuclear–mononuclear cocrystals,^{81,89} trinuclear–mononuclear cocrystals⁹⁰ etc. A brief survey of those compounds is summarised in this review article. Single compartmental Salen-type Schiff base ligands in which aldehyde part is salicylaldehyde and 2-hydroxyacetophenone and the diamine parts comes from ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1-methylethylenediamine, 1,1-dimethylethylenediamine, 2,2-dimethyl-1,3-

diaminopropane, o-phenylenediamine, trans-1,2-diaminocyclohexane are considered in this survey. The primary aim of this survey is to mention which second metal ions are used in the copper (II)/nickel(II)-second metal ion compounds and so definitely the types of compounds are not restricted among the types mentioned in this review article.

Structural discussion

A brief structural survey of Cu(II)/Ni(II)-second metal (s-, p-, d¹⁰-, 3d-, 4f-block metal) homo/hetero nuclear coordination compounds derived from single compartmental salicylaldehyde-diamine and acetophenone-diamine ligand systems have been mentioned in the following five subsection. The structure and abbreviation of ligand systems considered [salicylaldehyde-diamine (H₂L^{sal/acpn-diamine}), 2-hydroxyacetophenone-diamine (H₂L^{acpn-diamine})] in this survey are demonstrated in Table 1. The coordination number of second metal centre(s) and the ligand systems from which the different types of Copper(II)/nickel(II) s-, p-, d¹⁰-, 3d- and, 4f- metal ion compounds are reported (which are mentioned in this survey) also summarized in the Tables 2, 3 and 4 respectively in the subsections.

Table 1: Chemical structures and abbreviation of H₂L^{sal/acpn-diamine} ligands

Chemical Structure	Abbreviation	Chemical Structure	Abbreviation
	H ₂ L ^{sal/acpn-en}		H ₂ L ^{sal/acpn-2,2Mepn}
	H ₂ L ^{sal/acpn-1-Meen}		H ₂ L ^{sal/acpn-bu}
	H ₂ L ^{sal/acpn-1,1-Me2en}		H ₂ L ^{sal/acpn-hex}
	H ₂ L ^{sal/acpn-Pn}		H ₂ L ^{sal/acpn-op}

Copper(II)/nickel(II)-s block metal ion complexes

Among the alkali metal ions, only few compounds of sodium (I)¹⁴⁻¹⁸ are known. Regarding the alkaline earth metal ions, only one barium(II) system (Ni^{II}Ba^{II}Ni^{II}) is known.¹⁹ The sodium(I) systems include pentanuclear triple-decker Ni^{II}₃Na^I₂,¹⁴ hexanuclear Ni^{II}₅Na^I₁,¹⁵ trinuclear Cu^{II}Na^ICu^{II},^{16,17} trinuclear Ni^{II}Na^INi^{II},¹⁵ trinuclear Cu^{II}Na^ICu^{II} based polymer,¹⁸ trinuclear Cu^{II}₃Na^I₁ etc. In all the above mentioned copper(II)/nickel(II)-

sodium(I) compounds and one nickel(II)-barium(II) compounds the copper(II)/nickel(II) centre is tetra coordinated by two bridging phenoxo-oxygen atoms and two imine nitrogen atoms of the Schiff base ligand and adopt a square-planer/distorted square-planar geometry, except one trinuclear Cu^{II}Na^ICu^{II} compound (derived from H₂L^{acpn-pn}) in which copper(II)/nickel(II) centre is penta-coordinated with the axial position occupied by one bridging phenoxo oxygen atom of adjacent Cu^{II}L^{acpn-pn} mononuclear

unit. Whereas in all the above mentioned copper(II)/nickel(II)-sodium(I) compounds^{14–18} the sodium(I) centre is hexa-coordinated by six bridging phenoxo oxygen atoms^{15,16} or by four bridging phenoxo oxygen atoms and two oxygen atoms of perchlorate/isothiocyanate^{14–18} ligand except one pentanuclear triple-decker $\text{Ni}^{\text{II}}_3\text{Na}^{\text{I}}_2$ compound¹⁴ (derived from $\text{H}_2\text{L}^{\text{sal-opda}}$) and one trinuclear $\text{Cu}^{\text{II}}\text{Na}^{\text{I}}\text{Cu}^{\text{II}}$ compound¹⁷ (derived from $\text{H}_2\text{L}^{\text{acpn-1Meen}}$ in which sodium(I) centre is hepta-coordinated with the 7th position occupied by a oxygen atom of water molecule). For pentanuclear triple-decker $\text{Ni}^{\text{II}}_3\text{Na}^{\text{I}}_2$ compound¹⁴ each sodium(I) centre is hexa-coordinated with four bridging phenoxo oxygen atoms and one nitrogen atom of terminal cyano group and one nitrogen atom of bridging cyano group and is sandwiched between two Ni^{II} -mononuclear units. whereas hexanuclear $\text{Ni}^{\text{II}}_5\text{Na}^{\text{I}}_2$ system¹⁵ consists of tetrametallic cluster ion $[\{\text{Ni}(\text{H}_2\text{L}^{\text{sal-1Meen}})\}_3\text{Na}]^+$ with encapsulated sodium by three $[\text{Ni}(\text{H}_2\text{L}^{\text{sal-1Meen}})]$ units and two mononuclear $[\text{Ni}(\text{H}_2\text{L}^{\text{sal-1Meen}})]$ units. The only example of barium(II) system is a trinuclear double-decker $\text{Ni}^{\text{II}}\text{Ba}^{\text{II}}\text{Ni}^{\text{II}}$ compound¹⁹ in which the barium(II) centre is eight-coordinated by four bridging phenoxo oxygen atoms of two schiff base ligand, three oxygen atoms of perchlorate and one oxygen atom of furan ring forming a distorted square antiprismatic geometry and the barium(II) cation is sandwiched between two Ni^{II} -mononuclear units.¹⁹ Among the above mentioned systems crystal structure of pentanuclear triple-decker $\text{Ni}^{\text{II}}_3\text{Na}^{\text{I}}_2$ compound is shown in Figure 1.

Copper(II)/nickel(II)-p block metal ion complexes

A few dinuclear $\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}$ ^{20,21} and trinuclear $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}}$,^{22,23} dimer-of-dinuclear $[\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}]_2$ (linker is N,N-dimethylformamide molecules),²¹ dinuclear $\text{Cu}^{\text{II}}\text{Bi}^{\text{III}}$ ²⁴ and $\text{Ni}^{\text{II}}\text{Bi}^{\text{III}}$ ²⁴ compounds are known. For the dinuclear $\text{Cu}^{\text{II}}\text{Bi}^{\text{III}}$, $\text{Ni}^{\text{II}}\text{Bi}^{\text{III}}$ and trinuclear $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}}$ compounds^{22,23,24} the copper(II)/nickel(II) centre are tetra coordinated by two bridging phenoxo-oxygen atoms and two imine nitrogen atoms of the Schiff base ligands to adopt a square planer/distorted square-planar geometry. Whereas for the dinuclear $\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}$ and dimer-of-dinuclear $[\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}]_2$ compound²¹ the nickel(II) centre(s) are hexa-coordinated by two bridging phenoxo-oxygen atoms and two imine nitrogen atoms of the Schiff base ligands and axial positions are occupied by two nitrogen atoms of two solvent pyridine ligands in dinuclear $\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}$ compound^{20,21} and by oxygen atom of the water molecule and N atom of the SCN^- group in dimer-of-dinuclear $[\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}]_2$ compound²¹ to adopt an octahedral geometry and slightly distorted octahedral geometry respectively.

However the $\text{Pb}(\text{II})$ centre(s) are, i) four coordinated involving two phenoxo oxygen atoms of the Schiff base ligand and two chlorine atoms with heavily distorted tetrahedral environment for the dinuclear $\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}$ compound,^{20,21} ii) hexa-coordinated involving four bridging phenoxo-oxygen atoms of two Schiff base ligand and two $\text{Cl}^-/\text{I}^-/\text{SCN}^-$ ligand with a distorted octahedral geometry for trinuclear $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}}$ compounds,^{22,23} iii) hexa-coordinated involving two phenoxo-oxygen atoms of Schiff base ligand, two bridging S atoms SCN^- group and two bridging O atoms of N,N-dimethylformamide molecules with a highly distorted octahedral geometry for dimer-of-dinuclear $[\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}]_2$ compound²¹ and iv) octa-coordinated with two phenoxo-oxygen atoms of Schiff base ligand and four oxygen atoms of two salicylate ion with approximately a capped pentagonal bipyramidal geometry for dinuclear $\text{Cu}^{\text{II}}\text{Bi}^{\text{III}}$ and $\text{Ni}^{\text{II}}\text{Bi}^{\text{III}}$ compounds.²⁴ Among the above mentioned systems crystal structure of dimer-of-dinuclear²¹ $[\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}]_2$ is shown in the Figure 2.

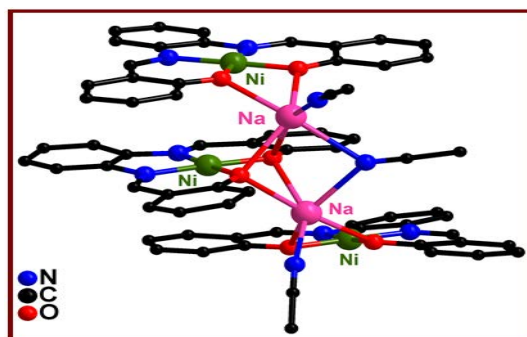


Fig. 1. Crystal structure of $[(\text{Ni}^{\text{II}}\text{L}^{\text{sal-op}})_3\text{Na}_2(\text{CH}_3\text{CN})_3][\text{NiEt}_3\text{Py}_4]\cdot\text{CH}_2\text{CN}$ (Py = pyrrolyl). It is a pentanuclear $\text{Ni}^{\text{II}}_3\text{Na}^{\text{I}}_2$ complex showing triple-decker topology. Anions, solvent acetonitrile molecule and all the hydrogen atoms are omitted for clarity.¹⁴

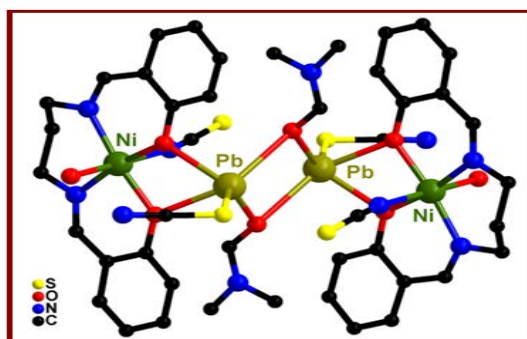


Fig. 2. Crystal structure of $[\text{Ni}^{\text{II}}\text{L}^{\text{sal-op}}\text{Pb}^{\text{II}}(\text{SCN})_2(\text{dmf})(\text{H}_2\text{O})_2]_2$. It is a dimer-of-dinuclear system in which two dinuclear $\text{Ni}^{\text{II}}\text{Pb}^{\text{II}}$ units are interlinked by two N,N-dimethylformamide molecules. Hydrogen atoms are not shown for clarity.²¹

Copper(II)/nickel(II)-d¹⁰ metal ion complexes

Several compounds are known containing copper(II)/nickel(II) and d¹⁰ metal ion such as Zn^{II}, Cd^{II} and Hg^{II}.²⁵⁻⁴⁶ The types of compounds include dinuclear Cu^{II}Zn^{II}, Ni^{II}Zn^{II}, Cu^{II}Hg^{II} and Ni^{II}Hg^{II},²⁵⁻³³ dinuclear Cu^{II}Cd^{II} based polymer (linker is dicyanamide),³⁴ dinuclear Cu^{II}Hg^{II} based polymer (linker is azide),³⁵ trinuclear Cu^{II}Zn^{II}Cu^{II}, Ni^{II}Zn^{II}Ni^{II}, Cu^{II}Cd^{II}Cu^{II}, Ni^{II}Cd^{II}Ni^{II} and Cu^{II}Hg^{II}Cu^{II},³⁶⁻⁴² and dimer-of-dinuclear [Ni^{II}Cd^{II}]₂ (linker is chloride),⁴⁴ dimer-of-dinuclear [Cu^{II}Hg^{II}]₂ (Hg-C bond is linker),³² dimer-of-dinuclear [Cu^{II}Hg^{II}]₂ (linker is chloride),⁴⁵ dimer-of-trinuclear [Cu^{II}Cd^{II}Cu^{II}]₂ (linker is dca),⁴⁶ Cu^{II}Cd^{II}Cu^{II} based polymer⁴⁶ etc.

It has been observed that for dinuclear Cu^{II}Zn^{II} and Cu^{II}Hg^{II},^{25-27,31,32} trinuclear Cu^{II}Zn^{II}Cu^{II}, Cu^{II}Cd^{II}Cu^{II} and Cu^{II}Hg^{II}Cu^{II} compounds^{36,37,39-41,43} in most of the cases the copper(II) centre(s) are tetra-coordinated and in few cases copper(II) centre(s) are penta-coordinated with the axial position occupied by oxygen atom of bridging acetate/formate/nitrate ligand or oxygen atom of water/N,N'-dimethylformamide molecule or nitrogen atom of picoline/pyrazine/azide/dicyanamide/thiocyanate ligand, but for dinuclear Ni^{II}Zn^{II}, Ni^{II}Hg^{II}, trinuclear Ni^{II}Zn^{II}Ni^{II}, and Ni^{II}Cd^{II}Ni^{II} compounds^{28,29,33,38,42} in most of the cases nickel(II) centre(s) are penta/hexa-coordinated with the axial position occupied by oxygen atom of bridging acetate/formate/nitrate ligand or oxygen atom of methanol/N,N'-dimethylformamide molecule or nitrogen atom of picoline/pyrazine/azide/dicyanamide/thiocyanate ligand. For all the above mentioned compounds the equatorial positions of copper(II)/nickel(II) centre are occupied two bridging phenoxo oxygen atoms and two imine nitrogen atoms of the Schiff base ligand. The second metal centre i.e. Zn(II)/Hg(II) in all the above mentioned dinuclear compounds²⁵⁻³³ are slightly distorted tetrahedral/irregular tetrahedral geometry. However for dinuclear Cu^{II}Cd^{II} based polymer,³⁴ the Cd(II) centres are hexa-coordinated by two phenoxo oxygen atoms of Schiff base ligand and four N atoms from four dca ligands to form a distorted octahedral geometry. Moreover all the dca ligands in this compound bridged the Cd(II) ions in single bridge fashion to construct a 2-D structure and it displays a wave-like structure because of the "V" type conformation of the dca ligand. For dinuclear Cu^{II}Hg^{II} based polymer,³⁵ the Hg(II) centre is tetra-coordinated and the azide ion bridge through $\mu_{1,1}$

fashion to form a 1D helical chain. For the dimer-of-dinuclear [Ni^{II}Cd^{II}]₂, [Cu^{II}Hg^{II}]₂ compound^{44,45} in which chlorine atom is linker, the Hg(II)/Cd(II) centres are penta-coordinated with two phenoxo oxygen atom of Schiff base ligand, two bridging Cl atoms and one terminal chlorine atom forming a distorted square pyramidal geometry. However for dimer-of-dinuclear, [Cu^{II}Hg^{II}]₂ compound³² in which linker is Hg-C bond the Hg atom is tetra-coordinated with two phenoxo oxygen atoms of Schiff base ligand, one Cl atom and one imine carbon atom of Schiff base ligand. It is to be mentioned that the square pyramidal geometry is quite common for Cd^{II} ion but it is unusual for Hg^{II} ion.

On the other hand the second metal centre i.e. Zn(II)/Cd(II)/Hg(II) in all the above mentioned trinuclear compounds³⁶⁻⁴³ is hexa-coordinated by four bridging phenoxo oxygen atoms of two Schiff base ligands and two oxygen atoms of two bridging formate/acetate/nitrate or two nitrogen atoms of two bridging/terminal dca/azide/thiocyanato/isothiocyanato or sulphur atom of terminal thiocyanato ligand to adopt a octahedral/distorted octahedral geometry, except one trinuclear Cu^{II}Zn^{II}Cu^{II} compound³⁷ (derived from H₂L^{sal-pn}) in which the second metal centre hepta-coordinated with 7th position is occupied by Zn(II) centre. It has to be mentioned that among the above mentioned compound, only in one dinuclear Ni^{II}Zn^{II} and one trinuclear Cu^{II}Zn^{II}Cu^{II} compound,^{30,37} metal-metal (Ni-Zn/Cu-Zn) coordinate bond have been observed. For the dimer-of-dinuclear [Cu^{II}Hg^{II}]₂ and [Cu^{II}Cd^{II}]₂ compounds^{44,45} Cl-ion bridged by μ_2 -fashion to form tetranuclear compound. Among the above mentioned systems crystal structure of dinuclear [Ni^{II}L^{sal-1-Meen}HgCl₂]₂³³ is shown in Figure 3.

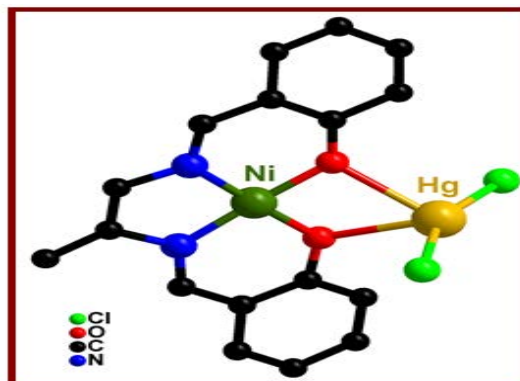


Fig. 3. Crystal structure of dinuclear compound [Ni^{II}L^{sal-1-Meen}HgCl₂]₂. Hydrogen atoms are not shown for clarity.³³

Table 2: The coordination number of second metal centre(s) (s-, p- and d¹⁰- metal ion) and the ligand systems from different types of Copper(II)/nickel(II) s-, p- and d¹⁰- metal ion complexes have been reported

	Ligand systems	Dinuclear(CN of second metal)	Trinuclear(CN of second metal)	Dimer-of-dinuclear/ polynuclear(CN of second metal)	Reference no.
s-block metal	H ₂ L ^{sal-en}	–	Ni ^{II} Ba ^{II} Ni ^{II} (8)	–	19
	H ₂ L ^{sal-1Meen}	–	Ni ^{II} Na ^I Ni ^{II} (6)	–	15
	H ₂ L ^{sal-pn}	–	Cu ^{II} Na ^I Cu ^{II} (6)	–	16
		–	Ni ^{II} ₃ Na ^I (6)	–	15
	H ₂ L ^{sal-opda}	–	Ni ^{II} ₃ Na ^I ₂ (6)	–	14
	H ₂ L ^{acpn-pn}	–	Cu ^{II} Na ^I Cu ^{II} (6)	–	18
		–	based polymer		
		–	Cu ^{II} Na ^I (6)	–	16
	H ₂ L ^{acpn-1-Meen}	–	Cu ^{II} Na ^I Cu ^{II} (7)	–	17
	p-block metal	H ₂ L ^{sal-en}	Cu ^{II} Bi ^{III} (8)	–	–
		Ni ^{II} Bi ^{III} (8)	–	–	24
H ₂ L ^{sal-pn}			Cu ^{II} Pb ^{II} Cu ^{II} (6)		22
		Ni ^{II} Pb ^{II} (4)		[Ni ^{II} Pb ^{II}] ₂ (6)	20,21
H ₂ L ^{acpn-pn}			Cu ^{II} Pb ^{II} Cu ^{II} (6)	–	23
d ¹⁰ -metal	H ₂ L ^{sal-en}	Ni ^{II} Zn ^{II} (4)	–	–	29
	H ₂ L ^{sal-2,2-Mepn}	Cu ^{II} Zn ^{II} (4)	Cu ^{II} Cd ^{II} Cu ^{II} (6)	–	25,40
		Ni ^{II} Zn ^{II} (4)	–	–	28
	H ₂ L ^{sal-pn}	Cu ^{II} Zn ^{II} (4)	Cu ^{II} Zn ^{II} Cu ^{II} (6,8)	–	26,36,37
		Ni ^{II} Zn ^{II} (4)	Ni ^{II} Zn ^{II} Ni ^{II} (6)	–	29,38
		Cu ^{II} Cd ^{II} (6)	Cu ^{II} Cd ^{II} Cu ^{II} (6)		
		based polymer			
		Cu ^{II} Cd ^{II} Cu ^{II} (6)	[Cu ^{II} ₂ Cd ^{II}] ₂ (4) dimer		34,39, 46
		based polymer			
		–	of trinuclear		
			Ni ^{II} Cd ^{II} Ni ^{II} (6)	–	42
		Cu ^{II} Hg ^I (4)	Cu ^{II} Hg ^I Cu ^{II} (6)	–	35,43
		based polymer			
		Ni ^{II} Hg ^I (4)		–	33
	H ₂ L ^{sal-bu}	Cu ^{II} Zn ^{II} (4)	Cu ^{II} Hg ^I Cu ^{II} (6)	[Cu ^{II} Hg ^I] ₂ (5)	26,43,45
H ₂ L ^{sal-hex}	Cu ^{II} Hg ^I (4)	–	–	31	
H ₂ L ^{acpn-en}	Cu ^{II} Zn ^{II} (6)	–	–	27	
H ₂ L ^{acpn-1-Meen}	Ni ^{II} Hg ^I (4)	–	[Ni ^{II} Cd ^{II}] ₂ (5)	33	
H ₂ L ^{acpn-pn}	–	–	[Cu ^{II} Hg ^I] ₂ (4)	32	
	–	Cu ^{II} Cd ^{II} Cu ^{II} (6)	Cu ^{II} ₃ Cd ^{II} (6)	41	
	Cu ^{II} Hg ^I (4)	Cu ^{II} Hg ^I Cu ^{II} (6)	–	32	

Copper(II)/nickel(II)–3d metal ion complexes

Several homonuclear copper(II) compounds are known.^{47–60} The types of such compounds include dinuclear Cu^{II}Cu^{II},^{47–50} dinuclear Cu^{II}Cu^{II} based polymer,⁵¹ trinuclear Cu^{II}Cu^{II}Cu^{II},^{52–55} dimer-of-dinuclear [Cu^{II}Cu^{II}]₂ (linker is azide or chloride or dca),^{50,56–59} In contrast, the number of nickel(II)–copper(II) compounds are only a few which include few trinuclear Ni^{II}Cu^{II}Ni^{II} compounds.^{60–62} The number of compounds obtained on reacting mononuclear copper(II) compounds with Ni^{II} is only a few.^{63–65} Two dinuclear Cu^{II}Ni^{II} systems published long ago in 1985 and 1989 and one trinuclear Cu^{II}Ni^{II}Cu^{II} compound⁶⁵ may be mentioned as examples of copper(II)–nickel(II) compounds. In contrast to

only a few copper(II)–nickel(II) compounds, the nickel(II)–nickel(II) compounds are several.^{66–71} Most of these systems are trinuclear Ni^{II}Ni^{II}Ni^{II} compounds^{67–70} and there is one interesting example of a octanuclear Ni^{II}₈ clusture (linker is chloride).⁷¹ Regarding copper(II)/nickel(II) as the first metal ion (in the N2O2 compartment) and cobalt(II) as the second metal ion, only a few dinuclear Cu^{II}Co^{II}/Ni^{II}Co^{II} and trinuclear Ni^{II}Co^{II}Ni^{II} compounds have been reported.^{62,72–75} Regarding copper(II)/nickel(II)–iron(II) compounds, there are only two examples and those are copper(II)–iron(II) systems.^{76,77} Those include trinuclear Cu^{II}Fe^{II}Cu^{II}⁷⁶ and tetranuclear Cu^{II}₃Fe^{II} based polymer.⁷⁷ With manganese(II) as the second metal ion, the number of compounds

are more in comparison to those in which iron(II)/cobalt(II) is second metal ion. The copper(II)/nickel(II)–manganese(II) systems include dinuclear $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ and $\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}$,^{78,79} trinuclear $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ ⁸⁰ and $\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}\text{Ni}^{\text{II}}$,⁶² tetranuclear $\text{Cu}^{\text{II}}_3\text{Mn}^{\text{II}}$ etc.⁸⁰

In all the reported compounds the coordination number of first metal centre i.e. copper(II)/nickel(II) centre is ranges from four to six. Whereas the coordination number of second metal centre is two/four/five/six/seven for copper(II), five/six/seven for nickel(II), four/six for cobalt(II), four/six for iron(II) and six for manganese(II) centre. However it is to be mentioned that among the above mentioned compounds, only in very few compounds, metal–metal coordination bond have been found which include dinuclear⁶⁴ $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ and trinuclear $\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$, $\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ ⁶⁷ derived from $\text{H}_2\text{L}^{\text{sal-en}}$ and $\text{H}_2\text{L}^{\text{sal-pn}}$ ligand system respectively. For the three dimer-of-dinuclear $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ compounds^{50,56–59} Cl⁻ ion bridged by μ_2 fashion, azide ion bridged by $\mu_{1,1}$ and $\mu_{1,3}$ fashion and dca ion bridged by $\mu_{1,5}$ fashion to form tetranuclear (dimer-of-dinuclear) compound. The octanuclear Ni^{II}_8 clusture⁷¹ consist of four

independent nickel atoms with three different coordination geometry, two nickel(II) centre are sit in the N₂O₂ cavity of Schiff base ligand with square-planar geometry, one nickel(II) centre is six-coordinated by two bridging phenoxo oxygen atoms of Schiff base ligand and four bridging μ_2 -Cl atoms forming a distorted octahedral geometry and another nickel(II) centre is five coordinated by two bridging phenoxo oxygen atoms of Schiff base ligands, two bridging μ_2 -Cl atoms and one terminal Cl atoms to adopt distorted square pyramidal geometry. The tetranuclear⁷⁷ $\text{Cu}^{\text{II}}_3\text{Fe}^{\text{III}}$ based polymer consists of trinuclear $\{\text{Cu}^{\text{II}}_2\text{Fe}^{\text{III}}\}$ unit and a mononuclear $\{\text{Cu}^{\text{II}}(\text{H}_2\text{L}^{\text{sal-1-Meen}})\}$ unit, arranged in helicoidal polymeric chains. Each copper(II) centre in trinuclear $\{\text{Cu}^{\text{II}}_2\text{Fe}^{\text{III}}\}$ unit is five coordinated and the copper(II) centre sits in the N₂O₂ cavity of Schiff base ligand and the fifth position is occupied by the bridging phenoxo oxygen atom of mononuclear $\{\text{Cu}^{\text{II}}(\text{H}_2\text{L}^{\text{sal-1-Meen}})\}$ unit to form polymeric chain. However the copper(II) centre in mononuclear $\{\text{Cu}^{\text{II}}(\text{H}_2\text{L}^{\text{sal-1-Meen}})\}$ unit is four coordinated in the N₂O₂ cavity of Schiff base ligand. Among the above mentioned systems crystal structure of octanuclear Ni^{II}_8 compound is shown in Figure 4.

Table 3: The coordination number of second metal centre (s) (3d-metal ion) and the ligand systems from which the above mentioned types of Copper(II)/nickel(II)-3d-metal ion complexes have been reported

Ligand system	Dinuclear (CN of 2 nd 3d metal ion)	Trinuclear (CN of 2 nd 3d metal ion)	Dimer-of-dinuclear (CN of 2 nd 3d metal ion)	Poly nuclear (CN of 2 nd 3d metal ion)	Reference no.
$\text{H}_2\text{L}^{\text{sal-en}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (2,5,6)	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (6,7)	$[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ (5)	–	47,52,56
	$\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ (6,7)	$\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	63,64,60
	$\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ (5)	$\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	66, 68
	$\text{Cu}^{\text{II}}\text{Co}^{\text{II}}$ (4,6)	–	–	–	72,73
	$\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ (6)	–	–	–	78
$\text{H}_2\text{L}^{\text{sal-opda}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (5)	–	–	octanuclear Ni^{II}_8 (5,6)	48, 71
$\text{H}_2\text{L}^{\text{sal-1-Meen}}$	–	–	$[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ (5)	–	58
$\text{H}_2\text{L}^{\text{sal-hex}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (5)	–	$[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ (4)	–	50
$\text{H}_2\text{L}^{\text{sal-pn}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (4)	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (4,5,6)	$[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ (5)	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (4) dinuclear based polymer	49,53, 57, 51
	$\text{Ni}^{\text{II}}\text{Co}^{\text{II}}$ (4)	$\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ (6,7)	–	$\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ (6) trinuclear based polymer	74, 61, 70
	–	$\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ (6,8)	–	–	67
	–	$\text{Ni}^{\text{II}}\text{Co}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	75
	–	$\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	79
$\text{H}_2\text{L}^{\text{sal-2,2-Me2pn}}$	–	$\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	62
	$\text{Ni}^{\text{II}}\text{Co}^{\text{II}}$ (6)	$\text{Ni}^{\text{II}}\text{Co}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	74, 62
	–	$\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	62
$\text{H}_2\text{L}^{\text{sal-bu}}$	$\text{Ni}^{\text{II}}\text{Co}^{\text{II}}$ (4)	$\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$ (6)	–	–	74, 69
$\text{H}_2\text{L}^{\text{acpn-en}}$	–	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (5)	–	$\text{Cu}^{\text{II}}_3\text{Fe}^{\text{III}}$ (6) based polymer	54, 77
$\text{H}_2\text{L}^{\text{acpn-pn}}$	–	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ (4,6)	$[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}]_2$ (5,6)	–	55, 59
	–	$\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$ (6)	–	–	65
	–	–	–	–	–
	–	$\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ (6)	–	$\text{Cu}^{\text{II}}_3\text{Mn}^{\text{II}}$ (6)	80

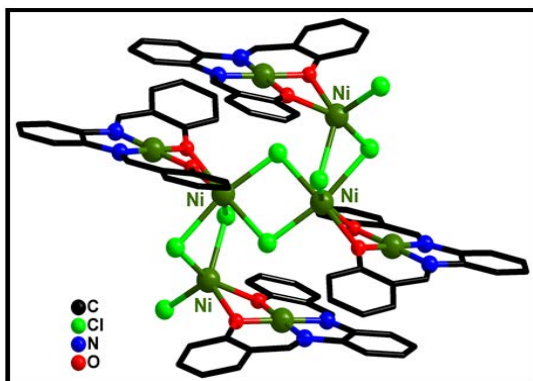


Fig. 4. Crystal structure of octanuclear $[Ni_8^{II}(L^{sal-op})_4Cl_6 \cdot (H_2O)_{0.5}]$ compound. Hydrogen atoms are omitted for clarity⁷¹

Copper(II)/nickel(II)–4f metal ion complexes

A number of copper(II)/nickel(II)–lanthanide compounds are known from this class of ligands.^{81–89} The types of systems include: (i) Dinuclear $Cu^{II}Pr^{III}$, $Cu^{II}Gd^{III}$, $Ni^{II}Pr^{III}$, $Ni^{II}Gd^{III}$ and $Ni^{II}Yb^{III}$,^{81–84} (iii) Trinuclear $Cu^{II}Ce^{III}Cu^{II}$, $Cu^{II}Sm^{III}Cu^{II}$ and $Cu^{II}Gd^{III}Cu^{II}$, $Cu^{II}Dy^{III}Cu^{II}$,^{85–87} (iii) Dimer-of-dinuclear $[Cu^{II}Pr^{III}]_2$ (linker is 4,4'-bipyridine, pyrazine),⁸¹ Dimer-of-dinuclear $[Cu^{II}Eu^{III}]_2$ (linker is nitrate),⁸⁸ $[2 \times 1 + 1 \times 1]$ Dinuclear–mononuclear cocrystals of i) one Dinuclear $Ni^{II}Pr^{III}$ and one mononuclear Ni^{II} units⁸¹ ii) one Dinuclear $Cu^{II}Er^{III}$ and one mononuclear Cu^{II} units⁸⁹ (iv) $[3 \times 1 + 1 \times 2]$ Trinuclear–mononuclear cocrystal of one $Cu^{II}Gd^{III}Cu^{II}$ and two Cu^{II} units.⁹⁰

For all the above mentioned copper(II)/nickel(II)–lanthanide compounds the copper(II)/nickel(II) ion is four coordinated with square planer geometry except the case of one $Cu^{II}Gd^{III}Cu^{II}$ and trinuclear $Cu^{II}Dy^{III}Cu^{II}$ compounds⁸⁷ (derived from H_2L^{sal-pn}) in which the copper(II) centre is five coordinated with bridging oxygen atom of trifluoro acetate ligand to form square pyramidal geometry. Whereas the coordination number of Ln(III) varies from seven to ten. Among the above mentioned systems crystal structure of $[3 \times 1 + 1 \times 2]$ trinuclear–mononuclear cocrystal of one $Cu^{II}Gd^{III}Cu^{II}$ and two Cu^{II} units are shown in Figure 5.

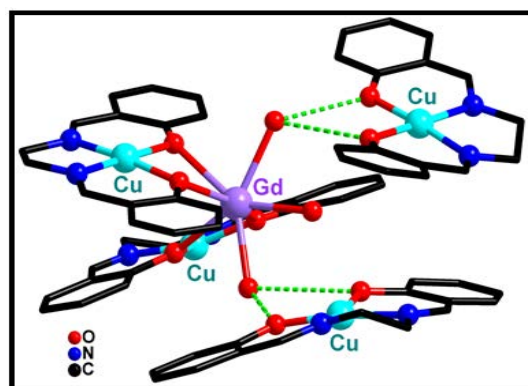


Fig. 5. Crystal structure of a pentanuclear $[3 \times 1 + 1 \times 2]$ cocrystal $[(Cu^{II}L^{sal-en})_2Gd^{III}(H_2O)_3]\{Cu^{II}L^{sal-en}\}_2(ClO_4)_3$. Hydrogen atoms and perchlorate ions are omitted for clarity⁹⁰

Table 4: The coordination number of second metal centre(s) (Ln^{III}-metal ion) and the ligand systems from which the above mentioned types of Copper(II)/nickel(II)-4f-block metal ion complexes have been reported

	Dinuclear (CN of Ln ^{III})	Trinuclear (CN of Ln ^{III})	Dimer-of-dinuclear/Cocrystal (CN of Ln ^{III})	Reference no.
H_2L^{sal-en}	–	$Cu^{II}Ce^{III}Cu^{II}(10)$	–	85
	$Cu^{II}Pr^{III}(8)$	–	Dimer-of-dinuclear	81
	$Ni^{II}Pr^{III}(9)$	–	$[Cu^{II}Pr^{III}]_2(9)$	81
	–	–	Cocrystal of one dinuclear $Ni^{II}Pr^{III}$ and one mononuclear Ni^{II} unit(9)	81
	$Cu^{II}Gd^{III}(7,9)$	–	Dimer-of-dinuclear $[Cu^{II}Eu^{III}]_2(9)$	88
$H_2L^{sal-opda}$	$Ni^{II}Gd^{III}(8)$	–	Cocrystal of one trinuclear $Cu^{II}Gd^{III}Cu^{II}$ and two mononuclear Cu^{II} unit(7,8,9)	83,84,90
	$Ni^{II}Yb^{III}(8)$	–	–	82
$H_2L^{sal-1,1-Me2en}$	–	$Cu^{II}Ce^{III}Cu^{II}(10)$	–	82
H_2L^{sal-pn}	–	$Cu^{II}Ce^{III}Cu^{II}(10)$	Cocrystal of one dinuclear $Cu^{II}Er^{III}$ and one Cu^{II} units(9)	86, 89
	–	$Cu^{II}Sm^{III}Cu^{II}(10)$	–	86
	–	$Cu^{II}Gd^{III}Cu^{II}(8,9)$	–	87
	–	$Cu^{II}Dy^{III}Cu^{II}(7)$	–	87
	$Cu^{II}Gd^{III}(9)$	–	–	83
$H_2L^{acpn-en}$	–	$Cu^{II}Gd^{III}Cu^{II}(7)$	Cocrystal of one Trinuclear $Cu^{II}Gd^{III}Cu^{II}$ and one Cu^{II} unit(7)	90

CONCLUSION

Compartmental Schiff base ligand and their metal complexes are one of the most important chemical classes of compounds having a variety of important feature and structural diversity. The nuclearity and dimensionality of the coordination compound derived from single compartmental Schiff bases ligand may be increased by employing bridging ligand like azide, dca, thiocyanate, nitrate, formate, acetate etc. Several review articles were published earlier on Schiff base compound and their catalytic activity, biological applications etc. But regarding the structural aspects of co-ordination compound derived from single compartmental acyclic Schiff base ligand having N-, O- donor centre in which the amine is a diamine is not reviewed yet. In these studies particular attention is devoted to copper (II)/nickel(II)-second metal ion compounds (s-, p-, d¹⁰-, 3d-, 4f- block metal) derived from single-compartmental acyclic salicylaldehyde-diamine and acetophenone diamine Schiff base ligand systems. The significance of this survey is to mention which second metal ions are used in the copper(II)/nickel(II)-second metal ion compounds and so definitely the types of compounds are not restricted among the types

mentioned. This survey also present the significant structural aspects of coordination compounds derived from acyclic single-compartmental diamine Schiff base ligand. The structural versatility and exciting structural aspects of eight salicylaldehyde-diamine and eight acetophenone-diamine single-compartmental Schiff base copper(II)/nickel(II)-second metal (s-, p-, d¹⁰-, 3d-, 4f- block metal) compounds have been reviewed in this review article. Therefore, it is to be expected that more unusual coordination architectures will be possible from single-compartmental diamine Schiff base ligand system and the outcome of such designed structure will be expected to have tremendous importance to coordination chemistry and crystal engineering.

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Conflict of Interest

The author states that there is no conflict of interest.

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