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Decizie de indexare a faptei de plagiat la poziţia

00362 / 23.01.2017

şi pentru admitere la publicare în volum tipărit

care se bazează pe:

A. Nota de constatare şi confirmare a indiciilor de plagiat prin fişa suspiciunii inclusă în decizie.

Fişa suspiciunii de plagiat / Sheet of plagiarism's suspicion

	Opera suspicionată (OS) **Suspicious work**	**Opera autentică (OA)** **Authentic work**
OS	COSTIŞOR, Otilia, and LINERT, Wolfgang. On polynuclear complexes in 3d-4f system. *Reviews in Inorganic Chemistry*. 25. p.13-54. 2005.	
OA	COSTIŞOR, Otilia, and LINERT, Wolfgang. 3d-4f coordination compounds. *Trends in Inorganic Chemistry*. 8. p.89-106. 2004.	

Incidenţa minimă a suspiciunii / Minimum incidence of suspicion

p.13:02- p.13:05	p.89:01s - p.89:06s
p.14:02 - p.14:21	p.89:23s - p.89:16d
p.14:22 - p.18:07	p.89:19d - p.91:21d
p.15: Structurile 1,2,3,4	p.90: Structurile 1,2,3,4s
p.16: Structurile 5,6	p.90: Structurile 5,6d
p.17: Structurile 7,8	p.91: Structurile 7,8s
p.18: Structura 9	p.91: Structura 9s
p.18:08-p.21:11	p.91:22d- p.92:16d
p.21:17-p.22:30	p.92:25d- p.93:07d

Fişa întocmită pentru includerea suspiciunii în Indexul Operelor Plagiate în România de la
Sheet drawn up for including the suspicion in the Index of Plagiarized Works in Romania at
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Notă: Prin „p.72:00" se înţelege paragraful care se termină la finele pag.72. Notaţia „p.00:00" semnifică până la ultima pagină a capitolului curent, în întregime de la punctul iniţial al preluării.

Note: By „p.72:00" one understands the text ending with the end of the page 72. By „p.00:00" one understands the taking over from the initial point till the last page of the current chapter, entirely.

B. Fişa de argumentare a calificării de plagiat alăturată, fişă care la rândul său este parte a deciziei.

Echipa Indexului Operelor Plagiate în România

Fişa de argumentare a calificării

Nr. crt.	Descrierea situaţiei care este încadrată drept plagiat	Se confirmă
1.	Preluarea identică a unor pasaje (piese de creaţie de tip text) dintr-o operă autentică publicată, fără precizarea întinderii şi menţionarea provenienţei şi însuşirea acestora într-o lucrare ulterioară celei autentice.	✓
2.	Preluarea a unor pasaje (piese de creaţie de tip text) dintr-o operă autentică publicată, care sunt rezumate ale unor opere anterioare operei autentice, fără precizarea întinderii şi menţionarea provenienţei şi însuşirea acestora într-o lucrare ulterioară celei autentice.	
3.	Preluarea identică a unor figuri (piese de creaţie de tip grafic) dintr-o operă autentică publicată, fără menţionarea provenienţei şi însuşirea acestora într-o lucrare ulterioară celei autentice.	✓
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5.	Republicarea unei opere anterioare publicate, prin includerea unui nou autor sau de noi autori fără contribuţie explicită în lista de autori	
6.	Republicarea unei opere anterioare publicate, prin excluderea unui autor sau a unor autori din lista iniţială de autori.	
7.	Preluarea identică de pasaje (piese de creaţie) dintr-o operă autentică publicată, fără precizarea întinderii şi menţionarea provenienţei, fără nici o intervenţie personală care să justifice exemplificarea sau critica prin aportul creator al autorului care preia şi însuşirea acestora într-o lucrare ulterioară celei autentice.	✓
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10.	Preluarea identică a unor fragmente de demonstraţie sau de deducere a unor relaţii matematice care nu se justifică în regăsirea unei relaţii matematice finale necesare aplicării efective dintr-o operă autentică publicată, fără menţionarea provenienţei, fără nici o intervenţie care să justifice exemplificarea sau critica prin aportul creator al autorului care preia şi însuşirea acestora într-o lucrare ulterioară celei autentice.	
11.	Preluarea identică a textului (piese de creaţie de tip text) unei lucrări publicate anterior sau simultan, cu acelaşi titlu sau cu titlu similar, de un acelaşi autor / un acelaşi grup de autori în publicaţii sau edituri diferite.	
12.	Preluarea identică de pasaje (piese de creaţie de tip text) ale unui cuvânt înainte sau ale unei prefeţe care se referă la două opere, diferite, publicate în două momente diferite de timp.	

Notă:

a) Prin „provenienţă" se înţelege informaţia din care se pot identifica cel puţin numele autorului / autorilor, titlul operei, anul apariţiei.

b) Plagiatul este definit prin textul legii[1].

> „ …*plagiatul – expunerea într-o operă scrisă sau o comunicare orală, inclusiv în format electronic, a unor texte, idei, demonstraţii, date, ipoteze, teorii, rezultate ori metode ştiinţifice extrase din opere scrise, inclusiv în format electronic, ale altor autori, fără a menţiona acest lucru şi fără a face trimitere la operele originale…*".

Tehnic, plagiatul are la bază conceptul de **piesă de creaţie** care[2]:

> *„…este un element de comunicare prezentat în formă scrisă, ca text, imagine sau combinat, care posedă un subiect, o organizare sau o construcţie logică şi de argumentare care presupune nişte premise, un raţionament şi o concluzie. Piesa de creaţie presupune în mod necesar o formă de exprimare specifică unei persoane. Piesa de creaţie se poate asocia cu întreaga operă autentică sau cu o parte a acesteia…"*

cu care se poate face identificarea operei plagiate sau suspicionate de plagiat[3]:

> *„…O operă de creaţie se găseşte în poziţia de operă plagiată sau operă suspicionată de plagiat în raport cu o altă operă considerată autentică dacă:*
> *i) Cele două opere tratează acelaşi subiect sau subiecte înrudite.*
> *ii) Opera autentică a fost făcută publică anterior operei suspicionate.*
> *iii) Cele două opere conţin piese de creaţie identificabile comune care posedă, fiecare în parte, un subiect şi o formă de prezentare bine definită.*
> *iv) Pentru piesele de creaţie comune, adică prezente în opera autentică şi în opera suspicionată, nu există o menţionare explicită a provenienţei. Menţionarea provenienţei se face printr-o citare care permite identificarea piesei de creaţie preluate din opera autentică.*
> *v) Simpla menţionare a titlului unei opere autentice într-un capitol de bibliografie sau similar acestuia fără delimitarea întinderii preluării nu este de natură să evite punerea în discuţie a suspiciunii de plagiat.*
> *vi) Piesele de creaţie preluate din opera autentică se utilizează la construcţii realizate prin juxtapunere fără ca acestea să fie tratate de autorul operei suspicionate prin poziţia sa explicită.*
> *vii) In opera suspicionată se identifică un fir sau mai multe fire logice de argumentare şi tratare care leagă aceleaşi premise cu aceleaşi concluzii ca în opera autentică…"*

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[1] Legea nr. 206/2004 privind buna conduită în cercetarea ştiinţifică, dezvoltarea tehnologică şi inovare, publicată în Monitorul Oficial al României, Partea I, nr. 505 din 4 iunie 2004

[2] ISOC, D. *Ghid de acţiune împotriva plagiatului: bună-conduită, prevenire, combatere*. Cluj-Napoca: Ecou Transilvan, 2012.

[3] ISOC, D. *Prevenitor de plagiat*. Cluj-Napoca: Ecou Transilvan, 2014.

Trends in
Inorganic Chemistry
Vol. 8, 2004

3d-4f coordination compounds

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Abstract. This paper reviews the coordination architectures obtained in 3d-4f metal ion systems along with a description of their general particularities. The work is organised roughly by the ligand nature. The structural particularities as well as some specific properties are discussed in detail.

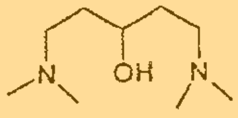
1. INTRODUCTION

There has been a great deal of recent interest in heterobinuclear complexes[1] containing both transitional metal and lantanide metal ions[2,3]. Studies on these complexes are mostly concerned on magnetic properties in conection with their aplication in advanced materials science and in medicinal inorganic chemistry. Lanthanide coordination chemistry is dominated by the oxygen-donor ligands. However, nitrogen-bonded complexes have also been obtained and well characterized. Certain key features must kept in mind when lanthanide chemistry is explored: the preferred high coordination number, their large ionic radii and their high charge. Lanthanide complexes are characterized kinetic lability evidentiated by formation of hydroxides in aqueous media. Amines alone are poor donors for lanthanides in water; however, incorporated into ligands which also contain oxygen donor atoms, they form quite stable Ln(III) complexes, much more stable than the analogous oxo acids. Their stability is increased when chelating ligands are present.

For the purpose of this review, we will make a recension of the 3d-4f coordination compounds along with a description of their properties compared to the parent precursors. We will describe some individual systems in more detail. The work is organised roughly by the ligand nature.

2. AMINOALCOHOLS AND AMINOPHENOLS AS LIGANDS

Tridentate aminoalcohols of the type 1, and aminophenols like 2, have been widely used to obtain homo- and heteropolynuclear complexes in which the oxygen atom bridges two metal ion thereby beeing favoured spin coupling. Binuclear blue complex $CuPr(1-H)_2(hfacac)_2(O_2CCF_3)L$, 3, (L = 2-methyl-2,4,6-tris (trifluoromethyl)-1,3-dioxane-4,6-diolato)) and the trinuclear one $LnCu_2(hfacac)(1-H)_3(O_2CCH_3)_2(O_2CCF_3)(hfacacH)(THF)$, 4, where Ln = Nd, Pr, have been reported for some of the lanthanide(III) metal ions[4]. The complexes can either be readily sublimed or thermally decomposed to the corresponding oxides, which along with their high solubility in organic solvents makes these compounds possible candidates as precursors for ceramic applications.



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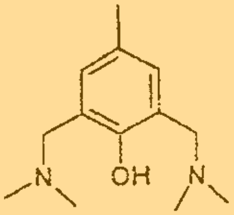

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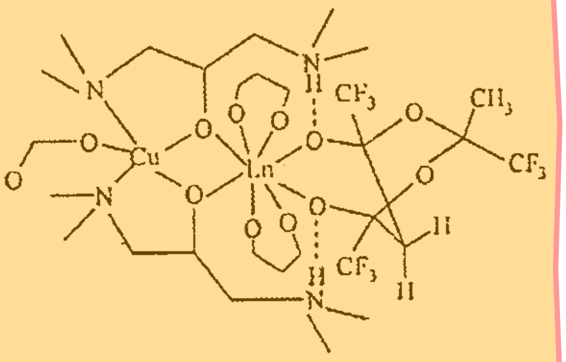

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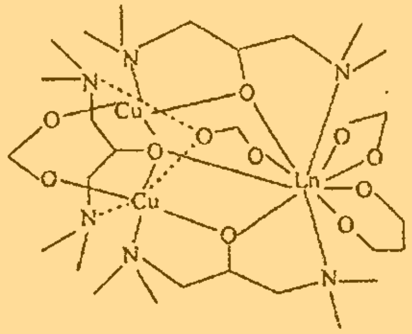

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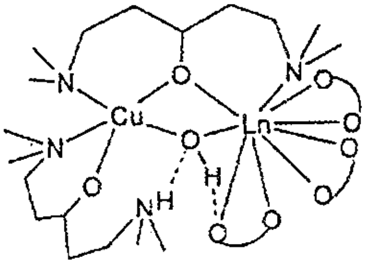
The binuclear compound $PrCu(2\text{-}H)(2)(OH)(hfacac)_3$, 5, and the tetranuclear one $[La^{III}Cu^{II}(2\text{-}H)(2)(OH)(O_2CCF_3)_3]_2$, 6, have been obtained stating form $Cu(2\text{-}H)_2(H_2O)$ which acts as ligand toward one lanthanide centre. Structural analyses show that the trigonal bipyramidal geometry of the copper centre in the precursor is preserved in the heterodinuclear complex but the nature of the donor atoms is now different.



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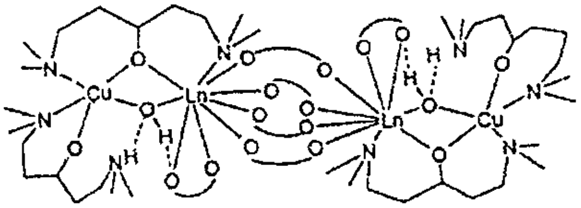

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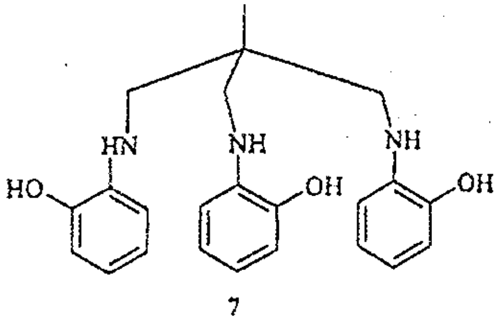
The compound 6 consists of two dinuclear units of $LaCu(2\text{-}H)(2)(\mu\text{-}OH)(O_2CCF_3)_3$ where the $La(O_2CCF_3)_3$ unit is linked to the copper(II) monomer unit *via* a hydroxo and a phenoxo bridge. The magnetic moment of 5 is slightly smaller than the theoretic value assuming that both Pr(III) and Cu(II) are noninteracting ions. At low temperature, antiferromagnetic interaction can be noticed.

Tripodal ligands 1,1,1-tris(((2-hydroxybenzyl)amino)methyl)ethane), 7, and tris (2-hydroxybenzylaminoethyl)amine, 8, are capable to bind a 3d an 4f metal ions simultaneously thanks to the flexibility of their arms. They can act in protonated or deprotonated form. The trinuclear cationic $[LnNi_2(7\text{-}3H)_2]^{2+}$ complexes have been obtained as a part of the following compounds: $[LnNi_2(7\text{-}3H)_2(CH_3OH)_{1/2}(CH_3CH_2OH)_{1/2}(H_2O)]ClO_4\cdot0.5CH_3OH\cdot0.5CH_3CH_2OH\cdot4H_2O$, 9, $[DyNi_2(7\text{-}3H)_2(CH_3OH)(H_2O)]ClO_4\cdot CH_3OH\cdot H_2O$ and $[YbNi_2(7\text{-}3H)_2(H_2O)]ClO_4\cdot2.58H_2O$ and their structure resolved[6]. For example, the solid-state structure of $[LaNi_2(7\text{-}3H)_2]^{2+}$ shows that La(III) is eight coordinated by two $[7\text{-}3H]^{3-}$ ligands, each of which is tridentate with respect to the La(III) ion and hexadentate with respect to one Ni(II) ion. Two solvent molecules complete the square antiprism coordination sphere around La(III).



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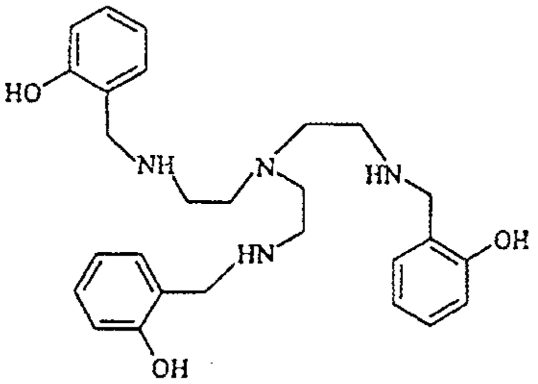

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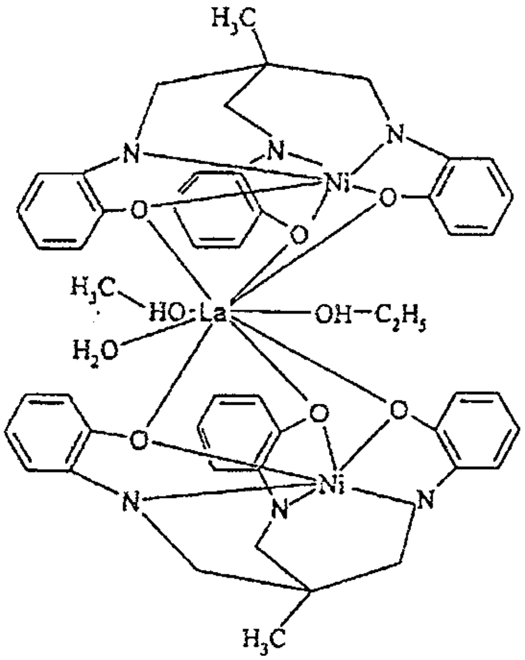

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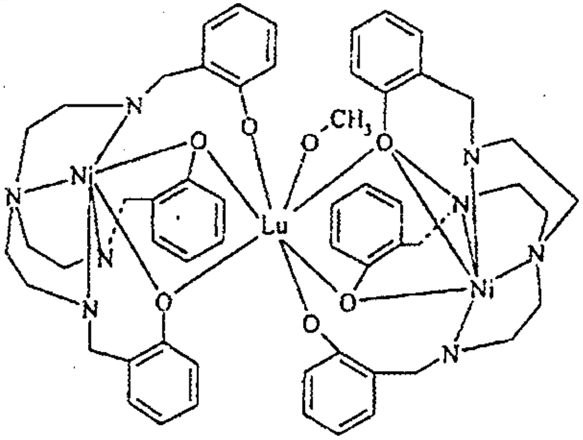
Each $[7\text{-}3H]^{3-}$ ligand encapsulates a Ni(II) ion *via* its three amine and three phenolato functions, rendering each Ni(II) coordination sphere approximately octahedral. Similar structures have been reported for the $[DyNi_2(7\text{-}3H)_2]^{2+}$ and $[YbNi_2(7\text{-}3H)_2(H_2O)]^{2+}$ cations. The magnetic behaviour of the compound containing $[LaNi_2(7\text{-}3H)_2]^{2+}$cation is consistent with the presence of two magnetically isolated octahedral Ni(II) centres whereas the other two complexes show antiferromagnetic exchange interactions between the Ln(III) and the Ni(II) ions.

Isostructural complexes, $[LnNi_2(8\text{-}3H)_2(CH_3OH)]X{\cdot}mCH_3OH{\cdot}nH_2O$, where for Ln = Pr, X= ClO_4 and for Ln = Sm, Tb, Er, Lu X = NO_3 containing a trinuclear unit **10**, have been obtained[7]. It has been established that each $[Ni(8\text{-}3H)]^-$ unit acts as a tridentate ligand toward the Ln^{III} ion *via* two bridging and one nonbridging phenolate donors. In all of the structurally characterised complexes, Ln^{III} is seven-coordinated with flattened pentagonal bipyramidal geometry.



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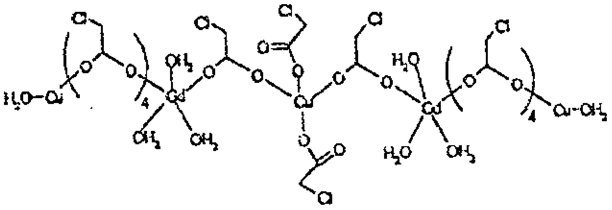
3. CARBOXYLATE AND CARBOXYLATE DERIVATIVES AS LIGANDS

3.1 Monocarboxylate Ligands

The ability of carboxylate groups to bridge metal ions and thus forming polynuclear compounds is well known. However the carboxylate-bridged mixed metal complexes involving both 3d and 4f metal ions is enough limited. Complexes containing only carboxylate groups as ligand and those containing aditionaly polydentate ligands have been obtained.

The centrosymmetric pentanuclear $[Cu_3Gd_2(O_2CCH_2Cl)_{12}(H_2O)_8]\cdot 2H_2O$, 11, complex bridged only by carboxylate groups has been reported[8]. Structural analyses have shown that cloroacetate anion acts as unidentate and bidentate ligand and that Gd(III) ion adopts an eight-coordinated distorted square-antiprism geometry.



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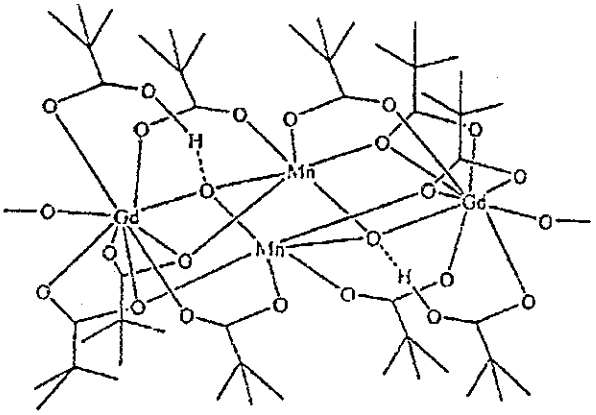
Cui et al[9] reported the syntheses of the heterometallic copper-lanthanide clusters $Cu_{12}La_6(\mu_3\text{-}OH)_{24}(\mu\text{-}O_2CCH_2Cl)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)][(NO_3)_4(OH)]\cdot 10H_2O$ and $Cu_{12}Nd_6(\mu_3\text{-}OH)_{24}(\mu\text{-}O_2CCCl_3)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)][O_2CCCl_3]_5\cdot 22H_2O$ using perchlorate anions a templates. All the compounds were studied by X-ray cristallography and it has been found that they contain the $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}]^{18+}$ core of pseudo-cubic *Oh* symmetry. A $\mu_{12}\text{-}ClO_4^-$ anion with the highest coordination number of twelve is encapsulated in this cluster. The complexes obey the Curie-Weiss law with θ of -11.5 and -1.6 K for $Cu_{12}La_6$ and $Cu_{12}Nd_6$, respectively. The $Cu_{12}Nd_6$ cluster exhibit a very strong antiferromagnetic interaction between pairs of Cu(II) ions which overcome the actually ferromagnetic copper(II)-neodymium(III) ineraction, and $Cu_{12}Nd_6$ cluster exhibit an overall weak antiferromagnetic interaction. Similar species in which piridinoacetate and pyridinepropionate (pyb) bridges Cu(II-Ln(III) ions through carboxylate groups to form heteropolynuclear species of the general type $Cu_{12}La_6(\mu_3\text{-}OH)_{24}(Pyb)_{12}(H_2O)_n(ClO_4)](ClO_4)_{17}\cdot xH_2O$ have been reported.

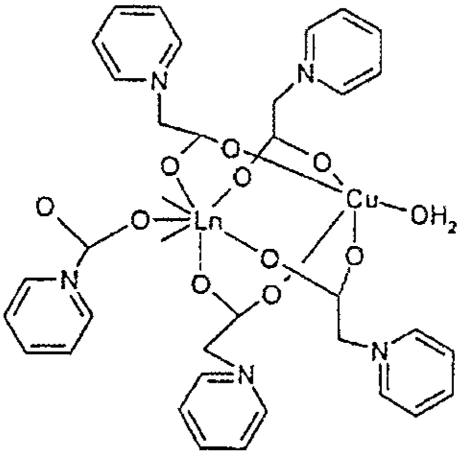
Using $Mn_6O_2(C_4H_8O)$ as starting reagent, Benelli et al[10] obtained two isostructural Mn(III)Ln(III) pivalates, $[Gd_2Mn_2O_2(O_2CCMe)_8(HO_2CCMe)_2]CH_2Cl_2$ where Ln = Gd, Dy. The X ray structural studies reveal a $\{Gd_2(\mu_3\text{-}O)Mn_2(\mu_3\text{-}O)Gd\}$, 12, core based on a Mn(III) di-μ-oxo-bridged dimmer, each oxide further bridging to a Gd(III) centre. Each Mn(III) ion has a distorted octahedral environment and each Gd (III) ion is nine coordinated with distorted capped square-antiprismatic geometry. Using a model based on a square with a metal at each corner, it has been calculated the exchange parameters for coupling between Mn(III) centre, Mn(III) and gadolinium(IIII) and gadolinium(III) centres, $J_2 = -62.91$, $J_1 = +2.44$ and $J_3 = -0.012\ cm^{-1}$, respectively.

Among the compounds containing both carboxylate and amino function, betaines occupy a special place. They adopts the zwiterionic form and acts as ligand only through carboxylate oxygen donors. Two types of carboxylate bridged $Cu^{II}_2Ln^{III}_2$ complexes formulated as $[Cu_2Ln_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$, where Ln = La, Ce, Gd and $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ where Ln = Gd, Sm and bet = betaine, (trimethylammonioacetate) were obtained[11]. The powder X-ray difraction studies showed that compounds in the first series are isomorphous. Structural studies on monocrystals show that the La-Cu and Ce-Cu complexes contain a tetranuclear $[Cu_2Ln_2(bet)_{10}(H_2O)_8]^{10+}$ cation in which each of the Cu atom is quadruply bridged to a Ln(III) ion by the μ_2-carboxylate groups into a dinuclear subunit. A pair of such dinuclear subunits is bridged by two carboxylate groups to form a tetranuclear cation. The two complexes $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ are isomorphous and their magnetic behaviour obeys the Curie-Weiss law, showing very weak antiferromagnetic interaction. Therefore, it may be concluded that shielding of the 4f electrons by the outer shell electrons very effectively precludes significant coupling interactions between the lanthanid 4f electrons and copper 3d electrons in a carboxylate-bridged system.

Yang et al[12] obtained two types of carboxylate-bridged copper(II)-lanthanide(III) complexes, $[CuLn(C_5H_5N^+CH_2CO_2^-)_5(H_2O)_5][ClO_4]_5\cdot 2H_2O$, 13, $(Ln^{III} = La^{III}, Nd^{III})$ and $[Cu_3Nd_2(C_5H_5N^+CH_2CO_2^-)_{10}(NO_3)_2(H_2O)_8][ClO_4]_{10}\cdot 4H_2O$ using pyridinioacetate as ligand in an one-step reaction strongly affected by the pH of the solutions. Thus, at low pH, the dinuclear complex is formed and further aggregates to construct the larger pentanuclear cluster whereas at pH ≥ 3.5, an octadecanuclear cluster is formed.

The octadecanuclear isomorphous clusters $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(C_5H_5N^+CH_2CO_2)_{12}(H_2O)_{18}(\mu_6\text{-}NO_3)](PF_6)_{10}(NO_3)_7\cdot 12H_2O$ where Ln = Sm^{III} or Gd^{III} [13] and $[Cu_{12}Ln_6(\mu\text{-}OH)_{24}(C_5H_5NCH_2CO_2)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)](ClO_4)_{17}\cdot nH_2O$ for Ln = Nd, Gd[14] have been obtained and their structural studies underline the role of the counterion in crystallization which, however, does not depend on the encapsulated anion. The structure of the





13

Sm-Cu complex has shown Cu...Cu distances in the range of 3.36-3.48 and Cu...Sm separation of 3.48-3.57 Å whereas the Sm(III) atoms are separated at distances of 7.02-7.07 Å and that the $C_5H_5N^+CH_2CO_2^-$ ligand act uniquely in the μ-carboxylato-*O-O'* mode, each bridging a copper(II) and a lanthanoid(III) ion. The magnetic behaviour of the Cu-Gd complex has been explored and the global antiferromagnetic interaction with C = 0.00331 Kcm^{3}mol^{-1} and θ = -1.46 K has been explained based on the structure of Sm-Cu complex as the differences between their core are minor. Thus, both a weak antiferomagnetic interaction between the Cu...Cu atoms and a weak ferromagnetic interaction between the Cu...Gd atoms has been concluded to coexist.

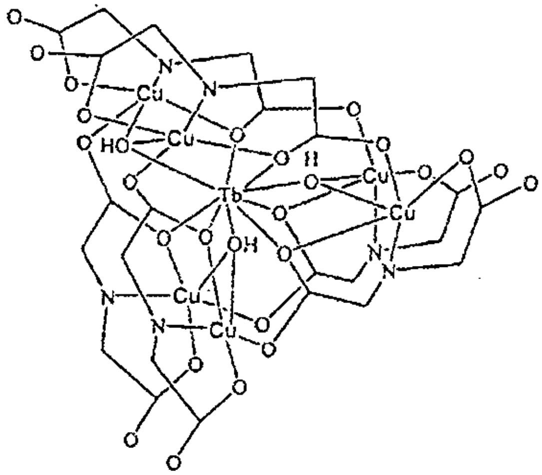
Using $C_5H_5N^+CH_2CH_2CO_2^-$ as ligand, the clusters $[Cu_{12}Ln_6(\mu_3\text{-}H)_{24}(C_5H_5NCH_2CH_2CO_2)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)](ClO_4)_{17}\cdot 16H_2O$ where Ln^{III} = Gd^{III}, Sm^{III} were obtained[15]. As in the previous reported $Cu_{12}Ln_6$ clusters, the perchlorate anion is used as template for the formation of the large polymetallic assemblies. The additional methylene group explains the presence of only ten of the $C_5H_5N^+CH_2CH_2CO_2^-$ ligands which act in the μ -carboxylato-*O-O'* mode, while the other two act in the carboxylato-*O-O'* mode.

3.2 Monocarboxylic amino-acid ligands

Taking advantage of the properties of the aminoacid ligands to bridge the metal centres, mixed-metal complexes have been designed and synthesized. Usually, the 3d-4f polymetallic compounds have been synthesized by using 3d metal complexes as ligands.

Starting from $[Ni(pro)_2]$, where pro stands for proline, as complex ligand, the complexes $[Ln\{Ni(pro)_2\}_6]X_3\cdot 6MeOH$, where for Ln = Sm, X = ClO_4^-, BF_4^-, PF_6^-, I^-, NO_3^-,[16] and for Ln = Eu,[17] X = ClO_4^- were obtained. It has been established that in all the complexes, the six $Ni(pro)_2$ units are coordinated to the rare earth metal ion which thus arises the coordination number of twelve with icosahedral geometry.

The isomorphous heteronuclear complexes $[LnCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4]\ (ClO_4)_2\cdot 25H_2O$, 14, where Ln = La - Ho and H_2L stands for aminodiacetic acid have been obtained[18, 19]. The structural analyses of the terbium(III) compound have shown that it is located in the centre of the trigonal prismatic cage formed by six Cu^{2+} ions. A ferromagnetic coupling between Tb^{3+} and Cu^{2+} ions has been noticed at low temperatures. Similar effect has been found for $[GdCu_6]$ compound whereas the magnetic behaviour of $[DyCu_6]$, $[HoCu_6]$, $[NdCu_6]$

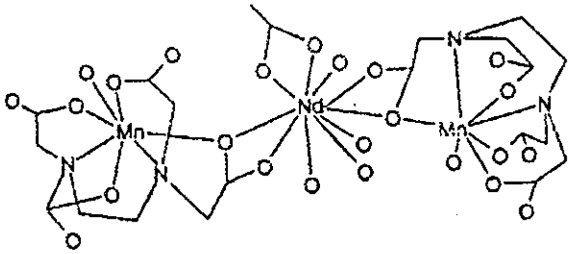


14

and $[PrCu_6]$ systems is affected by factors including Ln-Ln, Cu-Cu, Ln-Cu interactions, the ligand field effects of the Ln^{3+} ion and field saturation effects.

The isomorfous complexes $[LnCuCl(NTA)(H_2O)_6]ClO_4\cdot H_2O$ where Ln = La, Ce, Pr, Gd, Tb, Dy Ho, Er, Tm, and Lu, in which nitrilotriacetic anion act as a tripodal ligand have been obtained[20]. It has been found that the structure of the complexes is polymeric and strongly affected by the ionic radii of the lanthanide ion as well as by the nature of the counterion[21]. For example the coordination environment of the Gd(III) is nine and that of the Eu is eight. Except the La(III) compound, all the other exhibit an overall antiferromagnetic feature.

More rarely are the Mn-Ln and Co-Ln complexes. However, the heterometallic compounds $Nd_2Mn_3(edta)_3(H_2O)_{11}\cdot 12H_2O$, (15), and $Gd_2Co_3(edta)_3(H_2O)_{11}\cdot 12H_2O$ have been reported and demonstrated that they are isomorphous consisting of a two-dimensional heterometallic sheet[22].



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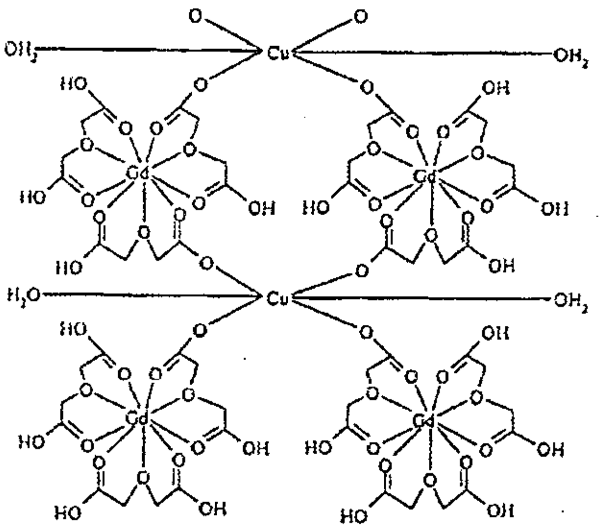
3.3. Dicarboxylate ligands

Discrete units and extended systems have been obtained by using dicarboxylate ligands. Extendend solids have been obtained by assembling lanthanide and copper ions in the 3D series of complexes $[Ln_2Cu_3\{O(CH_2COOH)_2\}_6\cdot(H_2O)_6.xH_2O]_n$, with Ln = Gd, Eu, Nd, Pr, Er[23]. Their structures have been resolved and it has been found that they all crystallize in the hexagonal systems. For example, the X-Ray studies of $[Gd_2Cu_3\{O(CH_2COOH)_2\}_6\cdot 9H_2O]$, 16, show a complicated three-dimensional network structure in which the Gd^{3+} ion is nine coordinated with a tricapped trigonal prism arrangement and the copper(II) ion has a distorted square-planar coordination geometry[24]. It has been noted that the Gd-O(ether) bond is longer than Gd-O(carboxylate) which prove that the coordination ability of carboxylato group is much stronger than that of the ether oxygen atom.

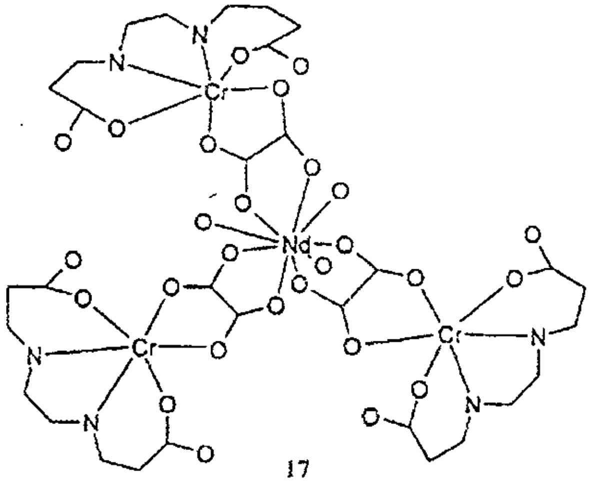


16

Extending the works, Rizzi et al[25] reported the complexes of the isostructural series of polymers formulated as $\{(Cu_3Ln_2(O(CH_2COO)_2)_6\}\cdot 12H_2O\}_n$, where Ln = Dy, Ho, Er. As in the previous compound, the Ln(III) ion coordinates to the two inner carboxylate oxygens and to the ether oxygen of the three symmetry-related $O(CH_2COO)_2^{2-}$ anions to define a tricapped trigonal prismatic environment. Each Cu atom coordinates to the remaining outer carboxylates oxygens belonging to four $O(CH_2COO)_2^{2-}$ anions and to two aqua ligands. The molar magnetic susceptibility were determined for the obtained compounds and bellow 50K antiferromagnetic interaction between copper ions in the extended structures has been proved. Also, the $\chi T(T) = f(T)$ curves profiles indicate that at low temperatures antiferromagnetic Ln - Cu (Ln = Dy, Ho, Er, Y) interactions are operative in the corresponding compounds.

Oxalate ion is a god candidate in preparing complexes which can act as ligands in order to obtain polynuclear complexes. Many oxalate-bridged complexes are well known for their ability to transmit electronic effects between paramagnetic centres separated from each other by more than 5 Å. It is well known that chromium (III) complexes are quite inert toward ligand substitution, allowing a good control over the reaction products. For this reason chromium-oxalate complexes have often been used as building blocks in assembling bi- and three dimensional networks.

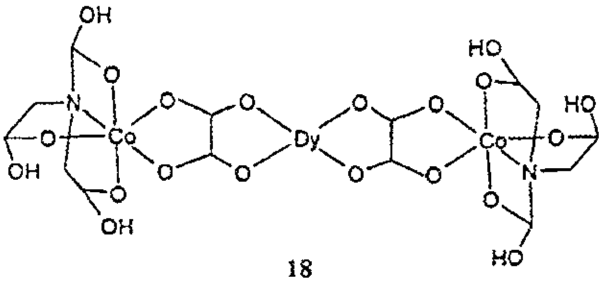
Polymeric 3d-4f coordination solids with stoichiometries $\{Ln^{III}Cr^{III}(ox)_3(H_2O)_4]_2 \cdot nH_2O$, where Ln = La, Ce, Pr, Nd, and *n* varies from 7 to 12, $[Eu^{III}Cr^{III}(ox)_3] \cdot 3(CH_3)_2SO \cdot 2H_2O$ and $[Tb^{III}Cr^{III}(ox)_3] \cdot 4(CH_3)_2NCHO \cdot H_2O$ have been obtained starting from tris(oxalate)chromium(III), $[Cr^{III}(ox)_3]^{3-}$ $(ox^{2-}=C_2O_4^{2-})$ as building block [26]. The crystal structures of $\{Ln^{III}Cr^{III}(ox)_3(H_2O)_4]_2 \cdot 12H_2O$, Ln = La, Ce show extended molecular array based on two types of symmetrically independent molecular chains with a ladder-type motif. Within the infinite ladder molecule, each Cr atom is surrounded by six oxygen atoms from three oxalate ligands and has slightly distorted octahedral coordination geometry. The Ln metal ions adopt a coordination number of ten, again with six oxygen atoms from the three bridging oxalate ligands and 4 additional oxygen atoms from coordinated water molecules. The study of the magnetic exchange interaction reveals the occurrence of an antiferromagnetic type interaction for Ce, Pr and Nd compounds facilitated by the convenient distances between the paramagnetic centres.



17

Using *unsym-cis*-$[Cr(eddp)(ox)]^-$ as a building block, where eddp stands for ehylenediamine-N,N'-dipropionate and serves as "end cap" ligand, the heteronuclear complex $\{Nd\{Cr(eddp)(ox)\}_3(H_2O)_3]\cdot 12H_2O$, sketched in 17, complex was synthesised[27].

Binuclear $[Dy\{Co(NTA)(\mu\text{-}ox)\}(H_2O)_7]Cl)$ and trinuclear $K\{Dy\{Co(NTA)(\mu\text{-}ox)\}_2(H_2O)_5]$, 18, complexes were obtained using $[Co(NTA)(ox)]^{2-}$ as building block[28].



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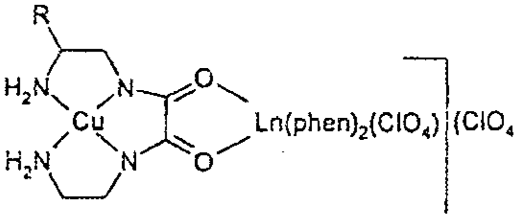
Heterobinuclear complexes $[(acac)_2Cr(ox)Ln(HBpz_3)_2]$ where Ln = Eu, Gd, Tb, Yb, Lu have been obtained starting from $[Cr(acac)_2(ox)]^-$ and $[Ln(HBpz_3)_2]^+$ as precursors, in molar ratio of 1:1[29]. The crystal structure of Cu-Yb compound shows that the Cr atom is located in a distorted octahedral environment and the Yb(III) ion has an eight-coordinate distorted square antiprismatic coordination geometry. The magnetic susceptibility data show a weak antiferromagnetic interaction between Gd(III) and Cr(III).

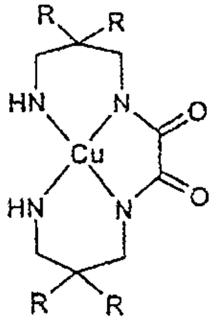
3.4. Amide as ligands

Oxamide and their derivatives have often been used to obtain discrete polynuclear complexes. They form stable complexes with some first row metal ions which thanks to the presence of the free coordination sites can further act as complex ligands. The copper(II) complexes of N,N'-bis(alkylaminoalkyl)oxamides. have been used as complex ligands to obtain binuclear complexes $Cu(L)Ln(phen)(ClO_4)_3$. 19 for Ln = Eu, Gd, Tb, Dy, Ho, Er[30] and 20 for Ln = La, Nd Gd, Dy, Ho, Er, Tb, and their structures have been formulated on the basis of spectral and magnetic studies[31]. The magnetic susceptibility measurements of Cu-Gd compound of the type 20 indicate a weak ferromagnetic interaction between the copper(II) and Gd(III) ions with J = 2.25 cm^{-1} while that of the type 19 shows antiferromagnetic interaction between Gd(III) and Cu(II).



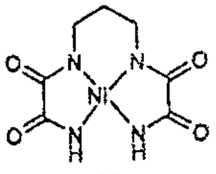
	R
19	H
20	CH_3

The discrete trinuclear compound $\{Gd(21)_2(H_2O)_4][NO_3]_3 \cdot 2H_2O$ has been obtained using the copper(II) precursor 21 as precursor. Structural analyses show the eight-coordinated gadolinium(III) ion and square-planar environment of the copper(II) ion. The Gd...Cu distances of 5.684 and 5.681 Å as well as the angle between the copper and gadolinium ions of 85.22(1)° lead to the shortest distances between the copper ions. These distances might explain the found values $J_{Gd-Cu} = -0.77(3)$ and $J_{GCu-Cu} = 0.42(4)$ cm^{-1}[32].



	R
21	CH_3
22	H

Heterotrinuclear complexes, $[Ni(L)\{Ln(HBpz_3)_2\}$, Ln = Eu, Tb or Yb and $[Ni(L)\{Ln[HB(pz)_3]_2\}_2]$, Ln = Sm to Lu, have been prepared when the complex ligand $[NiL]^{2-}$ = 23 and 24, respectively, were used. The two free O,O' sites of the complex ligands allow the formation of stable trinuclear Ln^{III}-Ni^{II}-Ln^{III} structures when the tripodal ligand $HB(pz)_3^-$ = hydrotris(pyrazol-1-yl)borate was used[33]. The crystal structure analyses of $[(23)Yb_2]$ and $[(24)Lu_2]$, 25, were performed and the distances Ni...Yb of 5.580 Å and Ni...Lu of 5.590 Å were found to be shorter than that in some Cu-Ln-oxamate complexes. Spectral studies as well as magnetic measurements support the square-planar environment of the nickel(II) ion. Magnetic studies on the $[(24)Gd_2]$ reveal the values of J = -0.002 cm^{-1} and g =2.03 which means that no interaction between the two paramagnetic gadolinium(III) centres exist.



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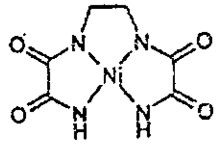

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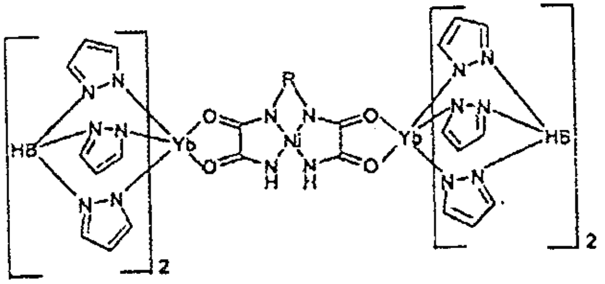


R= $-CH_2CH_2CH_2-$
$-CH_2CH_2-$

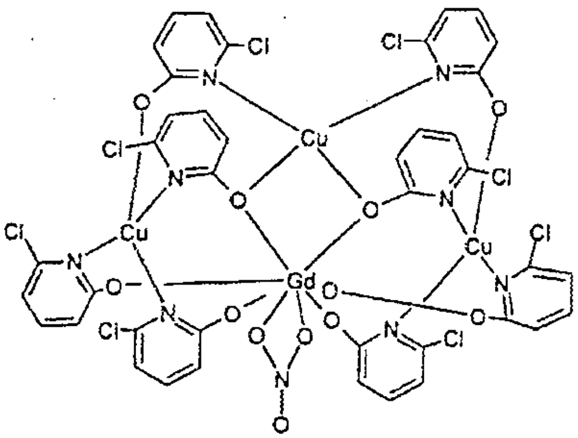
25

Pentanuclear Cu-Ln complexes of formula $\{Ln[22]_2[(22)(H_2O)]_2\}$ $[ClO_4]_3 \cdot 7H_2O$ (Ln = Dy, Gd), $\{Ln[22][(22)(H_2O)]_3\}[PF_6]_3 \cdot 4.5H_2O$ (Ln = Ho, Gd) have been reported and it has been found that these are isomorphous[34]. For the Gd complexes the magnetic susceptibility data have shown that the ground-state spin for the $[Gd^{III}Cu^{II}_4]$ unit is S=11/2, the Gd^{III}-Cu^{II} interaction being ferromagnetic.

4. Pyridine derivatives

The copper pyridonate complexes $([Cu_6Na(mhp)_{12}](NO_3)$, where mhp = 6-methyl-2-pyridonate, and $[Cu_2L_4]$ where L = 6-cloro-2-pyridonate (chp), 6-bromo-2-pyridonate (bhp) or 6-fluoro-2-pyridonate(fhp) have been used as ligands toward lanthanide(III) metal ions to obtain heterometallic complexes[35]. The studies reveal that the nuclearity and structure of the obtained compounds depend on the nature of the used pyridone, the solvent and the specific lanthanid involved. Thus, depending on the nature of the solvent, the complexes $[Cu_3Ln(chp)_8(NO_3)]$ (Ln = Gd, Pr, Nd, Sm, Er) and $[Cu_3Yb(chp)_8(Hchp)(NO_3)_2]$, 26, $[Cu_3Ln(bhp)_8(NO_3)]$ (Ln = Sm, Gd with Cu_3Ln core and $[\{CuLn(\mu\text{-}OH)(chp)_2(NO_3)_2(H_2O)_2\}_2]$, 27, (Ln = Yb, Er), $[\{CuYb(\mu\text{-}OMe)(chp)_2(NO_3)_2(MeOH)_2\}_2]$ and $(\{CuEr(\mu\text{-}OH)(bhp)_2(NO_3)_2(Hbhp)_2\}_2)$, $(\{CuLn(\mu\text{-}OMe)(bhp)_2(NO_3)_2(MeOH)_n\}_2$ (Ln = Pr, Nd, n=3; Gd, Er, *n* = 2),

$[Ln_2Cu_2(OMe)_2(mhp)_4(NO_3)_4(Hmhp)_2(MeOH)_4]$, (Ln = La, Ce, Nd) and $[Ln_2Cu_2(OMe)_2(mhp)_4(NO_3)_4(Hmhp)_2(MeOH)_2]$, (Ln = Gd, Dy, Yb) with Cu_2Ln_2 cores have been obtained[36].



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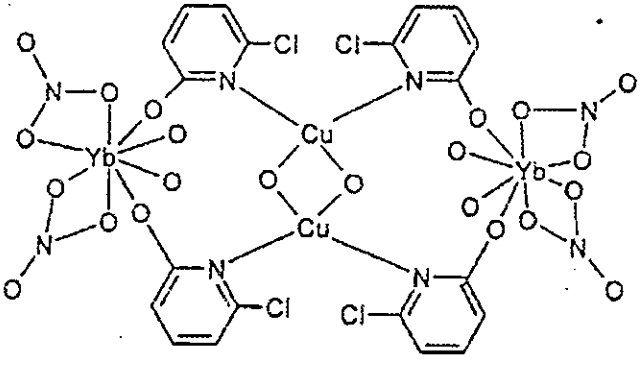
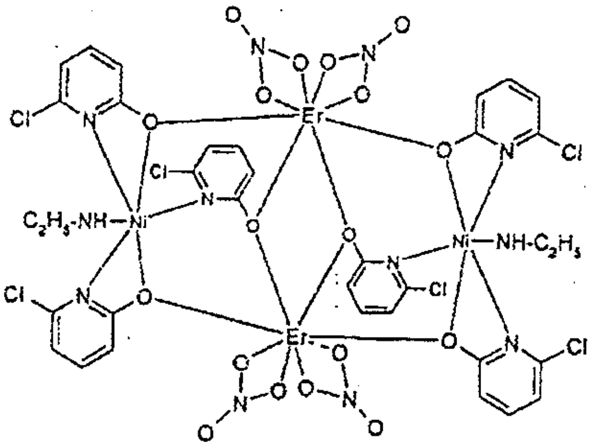


27

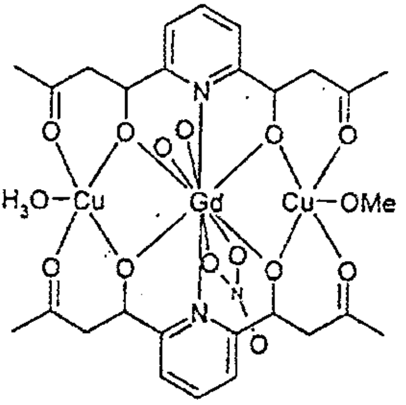
A somewhat unique high-nuclearity complex $[Cu_{12}La_5(\mu_3\text{-}OH)_{24}(NO_3)_{21.2}(Hmhp)_{13}(H_2O)_{5.5}](NO_3)_{2.8}\cdot 2Hmhp$ has been reported. Structural analyses show the presence of the $Cu_{12}O_6$ core and the arrangement of the copper(II) ion in the vertices of a cuboctahedron which further is located inside a cube of eight lanthanum ions.

The compounds of stoichiometry $[Ni_2Er_2(chp)_6(NO_3)_4(CH_3CN)_2]$, (28), and $[NEt_4]_2[Co_2Dy_2OH(chp)_6(NO_3)_5]$ have been reported[37]. The structural analyses show that the nickel compound is centrosymmetric and contains the central Er_2O_2 ring bridged to peripheral nickel atoms through six chp ligands.



28

The Cu-Gd trinuclear mixed metal compound $[Cu_2Gd(L)_2(NO_3)_2]NO_3$, 29, where L^{2-} is the 2,6-di(acetoacetyl)pyridine anion, has been obtained[38] and a ferromagnetic interaction between Cu^{II} and Gd^{III} ions corresponding to the M value of 9.05 Nβ at 50 kG, has been observed, in agreement with the expected value for ferromagnetically coupled Cu_2Gd (S_T=9/2).



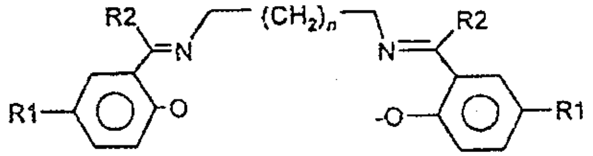
29

6. Schiff bases ligands

Polynuclear complexes, containing different donor groups along with the imines ones and with various shapes can be obtained. They can be synthesised by a direct metal - ligand way but also by a metal directed one. Open as well as closed systems can be obtained. The carbonyl compounds form the "head" of the ligands and diamines are the straps which bond the carbonyl groups belonging either to the same head or to a different one.

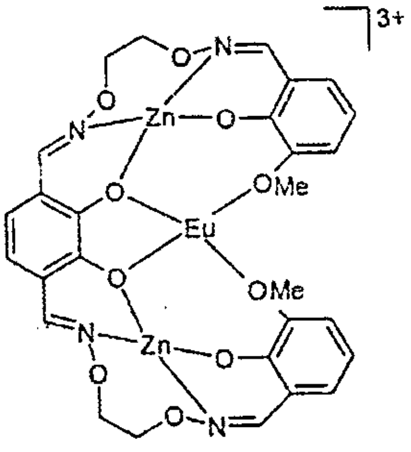
6.1. Tetradentate Schiff bases

The most comon ligands belong to the type of N,N'-ethylenebis(salicylaldimine) (SALEN). Heteropolynuclear complexes of the formula $[(Cu(30)_2Gd(H_2O)_3](ClO_4)_3\cdot 2Cu(30)\cdot 0.5C_2H_5NO_2$, $[(Cu(31))_2Gd(H_2O)_3](ClO_4)_3\cdot 2Cu(32)$ [39], $[Gd(hfa)_3Cu(30)]$, $[Y(hfa)_3Cu(30)]$, $[Gd(hfa)_3Cu(30)(Meim)]$, $[La(hfa)_3(H_2O)Cu(30)]$ and $[La(hfa)_3Ni(30)]$, where Ln = La, Gd, hfa = hexafluoroacetylacetonato and Meim = 1-methylimidazole [40], $\{CuGd(33)(NO_3)_3H_2O].Cu(33)$ [41], $Ln(L)_nX_3\cdot mH_2O$ where for L =Ni(32), Cu(32); X = NO_3^-, NCS^-, Cl^-, ClO_4^-; n = 1, 2; m = 0 - 4, [42] $(Cu(32))_2Ln(H_2O)(NO_3)_3\cdot 2EtNO_2$ where Ln = Eu(III), Gd(III))[43] have been obtained starting from the corresponding 3d-Schiff base precursor and the corresponding lanthanide complexes. In all the cases, the 3d metal ion occupies the N_2O_2 donor site and the oxygen atom bridges the two metal centres. The geometry of the 3d metal ions is preserved whereas the coordination number of the lanthanide ion is fulfiled by water molecules or by the counterions. In most of the cases, the complexes containing similar metal ions are isostructural. The study of the magnetic properties of the binuclear Cu-Gd complexes have shown that the copper(II) and gadolinium(III) ions are coupled in a ferromagnetic fashion with isotropic coupling constants of the order of five to seven wave numbers. The two copper(II) salicylaldiminate molecules in the unit cell of the $[(Cu(30))_2Gd(H_2O)_3](ClO_4)_3\cdot 2Cu(30)\cdot 0.5C_2H_5NO_2$ complex complicate the magnetic behaviour as they are rather well separated from the $GdCu_2$ units. Thus, an additional contribution to the magnetic susceptibility of the material can be noticed. Also, the presence of the triplet in the EPR spectrum of $(Cu(32))_2Eu(H_2O)(NO_3)_3\cdot 2EtNO_2$ proves the existence of a coupling between the two copper ions.



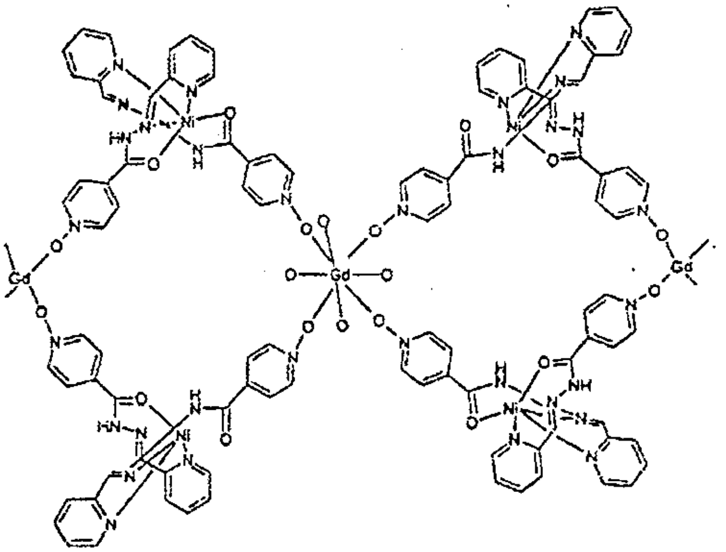
	n	R1	R2
30	2	H	H
31	2	H	CH3
32	3	H	H
33	2	OCH3	H

The heterotrinuclear complex 34 has been obtained [44] by transmetalation of the central 3d metal ion in the homotrinuclear precursor that contains the salen-type chelating moieties whose straps include *oxime* groups. The Zn(II) ions bind selectively to the two SALEM moieties and the europium(III) ion in the central cavity.



34

The one-dimensional lanthanide–transition heterometallic chains of squares, $\{LnNi_2L_3(HL)(DMF)_4(ClO_4)_4\cdot S\}_\infty$, 35, where Ln = Gd and Tb and HL stands for the Schiff base obtained by the condensation of 2-pyridylaldehyde with isonicotinic hydrazide N-oxide, S= solvent) and $\{LnNi_2L_4(DMF)_4(ClO_4)_3\cdot S\}_\infty$where Ln = Dy have been reported. The polynuclear compounds were synthesized by self-assembly of the well-designed orthogonal metalloligands $[Ni(HL)L]^+$ and the Ln(III) ions, which act as the bridging units and nodes respectively[45]. The X-ray structure of Gd compound show that the central Gd(III) ion has a slightly distorted square antiprism coordination geometry. The magnetic measurements for Gd(III) compound show that, the complex behaves as a ferromagnetic chain with antiferromagnetic interactions between the neighbouring paramagnetic centres with uncompensated spins. In addition, upon further cooling, the secondary effects such as zero-field splitting of the Ni(II) ions and/or interchain antiferromagnetic interactions occur.



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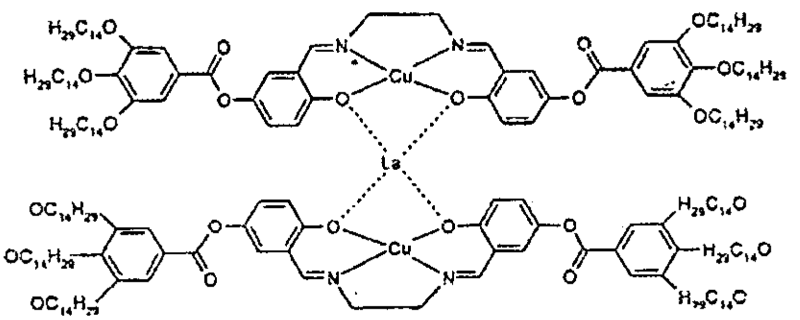


36

The first heteropolynuclear metallomesogens $[La(NO)_3\{Cu(X\text{-}SALEN)\}_2]$, **36**, and $[Gd(NO)_3Cu(X\text{-}SALEN)]$ that contain both a transition metal ion and a trivalent lanthanide ion have been reported[46].

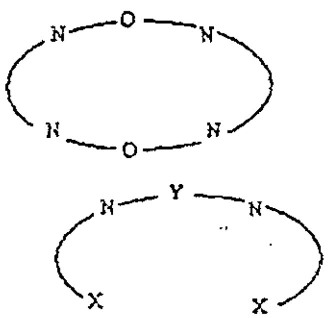
The compounds exhibit a hexagonal columnar mesophase over a wide temperature-range with rather low melting temperatures. Although the clearing point could be observed for the parent copper(II) complex, the mixed f-d complexes decomposed in the high-temperature part of the mesomorphic domain before clearing.

6.2 Compartmental ligands

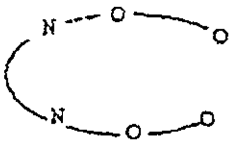
Dicarbonyl compounds forming the "head" of a Schiff base ligand[47, 48] suffer condensations with a wide range of diamines including, dialkylalkanediamines which make up the lateral units. An additional donor atom at the head unit bridges two metal ions. The appropriate chose of the amine straps allows selective coordination of metal ions of different size.

The types of compartmental ligands have been designed according to Scheme 1. The first type, a macrocyclic one, results from a [2+2] condensation of heads and lateral units. The other two types are acyclic ligands: one of them, an "end-off", the form B, in which one donor bridge is removed, and the second, a "side-off" form C, in which one non-donor bridge is removed.

A large variety of complexes with these shape have been synthesized and when the two coordination sites are occupied by different metal ions, heterodinuclear



end-off



side-off

Scheme 1

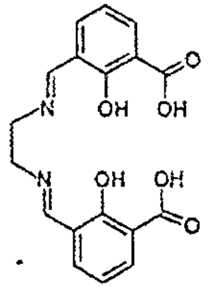
complexes result. Ligands containing phenolato group as an anionic oxygen donor are most comon for 3d-4f metal complexes. Such a ligand is hindered by the weak acidity of the hydroxyl group (pK_a of phenol ~ 10) and since the aqueous lanthanide ions are themselves weak Lewis acids which precipitates as hydroxidex above pH 8, they generally cannot complete with the hydrogen ion for complexation of phenols in water. The condensation can occur a half stage when open chain ligands are formed.

6.2.1. Open-chain ligands.

The complexes $[CoLa(37\text{-}4H)(CH_3OH)(NO_3)]$, $[CoNd(37\text{-}4H)(H_2O)_2(NO_3)]$ and $[CoGd(37\text{-}4H)(H_2O)(NO_3)]$.[49] $CuLn(37\text{-}2H)(NO_3)_3 \cdot 0.5CH_3OH$ (Ln = La, Nd, Eu, Gd or Ho), $CuGd(40\text{-}2H)(NO_3)_3 \cdot Me_2CO$ have been obtained[50].

Heterobinuclear complexes $[MLn(39\text{-}2H)(X)(solv)_n]$ (M = Cu or Ni, Ln = La, Eu, Lu,[51], X = NO_3 or Cl, solv = H_2O, methanol or dimethylsulphoxide (dmso)) have been obtained starting from corresponding 3d precursor complexes[52]. Also, a rare oxovanadium(IV)-4f mixed-metal compound, $VOLn(39\text{-}2H)(NO_3)(H_2O)_{2.5}$ where Ln = La, Eu, Gd have been reported[53]. In all the cases, the 3d metal ion occupies the endogenous N_2O_2 coordination site and Ln(III) ions are located in the exogenous O_4-coordination site.

The complexes containing gadolinium(III) and the 3d metal ions zinc(II) or nickel(II) and deprotonated Schiff bases 39, 46 or 47 as ligands have been obtained[54]. The complexes have been characterized by infrared, H-NMR, EPR and electronic spectra in order to formulate their structure. It has been proved that the nickel ion has a square planar geometry while zinc ion has a distorted tetrahedral geometry. These differences affect the magnetic moments of the complexes although the both 3d metal ions are diamagnetic. The differences are more visible when the lateral strap of the ligand is more rigid, like in 47 or 48[55].



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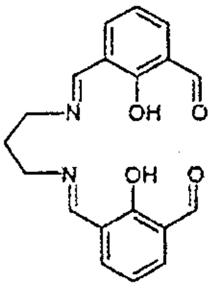

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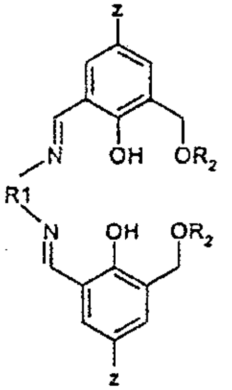


	R1	z	R2
39	$-CH_2-CH_2-$	H	H
40	$-CH_2-C(CH_3)_2-$	H	CH_3
41	$-CH_2-CH_2-$	H	CH_3
42	$-CH_2-C(CH_3)_2-CH_2-$	H	CH_3
43	$-CH_2-CH(CH_3)-CH_2-$	H	CH_3
44	$CH_2-CH(CH_3)-CH_2$	H	CH_3
45	$-CH_2-CH(COOH)-$	H	CH_3
46	$-CH_2-CH(CH_3)-$	H	H
47	$-C_6H_4-$	H	H
48	$-C_6H_4-$	Cl/CH_3	H

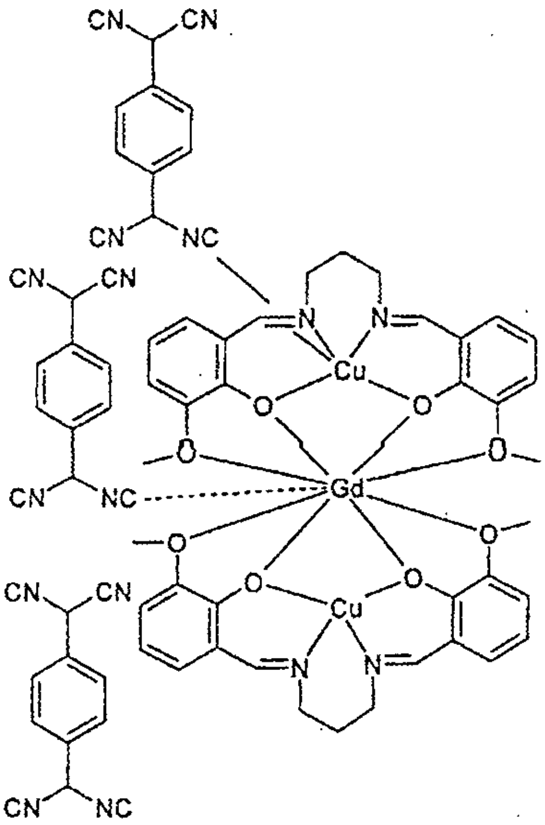
Costes et al[56] obtained the discrete binuclear complex $Ni_2Gd(42\text{-}2H)(H_2O)(NO_3)_3$. As in the previous cases, the nickel occupies the inner coordination site and has a distorted octahedral environment with the N_2O_2 atoms of the ligand almost coplanar and the apical positions occupied by the oxygen atoms of two water molecules. The profile of the curve X_MT vs T indicates ferromagnetic interactions between the two metal centres.

The binuclear Fe^{II}-Gd^{III}) complexes $Fe(42\text{-}2H)(CH_3OH)Gd(NO_3)_3(CH_3OH)_2$, $Fe(43\text{-}2H)(CH_3)_2CO)Gd(NO_3)_3$, $Fe(43\text{-}2H)((CH_3)_2CO)Gd(NO_3)_3$ have been obtained[57]. The experimental magnetic susceptibility and magnetization data indicate the occurrence of weak Fe^{II}-Gd^{III} ferromagnetic interactions.

Heterometallic compounds containing deprotonated ligands **41**, **42**, and **44** have been obtainined for Cu-Gd[58], Zn-Pr[69] pairs of ions. The Zn-Pr complexes have been obtained starting from Pr(III) – Schiff bases complexes, $Pr(41\text{-}2H))(NO_3)_3\cdot H_2O$, $Pr(44\text{-}2H)(NO_3)\cdot H_2O\cdot CH_3OH$ as precursors. The structural studies show that the rare earth metal ion occupies the O_2O_2 coordination site as in the precursors while zinc(II) ion penetrate the N_2O_2 sites.

Madalanet al[60] obtained $[\{Cu(40\text{-}2H)\}_2Gd(TCNQ)_2]\cdot TCNQ\text{-}CH_3OH\cdot 2CH_3CN$, where $TCNQ^{\cdot}$ stands for anion of 7,7,8,8- tetracyano-p-quinodimethane. The compound presents an infinite chain structure in running along the crystallographic axis. This arrangement is favoured by the presence of a TCNQ unit which coordinate to Gd^{3+} and to one TCNQ that further binds two adjacent Cu^{2+} as can be seen in the formula 49. The value of X_MT at room temperature is lower than that expected for six uncoupled spin carriers: two copper(II) ions ($S = 1/2$), one gadolinium(III) ion ($S = 7/2$), and three $TCNQ^{\cdot-}$ radicals ($S = ½$). This can be explained by strong antiferromagnetic coupling of the six stacked $TCNQ^{\cdot-}$ radicals connecting the $[Cu_2Gd]$ units. Also, a two - dimensional coordination polymer of the formula $[\dot{C}uPr(44\text{-}2H)(NO_3)_2(IN)]$ where IN stands for isonicotinate ion, has been obtained[61] using $CuPr(44\text{-}2H)(NO_3)_3$ as building block interconnected through the pyridyl moieties of the isonicotinato bridges.

Additional potential donor groups may be present like in **45**. The heterometallic compound $CuGd(45\text{-}3H)(NO_3)_2\cdot 2H_2O$, has been obtained and structural investigation has demonstrated that the pendant carboxylate group is involved in the intermolecular links to Gd(III) ion in a neighbouring unit, thus favouring the ferromagnetic interaction between Cu(II) and Gd(IIII) belonging to the different units.



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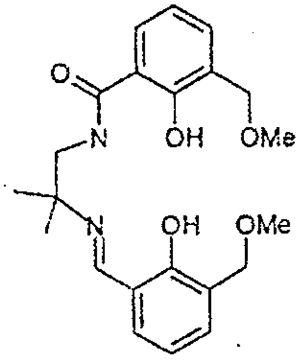
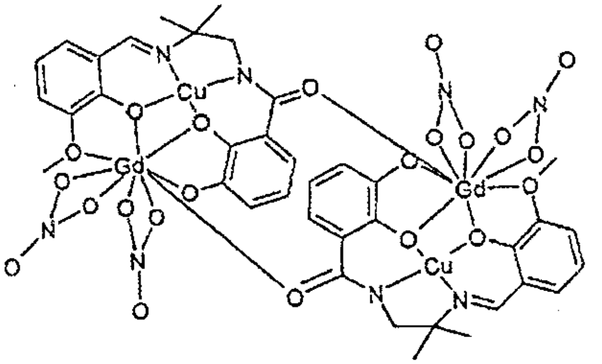


50

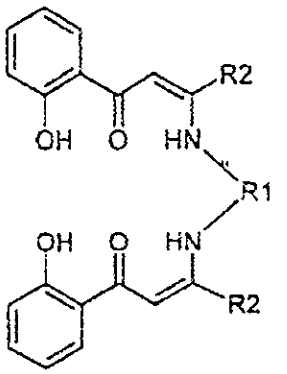
The Schiff base containing only an imino group, 50, has been successfully used to design and obtain 3d-4f metal complexes. Thus, $[CuGd(50\text{-}2H)(NO_3)_2\cdot CH_3OH]_2$, 51, has been obtained and X ray structural analyses have shown its dimeric nature.



51

Kido et al[62] reported the synthesis of a series of tetranuclear 3d-4f compounds of the general formula $[M(50\text{-}2H)Ln(hfac)_2]_2$, where M^{II}, Ln^{III} pair of ions are Cu, Eu; Cu, Gd; Cu, Tb; Cu, Dy; Ni, Eu; Ni, Gd; Ni, Tb or Ni, Dy and Hhfac = hexafluoroacetylacetone by assembling K[M(50-3H) and lanthanoid complexes precursors. The powder X-ray diffraction show that complexes belonging to each of the series Cu^{II}-Ln^{III} and Ni^{II}-Ln^{III} has been found to be isomorphous. The crystal structures of the Cu-Gd and Cu-Tb complexes showed the presence of the cyclic cylindrical arrangenments of the tetranuclear Cu_2Ln_2 units in which the copper(II) complexes act as bridging ligand-complexes to the two adjacent rare earth ions. It has been established that the 3d and 4f magnetic ions are arranged alternately and have suitable molecular design to produce a large magnetic moment and a large magnetic anisotropy. The temperature dependent magnetic susceptibilities and the field magnetic magnetizations have been measured for four pairs of $Cu^{II}_2Ln^{III}_2$ and Ni^{II}_2 Ln^{III}_2, in which compound Ni^{II}_2 Ln^{III}_2 containing diamagnetic Ni^{II} ion was used as reference to evaluate the Cu^{II}-Ln^{III} magnetic interaction following the empirical approach developed by Kahn et al[63]. The magnetic interaction between copper(II) and either Eu(III), Gd(III), Tb(III) or Dy(III) ions was found to be ferromagnetic.

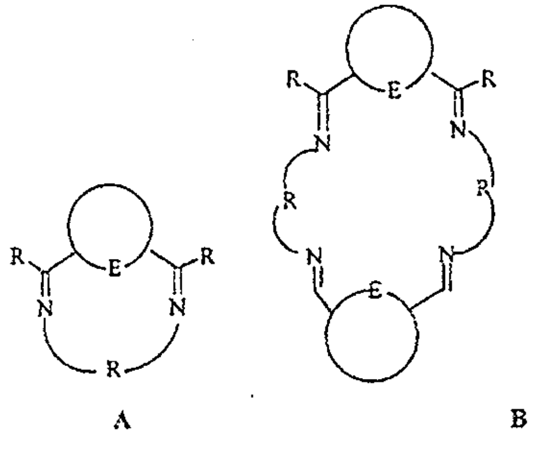
The reaction of the mononuclear chelates [M(L-2H)] with the required rare earth metal salts, in the presence of LiOH, resulted in the heterodinuclear complexes of the general formula $[Ln(OH)M(L)]\cdot nH_2O$, where M = Cu or Ni and for L = 52, Ln = La-Eu[64] and for L = 53, Ln = La-Lu[65]. In the 3d precursors the metal ion occupies the inner compartment. Spectral data show that the 3d metal ions preserve their position and are almost square planar. These data corroborated by the magnetic moments show that the divalent cations are unaffected by the presence of the lanthanide cation in the neighbouring cavity. For example, all the nickel - spin – paired lanthanide(III) complexes are diamagnetic while the complexes with spin-unpaired lanthanide(III) cations exhibit magnetic moments due to the lanthanide ion.



	R	R_2
52	$-H_2C\text{-}CH_2-$	C_2H_5
53	$-H_2C\text{-}CH_2-$	CH_3

6.2.2. Cyclic compartmental ligands

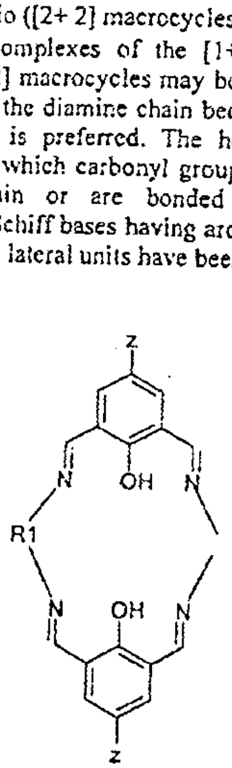
Cyclic Schiff base systems[66] are of the type reported bellow (Scheme 2). The type A results in 1:1



Scheme 2 Schematic representation of the [1+1] and [2+2] Schiff base macrocycles

condensation (termed [1+ 1] macrocycles) of precursors whereas the type B is formed when the precursors are in 2:2 molar ratio ([2+ 2] macrocycles).

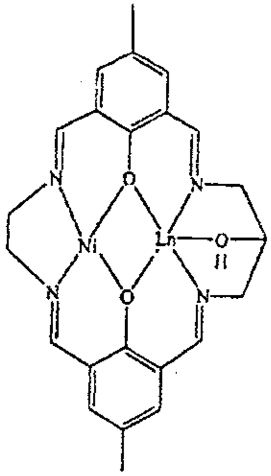
The metal complexes of the [1+1] are mononuclear whereas [2+2] macrocycles may be mono- or bi-nuclear in nature. As the diamine chain became longer a [1 + 1] condensation is preferred. The head units consist of molecules in which carbonyl groups are included in an aliphatic chain or are bonded to an unsaturated heterocycle. Schiff bases having aromatic head units and rigid aromatic lateral units have been also reported.



	Z	R1	R2
54	Cl	$-(CH_2)_2-NH-(CH_2)_2-$	$-(CH_2-)_2-NH-(CH_2)_2-$
55	H	$(CH_2)_3N(C_2H_4)_2N(CH_2)_3$	$(CH_2)_3N(C_2H_4)_2N(CH_2)_3$
56	CH_3	$-C_6H_4-$	$-C_2H_4-$
57	CH_3	$-C_6H_4-$	$-C_6H_4-$
58	Cl	$-C_6H_4-$	$-C_2H_4-$

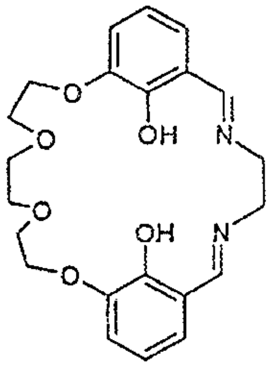
The 3d - 4f heterometallic complexes with compartmental ligands have been obtained both by direct metal-ligand route as well as by metal directed template one. It is well known that lanthanide(III) ions are effective template agents in the synthesis of macrocycles particularly in the preparation of mono-, bi- and polynuclear compounds[67]. For example, template condensation of [N,N'-phenylene-bis(3-formyl-5-chlorosalicylideneiminato]copper(II) with 1,2-diamino-ethane in the presence of $La(NO_3)_3 \cdot 6H_2O$ lead to $Cu_2La(58\text{-}3H)(NO_3)_2(OH)$. A second route consists of the reaction between preformed ligands 56 or 58 with copper(II) salt. This second route needs special conditions as a mismatch between the ionic radii of the rare earth ions and the N_2O_2 cavity exist. Actually, structural analyses have show that the lanthanide ions are situated above or below the plane. The proposed structure involves a sandwiched lanthanide ion by the vacant N_2O_2 site of the two CuL entities. The complex is labile in solution which can be explained by the poor coordination to the La(III) ion

The binuclear complexes $[LnNiL]Cl_3$, (59), Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), or Eu(III) have been obtained in a stepwise synthetic strategy following the template effect of lanthanide ions. In the first stage, N,N'-bis(3-formyl-5-methylsalicylidene)-ethylenediaminato]nickel(II) has been obtained which further, leads to the product in a template reaction around La with and 2-hydroxypropylene-1,3-diamine[68]. Spectral studies reveal that the complexes have a similar structure and thermal behaviour studies show that the rate of decomposition process increases along the lanthanide ion series thus suggesting the poor match of the smaller Ln^{3+} ions with the coordinating compartment of the ligand. The X-ray crystal structure of $[LaNiL]Cl_3$ indicates the essentially planar backbone of the ligand and the asymmetry of the coordination environment of La(III) ion. The 2D ^1H NMR techniques and ^{13}C NMR spectroscopy support the idea that the solid state structure is preserved in solution.



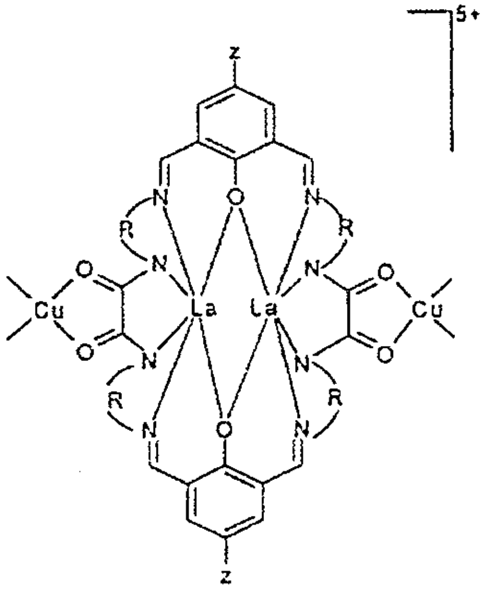
59

Asymmetric compartmental macrocycles containing additional donor atoms have been used to obtain heterodinuclear complexes. Vigato et al[69] obtained the asymmetrical ligand 60 which contains a crown-ether compartment appropriate to include a rare earth ion and a N_2O_2 coordination site which locate the 3d metal ion. The heterodinuclear complex $MLa(60\text{-}2H)(Cl)_2(OH) \cdot nH_2O$ (M = Cu, n=1; M = Ni, n =2), have been obtained when $La(H_2L_C)Cl_3$ reacted with the appropriate metal salt.



60

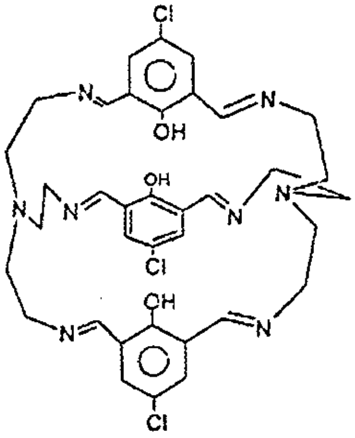
Heterodinuclear complexex ions 61 and 62, where Ln = La^{3+}, Dy^{3+}, Gd^{3+} have been obtained as perchlorates, acetates or nitrates, starting from the homodinuclear lanthanide complexes, $Ln_2(HL)(X)$, as precursors and copper(II) salts[70]. The nature of the complexes has been evidenced by scaning electron microscopy and EDX analyses. It has to be noted that the heterodinuclear dysprosium(III) precursor and the Dy_2-copper heterotrinuclear one have a similar magnetic moment at room temperature, of ~15.5 μB indicative of an antiferromagnetic exchange between paramagnetic ions, whereas in $Cu-La_2$ complexes, the magnetic contribution is given only by copper(II) ions in an interpolynuclear antiferromagnetic exchange interaction.



	R	Z
61	$-CH_2-CH_2-$	-Cl
62	$-CH_2-C(CH_3)_2-$	-Cl

6.2.3. Criptates

Qiu-Yun Chen et all[71] synthesized in two steps the d-f heteronuclear Robson-type cryptate $[GdNiL(DMF)](ClO_4)_2$, where L stands for 63. The first step involves the formation of the mononuclear Gd(III) cryptate precursor by the condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-clorophenol in the presence of Gd^{3+} ion whereas in the second one, the Gd(III) complex was reacted with nickel(II) perclorate. Actually, the second step referes to the substitution of one water molecule encapsulated in a mononuclear precursor complex $[Gd(H_3L)(NO_3)(H_2O)](ClO_4)_2$ by Ni^{2+} ion at controlled pH conditions. Magnetic measurements proved that the interaction between Ni and Gd is ferromagnetic with $g = 1.99$, $J = 0.56$ cm^{-1}.



63

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