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d–f Heteronuclear complexes: synthesis, structures and physicochemical aspects

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Abstract

This article concerns d–f heteronuclear complexes, focusing on recent progress in their synthesis, stereochemistry, magnetism, some other physicochemical properties, and potential use as new materials.

Keywords: d–f Complexes; Heteronuclear complexes; Crystal structures; Spin-exchange; Ferromagnetic interactions; Fluorescence; Luminescence

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1. Introduction

Studies of heteronuclear metal complexes started at the end of the 1960s due to an interest in the physicochemical properties arising from the presence of dissimilar metal ions in close proximity. The heteronuclear complexes first studied contained different d metal ions, and little attention was paid to d–f heteronuclear complexes until 1985 when Bencini reported unique magnetic properties for $Cu^{II}Gd^{III}$ complexes. In the first attempt to prepare discrete d–f complexes, Cu(salen) and analogous complexes of quadridentate Schiff bases were extensively used as 'complex ligands' to provide di(μ-phenoxo)$Cu^{II}Ln^{III}$ complexes. The synthetic strategy using appropriate d metal complexes as 'ligands' proved to be of general use for d–f complexes of various bridging ligands, such as oxamide, oxamidate. The emergence of compartmental ligands with two dissimilar metal-binding sites, one being specific for the d metal ion and another for the f metal ion, has greatly contributed to developments in the solution chemistry of d–f complexes. Now non-compartmental ligands such as diaminoalcohols, diaminophenols, carboxylates, amino acidates, betaines and 2-pyridones are shown to afford discrete d–f complexes, and rare d–f cluster compounds have been synthesized. The aim of this article is to review the types of d–f heteronuclear complexes, illustrate some typical characteristics and provide a useful foundation for future research in this little-studied area.

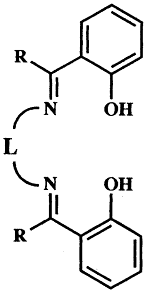
A class of lanthanide (Ln) analogs of Prussian blue has been derived from hexacyanometallate(III) ions. Most of them are thought to be double salts, but the presence of the M^{III}–CN–Ln^{III} linkage is clearly demonstrated for some Ln analogs of Prussian blue. However, they are not included in this article.

2. Synthesis and structures

2.1. d–f Complexes of tetradentate Schiff base ligands

Metal complexes of tetradentate Schiff bases (**1**) were extensively used by Sinn and Harris [1] as 'complex ligands' for providing transition metal dinuclear MM′ and trinuclear MM′M complexes. This method was successfully applied for preparing d–f heteronuclear complexes [2]. Dinuclear Ln{Cu(saltn)}$(NO_3)_2(H_2O)_2$ (Ln =

Eu–Lu) and trinuclear Ln{Cu(saltn)}$_2$(NO$_3$)$_3$ (Ln = La–Sm) were prepared by the reaction of Cu(salen) with Ln^{III} nitrate. Similarly, dinuclear Ln{Ni(saltn)}-(NO$_3$)$_3$(H$_2$O)$_2$ (Ln = Eu–Lu) and trinuclear Ln{Ni(saltn)}$_2$(NO$_3$)$_3$ (Ln = La–Sm) were prepared [3]. It appears that heavier lanthanide ions with a smaller ionic radius (Eu–Lu) cannot accommodate simultaneously two complex ligands. In accord with this, the apparently trinuclear Er{Cu(saldmen)}$_2$(NO$_3$)$_3$(H$_2$O) actually consists of dinuclear Er{Cu(saldmen)}(NO$_3$)$_3$(H$_2$O) and mononuclear Cu(saldmen) [4]. Trinuclear M^{II}Ln^{II}M^{II} (M = Cu, Ni) complexes are obtained with various anions such as thiocyanate, perchlorate or chloride, whereas only dinuclear M^{II}Ln^{III} complexes are isolated with nitrate ion. In all the MLn nitrate complexes the nitrate group functions as a chelating end-cap ligand to the Ln ion.



R	L	abbreviation
H	-CH$_2$CH$_2$-	H$_2$salen
H	-C(CH$_3$)$_2$CH$_2$-	H$_2$saldmen
H	-CH$_2$CH$_2$CH$_2$-	H$_2$saltn
H	-C$_6$H$_4$-o-CH$_2$-	H$_2$salabza
CH$_3$	-CH$_2$CH$_2$-	H$_2$acpen

1

A crystal of Gd{Cu(acpen)}$_2$(H$_2$O)$_3$(ClO$_4$)$_3$·2Cu(acpen) consists of a trinuclear GdCu$_2$ unit and two isolated Cu(acpen) molecules [5]. The trinuclear unit is formed by the coordination of two Cu(acpen) molecules to Gd through the two phenolic oxygen atoms with a Cu–Gd separation of 3.367(2) Å (Fig. 1). The Gd has seven-coordinate geometry with the further coordination of three water molecules. The Cu(O)$_2$Gd bridge is asymmetric and the Gd–O bond distances are about 0.45 Å longer than the Cu–O distances. Gd{Cu(saltn)}$_2$(H$_2$O)(NO$_3$)$_3$·2C$_2$H$_5$NO$_2$ has a discrete trinuclear core [6] where the Gd is nine-coordinated with two bidentate Cu(saltn) molecules, two bidentate nitrate ions and one water molecule.

Discrete dinuclear d–f complexes can be obtained when an appropriate ‘end-cap’ ligand is used for the f metal ion [7,8]. Typical examples are Ln{M(salen)}(hfa)$_3$ (Ln = Gd, Y; M^{II} = Cu, Ni; hfa$^-$ = hexafluoroacetylacetone) prepared by the reaction of stoichiometric amounts of Ln(hfa)$_3$ and M(salen) [7]. The X-ray structural study for Gd{Cu(salen)}(hfa)$_3$ indicates a square antiprism polyhedron about the Gd with the coordination of one Cu(salen) and three hfa ligands (Fig. 2). The Cu(O)$_2$Gd core has a butterfly shape; the GdO1O2 and CuO1O2 planes are bent at the O1–O2 edge with a dihedral angle of 47.0°. Because of this large bend, the interatomic Cu–Gd distance is short (3.198(2) Å).

In a similar way, Ln{Cu(saltn)}(hfa)$_3$ [9] and LnCu(salabza)(hfa)$_3$ (Ln = Gd, Lu) [10,11] were obtained. In the synthesis of the former complex, tetranuclear Ln$_2$Cu$_2$

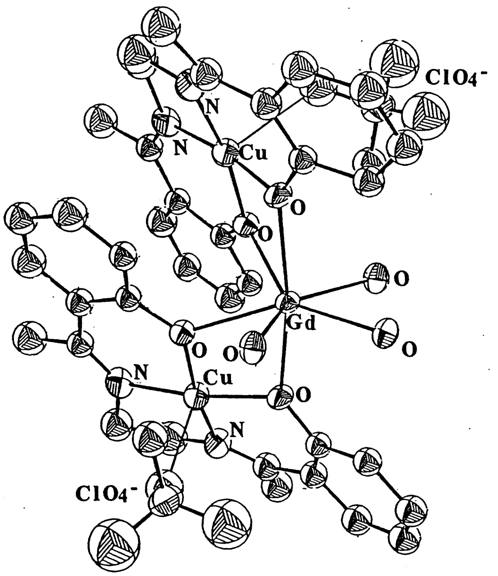


Fig. 1. Structure of $\mathrm{Gd\{Cu(acpen)\}_2(H_2O)_{3(}ClO_4)_2\cdot 2Cu(acpen)}$.

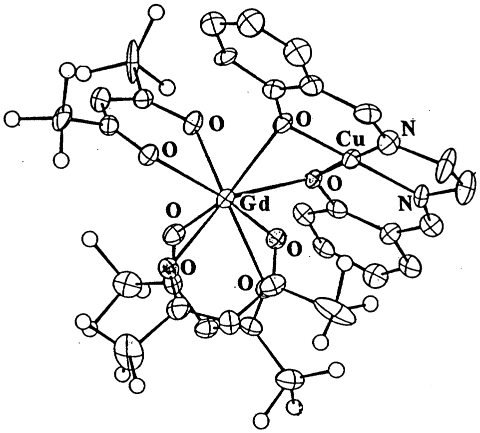
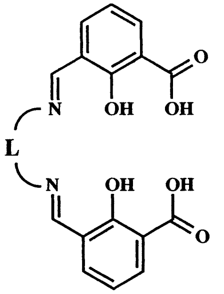


Fig. 2. Structure of $\mathrm{Gd\{Cu(salen)\}(hfa)_3}$.

complexes $\mathrm{[LnCu(satn)(hfa)_3(OH)]_2}$ (satn = *N*-(3-aminopropyl)salicylaldiminate) were obtained as a byproduct. The $\mathrm{Dy_2Cu_2}$ complex has a dimer-of-dimers structure, where the dinuclear DyCu unit is formed by the bridge of the phenolic oxygen of the satn ligand and a hydroxo group, and the two DyCu units are linked by the out-of-plane OH–Dy bonding.

2.2. d–f Complexes of compartmental Schiff base ligands

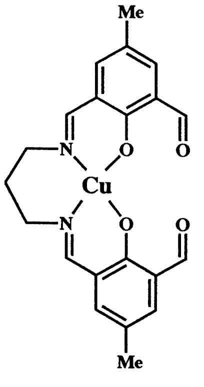
Schiff bases derived from the 2:1 condensation between 3-formylsalicylic acid and a diamine (**2**) are compartmental ligands having dissimilar N_2O_2 and O_4 metal-binding sites sharing the two phenolic oxygen atoms. They show a specificity for the d metal ion with the N_2O_2 site [12,13] and a specificity for the f metal ion with the O_4 site [14]. In general, mononuclear d metal complexes were prepared and used for the reaction with Ln ion in the presence of LiOH. By this stepwise method the following d–f complexes have been prepared: $Cu^{II}Ln^{III}$ [14], $Co^{II}Ln^{III}$ [15,16], $Ni^{II}Ln^{III}$ [17], $V^{IV}(=O)Ln^{III}$ [18] and $Pd^{II}Ln^{III}$ [19]. In a series of CuLn complexes, $LnCu(csalen)(NO_3)(H_2O)_n$, those with lighter Ln ions (La–Gd) were obtained as tetrahydrates whereas those with heavier Ln ions (Tb–Lu) yielded pentahydrates [14]. Similarly, the $V^{IV}(=O)Ln^{III}$ complexes of csalen ligand were obtained as tetrahydrates for Ln = La, Pr and Eu, but as pentahydrates for Ln = Gd and Tb [18]. This is in conflict with the general concept that lighter Ln ions can assume a larger coordination number. Such an increasing trend in the number of hydration water on going from lighter Ln ions to heavier ones was observed for $Ln\{M(saltn)\}_2(NCS)_3 \cdot nH_2O$ (Ln = La–Lu; M = Cu, Ni) [3].



L	abbreviation
$-CH_2CH_2-$	H_4csalen
$-CH_2CH(CH_3)-$	H_4csalpn
$-CH_2CH_2NHCH_2CH_2-$	H_4csaldien

2

Cu(fsaltn) (**3**) of *N*,*N*′-1,3-trimethylenedi(3-formyl-5-methylsalicylideneimine) combines a Ln^{III} ion with its O_4 metal-binding site providing $LnCu(fsaltn)(NO_3)_3$



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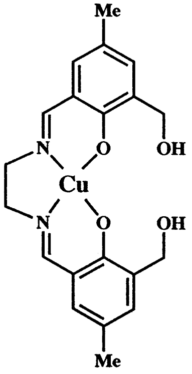
(Ln = La, Nd, Eu, Gd, Ho) [20]. Cu(H_2hmsalen) (**4**) of *N*,*N*′-ethylenedi(3-hydroxymethyl-5-methylsalicylideneamine) (H_4hmsalen) similarly accommodates a Ln ion in its O_4 metal-binding site providing LnCu(hmsalen)(NO_3)(H_2O)$_n$ [21]. Notably, the two hydroxymethyl groups of the ligand are deprotonated in the LnCu complexes.



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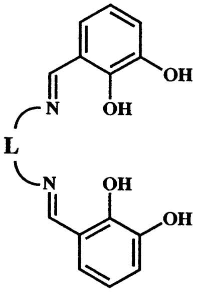
3-Hydroxysalicylaldehyde–diamine Schiff bases (**5**) are good compartmental ligands for providing d–f heterodinuclear complexes [22,23]. *N*,*N*′-Ethylenedi(3-hydroxysalicylideneaminato)copper(II) Cu(H_2osalen) was prepared and reacted with Ln^{III} nitrates in the presence of LiOH to afford $Cu^{II}Ln^{III}$ (Ln = La, Y) complexes. Similarly, $Cu^{II}Ln^{III}$, $Ni^{II}Ln^{III}$, and $V^{IV}(O)Ln^{III}$ complexes were derived from osalen^{4-} and homologs [22–31].



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In the crystal of CuY(osalen)(NO_3)(dmso)$_2$ [22], the Cu is bound to the salen-like N_2O_2 site and the resulting Cu(osalen)$^{2-}$ combines the Y with four phenolic oxygens (Fig. 3). The Y has an eight-coordinate geometry with further coordination of a bidentate nitrate ion, a dmso molecule and a phenolic oxygen from an adjacent molecule. Thus, the complex has a ‘dimer-of-dimers’ structure. The dimeric core, except for the exogenous ligating groups, forms a near coplane. Analogous ligands, having an additional donor atom in the lateral chain, generally provide dinuclear Ln^{III} complexes [27].

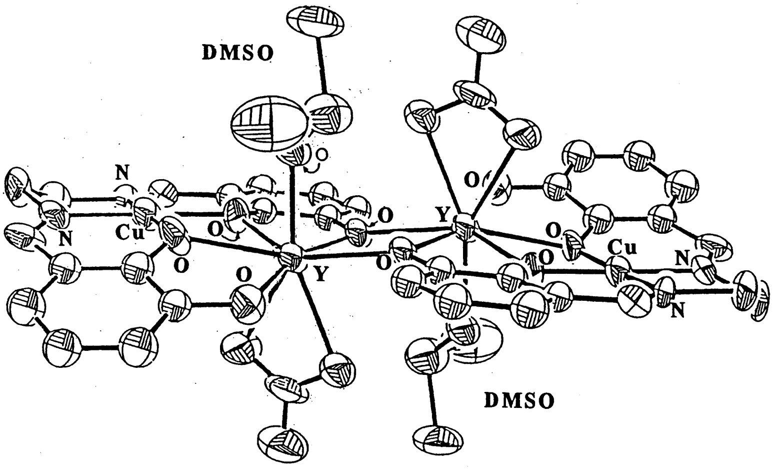


Fig. 3. Structure of CuY(osalen)(NO_3)(dmso)$_2$.

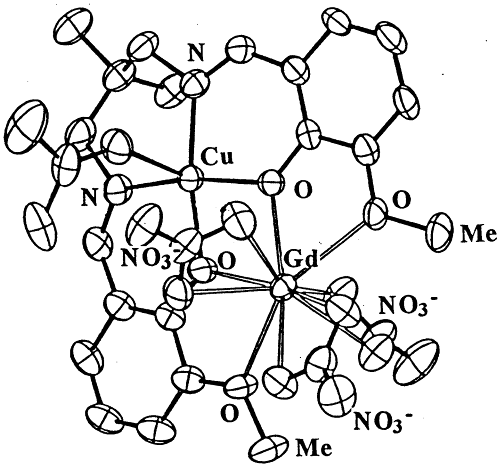
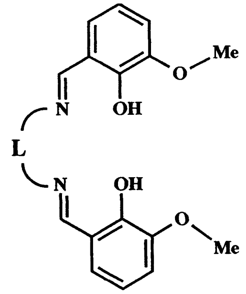


Fig. 4. Structure of GdCu(mosaldmen)$(NO_3)_3$.

Costes used 3-methoxysalicylaldehyde–diamine Schiff bases (**6**) as compartmental ligands for providing d–f dinuclear complexes [4,32–37]. The Schiff bases derived from the 1:1:1 condensation of 3-methoxysalicylaldehyde, diacetyl monooxime and a diamine (**7**) were also used for providing CuGd complexes [38]. The crystal structure of GdCu(mosaldmen)$(NO_3)_3$ is given in Fig. 4. The ligand accommodates the Cu in the salen-like site, and the resulting Cu(mosaldmen) combines the Gd with its two phenolic and two methoxy oxygen atoms providing a deca-coordinate environment about the Gd together with three bidentate nitrate ions. It is known that 3-methoxysalicylaldehyde (Hmosal) itself and the Schiff base with ammonia (Hmosalim) also form discrete CuLn and CoLn complexes [33,39]. An X-ray crystallographic study of GdCu(mosalim)$_2$(MeOH)(NO$_3$)$_3$ indicates a *cis* arrangement of the two ligands, providing the two imine nitrogens and the two phenolic oxygens for the accommodation of the Cu and the two phenolic oxygens and the two methoxy oxygens for the accommodation of the Gd (Fig. 5). The core structure of this compound resembles that of Cu(mosalpn)Gd(NO$_3$)$_3$. A similar *cis* arrangement of two mosal ligands has been demonstrated for PrCo(mosal)$_2$(H$_2$O)$_2$(NO$_3$)$_3$ [39] where the Co has a six-coordinate structure with further coordination of two water molecules.



L	Abbreviation
-CH(CH$_3$)CH$_2$-	H$_2$mosalpn
-CH$_2$CH$_2$CH$_2$-	H$_2$mosaltn
-C(CH$_3$)$_2$CH$_2$-	H$_2$mosaldmen
-CH$_2$C(CH$_3$)$_2$CH$_2$-	H$_2$mosaldmtn

6

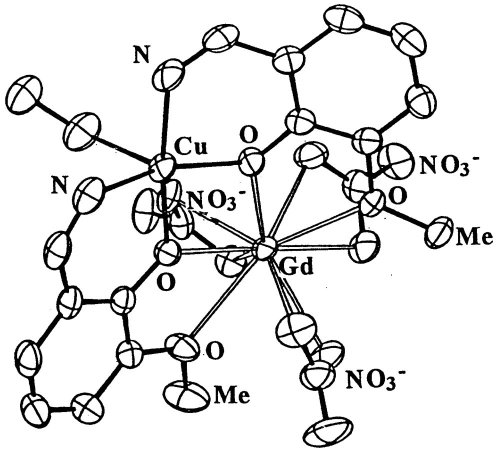
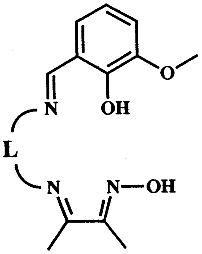
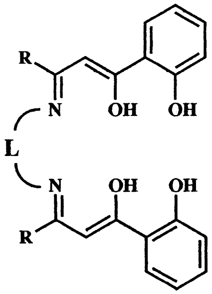


Fig. 5. Structure of GdCu(mosalim)$_2$(MeOH)(NO$_3$)$_3$.



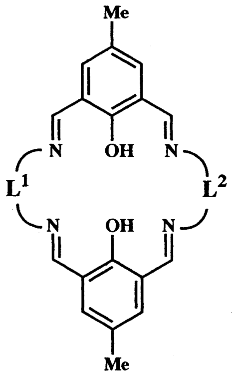
7

Diamine Schiff bases derived from *o*-(β-acylacetyl)phenols (**8**) have dissimilar N_2O_2 and O_4 metal-binding sites sharing two enolate oxygen atoms [40–42]. Mononuclear Ln complexes with the metal in the O_4 site can be derived, but those complexes hardly accommodate d metal ions in the N_2O_2 site. On the other hand, mononuclear Ni^{II} and Cu^{II} complexes with the metal in the N_2O_2 site can incorporate Ln ion with its O_4 site affording $MLn(L)(OH)(H_2O)_{2-3}$.



8

Dinuclear $Cu^{II}Ln^{III}$ complexes of the macrocyclic ligands $H_2(L^{m;n})$ (**9**) were synthesized by reacting *N*,*N*′-alkane- or *N*,*N*′-*o*-phenylenedi(3-formyl-5-methylsalicylideneaminato)copper(II) with a diamine in the presence of a Ln ion [43–45]. Notably, coordination-position isomeric $CuLn(L^{2,3})(NO_3)(H_2O)_n$ (**10 a**) and $LnCu(L^{2,3})(NO_3)(H_2O)_n$ (**10 b**) have been obtained. The former complexes are yellowish brown and have a d–d band maximum due to Cu^{II} at ~18,000 cm^{-1}, whereas the latter complexes are green and have a d–d maximum at ~16,000 cm^{-1}. The macrocycles $(L^{2,2'})^{2-}$ and $(L^{2',2'})^{2-}$ afforded trinuclear $LnCu_2$ complexes, where two $Cu(L^{2,2'})$ (or $Cu(L^{2',2'})$) units sandwich one Ln ion with the vacant N_2O_2 site [46]. The macrocycle $(L^{2,3(OH)})^{2-}$, having a hydroxy group at the center carbon of the trimethylene chain, forms dinuclear $LnNi(L^{2,3(OH)})Cl_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu) where the hydroxy group is involved in coordination to the La ion [47].



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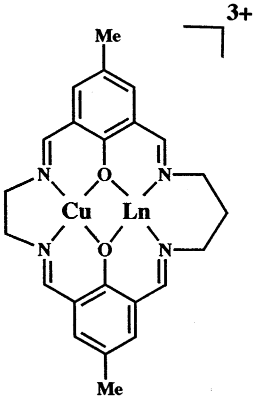
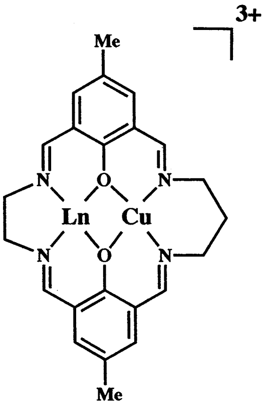
L^1	L^2	abbreviation
$-CH_2CH_2-$	$-CH_2CH_2CH_2-$	$H_2(L^{2,3})$
$-CH_2CH_2-$	$-CH_2CH(OH)CH_2-$	$H_2(L^{2,3(OH)})$
$-CH_2CH_2-$	o-phenylene	$H_2(L^{2,2'})$
o-phenylene	o-phenylene	$H_2(L^{2',2'})$

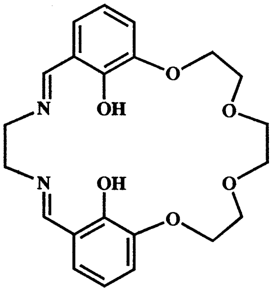


10a



10b

$H_2(O_6salen)$ (**11**) is a macrocyclic analog of mosalen [48]. The Ln complex $[La\{H_2(O_6salen)\}(H_2O)_4]Cl_3$ has the metal ion in the crown-ether-like O_6 site. It reacts with M^{II} ion to afford $LaM(O_6salen)Cl_2(OH)(H_2O)_2$ ($M = Cu$, Ni), but their crystal structures have not been determined.



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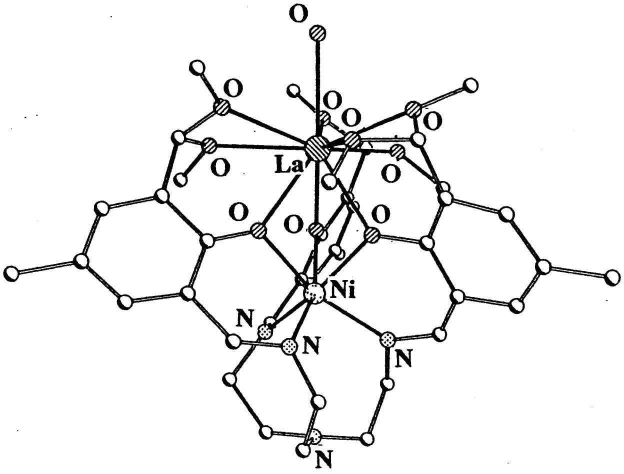
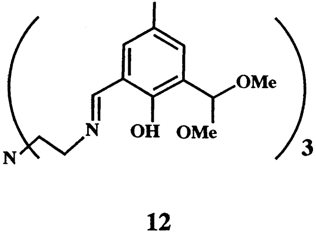


Fig. 6. Structure of LaNi(dmmsaltren)$(H_2O)(ClO_4)_2$.

Various acyclic and macrocyclic compartmental ligands having larger cavities for coordination have been developed by Vigato et al. [49–53]. Those ligands generally show a low selectivity for d and f metal ions and afford homodinuclear Ln complexes.

A tripodal ligand, tri{3-di(methyloxy)methyl-5-methylsalicylideneaminoethyl}-amine (H_3dmmsaltren) (**12**), has the inner N_4O_3 and the outer O_9 metal-binding sites sharing the three phenolic oxygen atoms [54]. It forms Ln(H_3dmmsaltren)-$(H_2O)_{0-1}(ClO_4)_3$ (Ln = La, Pr and Gd as monohydrates and Ln = Y as an anhydrate) where the Ln resides in the outer O_9 site. The monohydrates have a deca-coordinate trirhombohedral geometry about the metal with further donation of a water molecule. The Y complex has a nine-coordinate geometry about the metal based on a tricapped trigonal prism. The La complex reacts with Ni^{II} ion in acetonitrile in the presence of ethyldiisopropylamine to form LaNi(dmmsaltren)$(H_2O)(ClO_4)_2$. The Ni existing in the inner site has a six-coordinate geometry with the three imine nitrogens and the three phenolic oxygen atoms; the bridgehead nitrogen being free from coordination (Fig. 6). The La in this complex has a ten-coordinate geometry similar to that of the mononuclear La precursor. The Ni–La interatomic separation is 3.255(5) Å. In a similar way the GdNi, EuNi and PrNi complexes were obtained.



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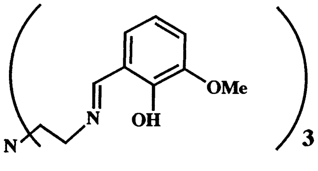
A related tripodal ligand, tri{*N*-(3-methoxysalicylidene)aminoethyl}amine (H_3vantren) (**13**), was utilized by Costes for the study of a $Fe^{III}Gd^{III}$ complex [55]. The ligand has an inner N_4O_3 site and an outer O_6 site for stepwise complexation of different metal ions. Mononuclear Fe(vantren) has the metal in the inner site with the bridgedhead nitrogen not being involved in coordination [56,57] and accommodates Gd ion in the outer site to give FeGd(vantren)$(NO_3)_3 \cdot 2H_2O$.



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2.3. d–f Complexes with diaminoalcohols and diaminophenols

Wang et al. reported d–f complexes of 2,6-bis(dimethylaminomethyl)-4-methylphenol (Hbdmmp) (**14**) [58]. Cu(bdmmp)$_2$(H_2O) was prepared and reacted with Pr(hfa)$_3$ to afford PrCu(bdmmp)(Hbdmmp)(μ-OH)(hfa)$_3$, where the Pr(hfa)$_3$ unit is linked to Cu(bdmmp)(Hbdmmp) through the phenoxo oxygen of bdmmp and a hydroxo oxygen in a Pr–Cu separation of 3.538(2) Å (Fig. 7). One amine nitrogen of the bdmmp is coordinated to the Pr atom. The Pr–N bond distance (2.90 Å) is much longer than the Pr–O bond distances (2.424–2.54 Å).

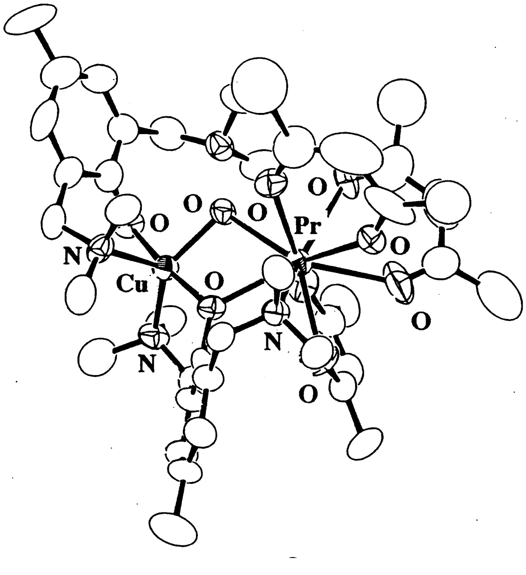


Fig. 7. Structure of PrCu(bdmmp)(Hbdmmp)(OH)(hfa)$_3$.

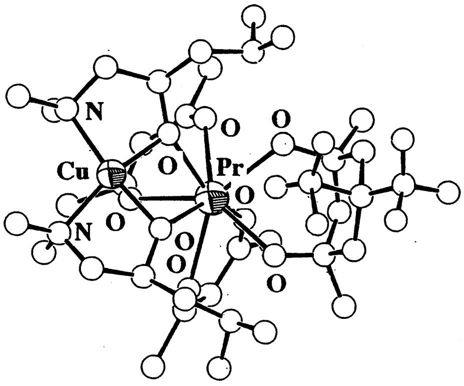
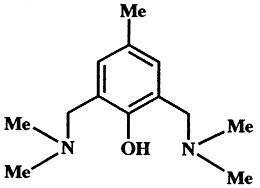


Fig. 8. Structure of $PrCu(Hbdmap)_2(hfa)_2(O_2CCF_3)L$ (L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolate).



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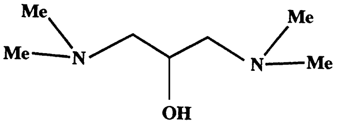
The reaction of $Cu(bdmmp)_2(H_2O)$ with $La(O_2CCF_3)_3$ in THF gave $[LaCu(bdmmp)(Hbdmmp)(OH)(O_2CCF_3)_3]_2$ that has a dimer-of-dimers structure based on a dinuclear unit similar to $PrCu(bdmmp)(Hbdmmp)(\mu\text{-}OH)(hfa)_3$. The two LaCu units are linked by four μ-η^1,η^1-trifluoroacetato bridges at the La site.

The d–f complexes of 1,3-bis(dimethylamino)-2-propanol (Hbdmap) (**15**) are also known [59–61]. A reaction of Hbdmap with $Pr(hfa)_3$ and $Cu(OCH_3)_2$ afforded $PrCu(Hbdmap)_2(hfa)_2(O_2CCF_3)L$ (L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolate). The trifluoroacetate ion arose from the decomposition of the hfa ligand ($F_3C\text{–}CO\text{–}CH_2\text{–}CO\text{–}CF_3 + H_2O = CF_3COOH + CF_3\text{–}CO\text{–}CF_3$) and the ligand L is produced by the cycloaddition of 1,1,1-trifluoro-2,2-propanediol to hfa. 1,1,1-Trifluoro-2,2-propanediol is the hydrated form of 1,1,1-trifluoroacetone, which is another decomposition product of hfa. The Cu has a five-coordinate geometry with two bidentate Hbdmap ligands and a unidentate trifluoroacetate ligand. The Pr ion is bridged to the Cu unit through the two oxygen atoms from two Hbdmap ligands with a Cu–Pr separation of 3.355(3) Å (Fig. 8). The Pr is surrounded by eight oxygen atoms, four from two hfa ligands, two from the bridging Hbdmap ligands and two from the ligand L.



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Other 3d–4f complexes with Hbdmap are $LnCu_2(bdmap)_3(O_2CCF_3)_4$ (Ln = La, Nd) [61] and $LnCu_2(bdmap)_3(hfa)(AcO)_2(O_2CCF_3)(Hhfa)(THF)$ (Ln = Pr, Nd) [60]. In the former, a dinuclear Cu unit is formed by combining two Cu(bdmap-N,O) entities with one trifluoroacetate ligand and one bdmap ligand, and to this dinuclear unit is linked $Ln(O_2CCF_3)_3$ through the oxygen atoms of all three bdmap ligands. In the latter complexes the trifluoroacetate ion is again a decomposition product of the hfa ligand. In the $NdCu_2$ complex of this type, one bdmap ligand functions as a μ^3-bridge with its oxygen, making bonds to the three metal ions in a triangular arrangement. The remaining two bdmap ligands and one acetate group act as supporting bridges of the triangular core.

2.4. d–f Complexes of carboxylates, amino acidates and betaines

A pentanuclear Cu_3Gd_2 complex, $[Cu_3Gd_2(O_2CCH_2Cl)_{12}(H_2O)_8]\cdot 2H_2O$, was obtained by a reaction of Cu^{II} nitrate and Gd^{III} nitrate in an aqueous solution of chloroacetic acid at pH 3.0–3.5 [62]. It has a linear Cu–Gd–Cu–Gd–Cu chain structure formed by linking two dinuclear $\{CuGd(\mu\text{-}O_2CCH_2Cl)_4\}$ subunits at the Gd site to the central Cu^{II} by a single *syn,anti*-carboxylato-O,O′ bridge.

$[Nd_3Cr_2(\mu\text{-}AcO)_6(\mu\text{-}OH)_6(H_2O)_9]Br_3\cdot NaBr\cdot 8H_2O$ [63] has a $\{Nd_3(OH)_6\}$ core of a triangular arrangement of three Nd^{III} ions with the $Nd(\mu\text{-}OH)_2Nd$ linkage. Each of the two peripheral Cr^{III} ions is linked to the trinuclear core via three μ-OH groups and three $\mu\text{-}\eta^1,\eta^1$-acetate bridges.

Two isostructural $Mn_2^{III}Ln_2^{III}$ complexes with the pivalate ligand (Me_3CCOO^-), $[Mn_2Ln_2O_2(O_2CCMe_3)_8(HO_2CCMe_3)_2(MeOH)_2]\cdot CH_2Cl_2$ (Ln = Gd, Dy), have been obtained [64]. They have a di-μ-oxodimanganese(III) core to which two Ln ions are combined through the μ^3-oxo bridge. Eight pivalate ligands are involved in the bridge between Mn and Gd ions in the usual 1,3-bridging mode, and two pivalic acid molecules coordinate to the Ln ion as a unidentate ligand. $[Cu_3\{Gd(dgla)_3\}_2]\cdot 9H_2O$ derived from diglycolic acid has a network structure formed by assembling $[Gd(gly)_3]^{3-}$ with Cu^{II} ions through carboxylate bridges [65].

Amino acids are expected to function as ambidentate ligands, making a bond to a d metal ion through the amine nitrogen and to a f metal ion through the carboxylate oxygen, but d–f mixed-metal complexes with amino acids are limited. $[Sm\{Ni(pro)_2\}_6](ClO_4)_3\cdot 6MeOH$ was prepared by the reaction of bis(L-prolinato)nickel(II) with Sm^{III} perchlorate in methanol [66,67]. The $\{Ni(pro)_2\}$ entity has a *cis* arrangement of the pro ligands and six $\{Ni(pro)_2\}$ entities coordinate to the Sm through two carboxylate groups providing an icosahedral geometry about the metal (Fig. 9). Six $\{Ni(pro)_2\}$ molecules associate by the coordination of the outer carboxylate oxygen to the axial site of Ni of the adjacent molecule, forming a cavity encapsulating the Sm atom. The Ni_6Sm core is stable in solutions and the cyclic voltammogram shows one reduction step due to Sm^{III}/Sm^{II} and six oxidation steps due to the Ni centers.

Rare $LnCu_6$ complexes $[LnCu_6(\mu^3\text{-}OH)_3(Hida)_2(ida)_4](ClO_4)_2\cdot 25H_2O$ (Ln = La, Tb; H_2ida = iminodiacetic acid) were reported recently [68]. Each ida (or Hida) ligand functions as a tridentate ligand to one Cu and a unidentate ligand to the adjacent Cu, providing a cage for encapsulating the Ln ion (Fig. 10). Each of the three hydroxide ions is involved in a μ^3-bridge among two Cu and one Ln ions.

The edta complexes $Ln_2M_3(edta)_3(H_2O)_{11}\cdot 12H_2O$ ($M^{II}Ln^{III}$ = MnNd, CoGd) were obtained and the Nd_2Mn_3 complex was structurally characterized [69]. The $\{Mn(edta)(H_2O)\}^{2-}$ molecule acts as a bridge to adjacent Nd ions with its two carboxylate groups, forming a sheet structure based on an 12-membered M_6Ln_6

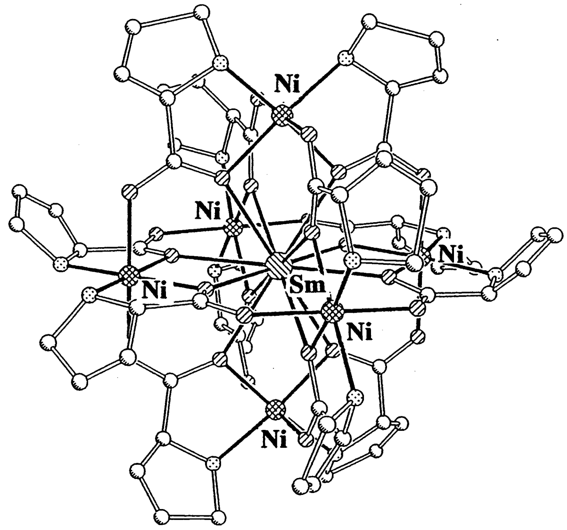


Fig. 9. Structure of $[Sm\{Ni(pro)_2\}_6](ClO_4)_3\cdot 6MeOH$.

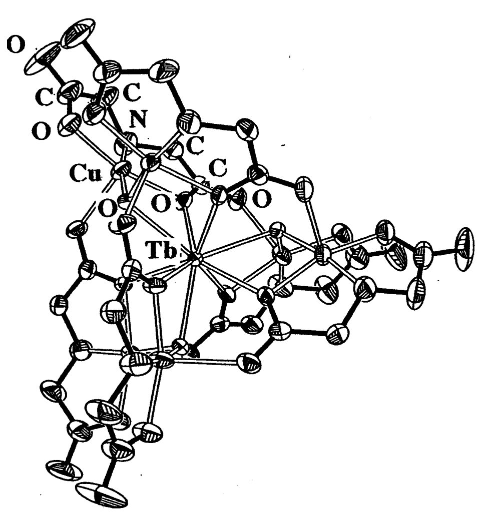


Fig. 10. Structure of $[TbCu_6(\mu^3\text{-}OH)(Hida)_2(ida)_4](ClO_4)_2\cdot 25H_2O$.

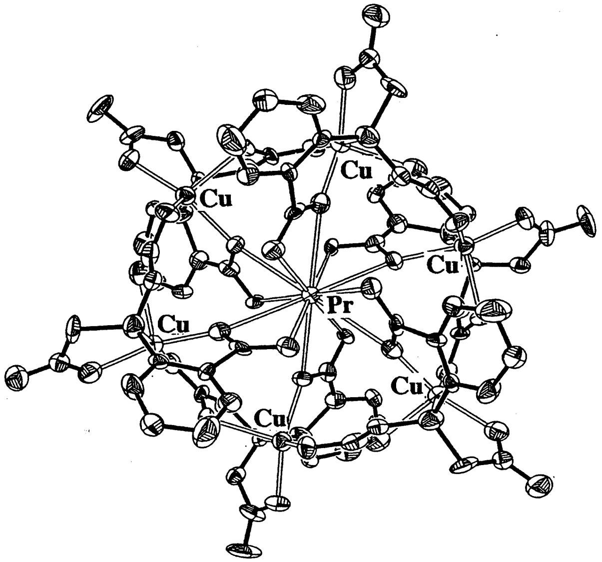


Fig. 11. Structure of $[PrCu_6(L)_6]^{3-}$ (H_3L = *N*-carboxymethyl-*N*-(*o*-carboxyphenyl)glycine.

motif. Each Nd has a ten-coordinate geometry with six carboxylate oxygens from three $\{M(edta)(H_2O)\}^{2-}$ molecules and four water molecules.

Novel $[Pr(H_2O)_{10}][PrCu_6(L)_6]\cdot 14H_2O$ was obtained using (H_3L =) *N*-carboxymethyl-*N*-(*o*-carboxyphenyl)glycine (Fig. 11) [70]. Each ligand employs the ring carboxylate group to connect one Cu and the Pr ion. One of the amino carboxylate groups coordinates to Cu in a monodentate fashion whereas another one bridges two neighboring Cu ions, providing a wheel-like structure for the $[PrCu_6(L)_6]^{3-}$ anion with the Pr at the center of the wheel.

Betaine ($Me_3N^+CH_2COO^-$; bet) has an advantage to overcome the charge-compensation problem in complexation of carboxylate ligands to a metal center. Two types of $Cu^{II}_2Ln^{III}_2$ complexes have been derived from $[Cu(bet)_4]^{2+}$: $[Cu_2Ln_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (Ln = La, Ce, Gd) and $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (Ln = Gd, Sm) [71]. In the former type, two dinuclear $\{CuLn(\mu\text{-}O_2CCH_2N^+Me_3)_4\}$ subunits are linked together at the Ln site by the $Ln(\mu\text{-}O_2CCH_2N^+Me_3)_2Ln'$ linkage into a tetranuclear core. In the latter type, two dinuclear $\{CuLn(\mu\text{-}O_2CCH_2N^+Me_3)_4\}$ subunits are linked at the Ln site by the $Ln(\mu\text{-}O_2CCH_2N^+Me_3)_4Ln'$ linkage.

Two types of CuLn complexes of pyridine betaine ($C_5H_5N^+CH_2COO^-$; pyb) have been obtained under acidic conditions (pH 2.5–3.0): $[CuLn(pyb)_5(H_2O)_5](ClO_4)_5\cdot 2H_2O$ (Ln = La, Nd) and $[Cu_3Nd_2(pyb)_{10}(NO_3)_2(H_2O)_8](ClO_4)_{10}\cdot 4H_2O$ [72]. The former has a dinuclear $\{CuLn(\mu\text{-}O_2CCH_2N^+C_5H_5)_4\}$ core (Fig. 12) which is the basic core structure in most d–f complexes derived from betaine and related ligands. The latter also has dinuclear $\{CuNd(\mu\text{-}O_2CCH_2N^+C_5H_5)_4\}$ as the subunit and two subunits are linked to another at the Cu site through a single *syn*,*anti*-μ-carboxylate-O,O′ bridge.

$[Cu_2Ln_2(tppp)_8(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ ($Ln^{III} = Eu$, Nd, Ce), derived from triphenylphosphoniopropionate ($Ph_3P^+CH_2CH_2COO^-$; tppp), also have two dinuclear $\{CuLn(\mu\text{-}tppp)_4\}$ subunits [73]. In this case the tetranuclear structure is formed by dimerizing two $\{CuLn(\mu\text{-}tppp)_4\}$ subunits at the Cu site through the $Cu(\mu\text{-}tppp)_2Cu'$ linkage.

Octadecanuclear $Cu_{12}Ln_6$ clusters, $[Cu_{12}Ln_6(\mu^3\text{-}OH)_{24}(H_2O)_{18}(pyb)_{12}(\mu^{12}\text{-}ClO_4)](ClO_4)_{17}\cdot nH_2O$ (Ln = Y, Nd, Gd), have been derived from pyridine betaine [74]. They have a discrete cationic core $[Cu_{12}Ln_6(\mu^3\text{-}OH)_{24}(\mu^{12}\text{-}ClO_4)]^{17+}$ in pseudo-*Oh* symmetry with six Gd ions at the vertices and 12 Cu ions at the midpoint of each edge of a regular octahedron. The metal framework is interconnected by 24 μ^3-OH ligands that are each linked to one Gd and two Cu ions. At the center of the core is encapsulated a $\mu^{12}\text{-}ClO_4^-$ anion. Similar core compounds have been derived from pyridiniumpropionate ($C_5H_5N^+CH_2CH_2COO^-$; pypro) and chloro- or trichloroacetate: $[Cu_{12}Ln_6(\mu^3\text{-}OH)_{24}(H_2O)_{16}(pypro)_{12}(\mu^{12}\text{-}ClO_4)](ClO_4)_{17}\cdot 16H_2O$ (Ln = Gd, Sm) [75] and $[Cu_{12}Ln_6(\mu^3\text{-}OH)_{24}(H_2O)_{18}(\mu\text{-}O_2CR)_{12}(\mu^{12}\text{-}ClO_4)]^{5+}$ (Ln = La, Nd; $R = CH_2Cl$, CCl_3) [76].

2.5. d–f Complexes of 2-pyridones

2-Pyridones are ambidentate ligands leading to the formation of d–f complexes in various oligomeric forms [77]. It is known that different d–f complexes result depending upon the pyridone ligand, the nature of the starting d-complex, the anion present, and the solvent used.

The reaction of 2-pyridone (Hhp) with $Cu(OH)_2$ and Ln nitrate formed Cu_4Ln_2 cage compounds, $Cu_4Ln_2(hp)_8(Hhp)_4(OH)_2(NO_3)_4(H_2O)_2$ (Ln = Gd, Dy) [78]. The six metal atoms in the cage are located at the vertices of a distorted octahedron with the two Ln atoms *trans* to one another (Fig. 13). Eight hp ligands are involved

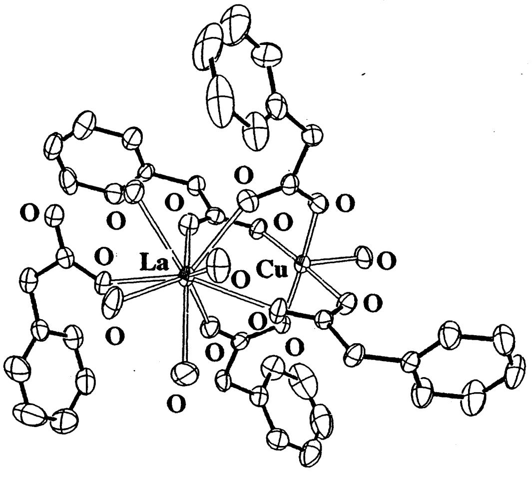


Fig. 12. Structure of $[CuLa(pyb)_5(H_2O)_5]^{5+}$.

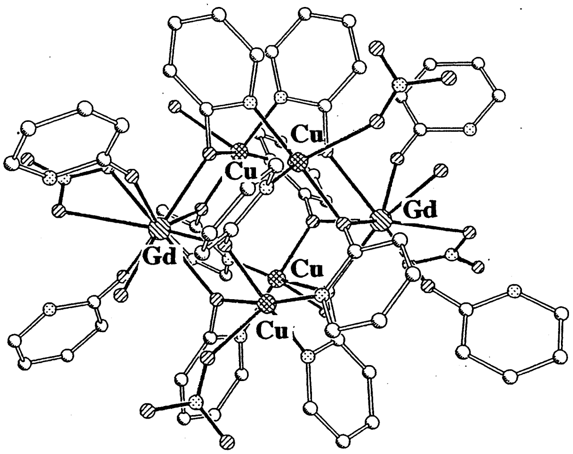


Fig. 13. Structure of $Cu_4Gd_2(hp)_8(Hhp)_4(OH)_2(NO_3)_4(H_2O)_2$.

in the bridge between the adjacent metal ions. A similar reaction using $Cu(OCH_3)_2$ led to a Cu_8Ln_2 cage, $Cu_8Y_2(\mu^4\text{-}O)_2(hp)_{12}(\mu\text{-}Cl)_2(NO_3)_4(H_2O)_2$ and $Cu_8Nd_2(\mu^4\text{-}O)_2(hp)_{12}(\mu\text{-}Cl)_2(OCH_3)_4(H_2O)_4$ [79]. They have a similar structure comprised of a $Ln_2Cu_4O_{10}Cl_2$ core and two peripheral Cu_2 units connected to the core through ambidentate hp ligands. In the central $Ln_2Cu_4O_{10}Cl_2$ core the two Ln ions are bridged by two oxo ligands, and the Ln ions are connected to four Cu^{II} ions through the two oxo ligands and eight oxygen atoms of hp ligands. Each chloride ion is involved in the bridge between a pair of Cu ions. The central core has a close resemblance to the atom arrangement of the $YBa_2Cu_3O_7$ superconductor. Deprotonation of the Hhp ligand, prior to the reaction with Cu^{II} nitrate and Ln^{III} perchlorate, leads to a Cu_4La_4 cage $[Cu_4La_4(hp)_8(Hhp)_8(ClO_4)_2(NO_3)_2\text{-}(OH)_4(CH_3O)_2](ClO_4)_2\cdot 2H_2O$ [80].

Dimeric $[Cu_2(chp)_4]$ (Hchp = 6-chloro-2-hydroxypyridine) can be used as the starting material for Cu–Ln compounds with the chp ligand [81,82]. A Cu_3La complex, $[Cu_3La(chp)_5(NO_3)_3(OMe)(MeOH)_2]$, was obtained by the reaction of $[Cu_2(chp)_4]$ with La^{III} nitrate in methanol–CH_2Cl_2, whereas a Cu_2La_2 complex, $[Cu_2La_2(chp)_8(Hchp)_2(NO_3)_2]\cdot 2Hchp\cdot 2MeCN$, was obtained by the reaction in acetonitrile. A similar reaction in ethanol gave $[Cu_3La(chp)_8(NO_3)(EtOH)]$. In the Cu_2La_2 complex a pair of La atoms are bridged by two chp ligands through the oxygen atom to give a $\{La_2O_2\}$ core. To each La of the dinuclear core are bonded three chp and one Hchp ligands through the oxygen atom, and all the pyridyl groups of the eight chp ligands are involved in the accommodation of Cu ions to provide two peripheral $\{CuN_4\}$ units. The Cu_3La complexes, $[Cu_3La(chp)_5\text{-}(NO_3)_3(OMe)(MeOH)_2]$ and $[Cu_3La(chp)_8(NO_3)(EtOH)]$, have a $\{CuLaO_2\}$ core bridged by two chp ligands through the oxygen atom, and two peripheral Cu units are combined to the $\{CuLaO_2\}$ core by ambidentate cph ligands.

A similar reaction of $[Cu_2(chp)_4]$ with Gd^{III}, Dy^{III} or Er^{III} nitrate in methanol led to $[Cu_3Ln(chp)_8(NO_3)(S)]$ (S = H_2O or $(H_2O)_{0.5}(MeOH)_{0.5}$) [83,84]. A similar reaction in CH_2Cl_2 gave $[Cu_3Ln(chp)_8(NO_3)]$ for Ln = Gd, Pr, Nd, Sm, Er and $[Cu_3Ln(chp)_7(Hchp)(NO_3)_2]$ for Ln = Yb and Y. In $[Cu_3Gd(chp)_8(NO_3)]$ (Fig. 14), a pair of Cu and Gd atoms are bridged by two chp ligands providing a $\{CuGdO_2\}$ core. Four chp ligands are further bonded to the Gd through the oxygen atom and two chp ligands are bonded to the Cu through the nitrogen atom. The six pyridyl nitrogens of the bridging and O-bonded chp ligands and two oxygens of the N-bonded chp ligands are involved in the accommodation of two Cu ions. A reaction of $[Cu_2(chp)_4]$ with Yb^{III} or Er^{III} nitrate in tetrahydrofuran gave $[Cu_2Ln_2(\mu\text{-}OH)_2(chp)_4(NO_3)_4(H_2O)_4]$ and a similar reaction in CH_2Cl_2–MeOH gave $[Cu_2Ln_2(\mu\text{-}OMe)_2(chp)_4(NO_3)_4(MeOH)_4]$. The former has a $\{Cu_2(\mu\text{-}OH)_2\}$ core

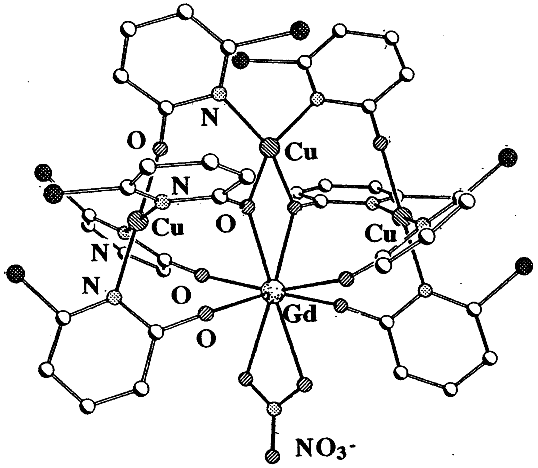


Fig. 14. Structure of $[Cu_3Gd(chp)_8(NO_3)]$.

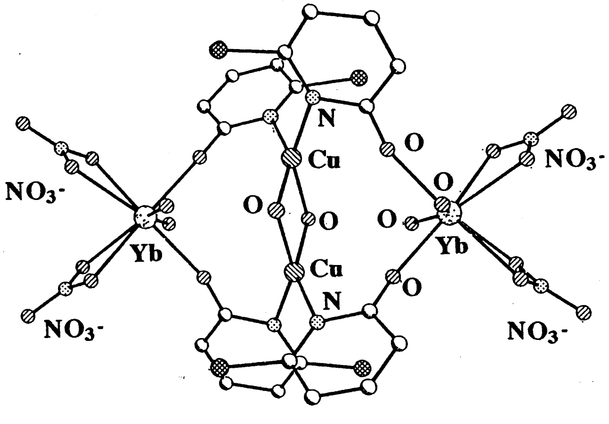


Fig. 15. Structure of $[\{CuYb(\mu\text{-}OH)(chp)_2(NO_3)_2(H_2O)_2\}_2]$.

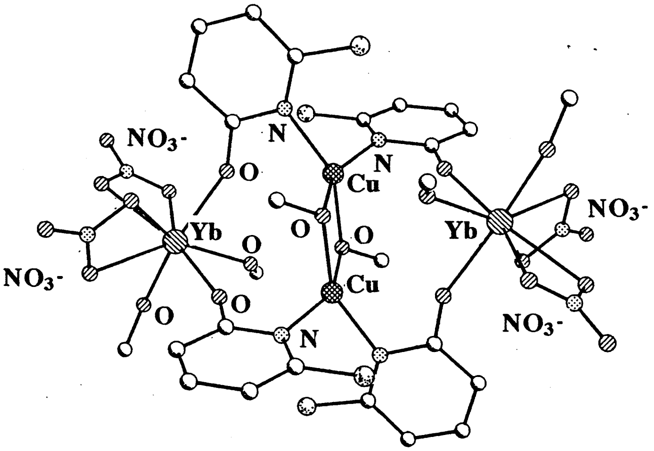


Fig. 16. Structure of $[\{CuYb(\mu\text{-}OMe)(chp)_2(NO_3)_2(MeOH)_2\}_2]$.

(Fig. 15) and the latter has a $\{Cu_2(\mu\text{-}OMe)_2\}$ core (Fig. 16), and to each dinuclear core are bonded peripheral two Ln units through ambidentate chp ligands.

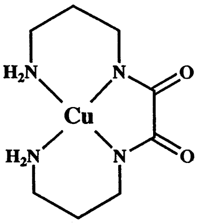
The reaction of dinuclear $[Cu_2(bhp)_4]$ (Hbhp = 6-bromo-2-pyridone) with Ln^{III} nitrate in CH_2Cl_2 gave $[Cu_3Ln(bhp)_8(NO_3)]$ for lighter Sm and Gd whereas $[Cu_2Er_2(\mu\text{-}OH)_2(bhp)_4(NO_3)_4(Hbhp)_4]$ for heavier Er [84]. The former complexes have a structure similar to that in Fig. 14. The latter has a $\{Cu_2(\mu\text{-}OH)_2\}$ core to which two peripheral Er units are linked through bhp ligands. A similar reaction in methanol gave $[Cu_2Ln_2(\mu\text{-}OMe)_2(bhp)_4(NO_3)_4(MeOH)_n]$ ($n = 6$ for Ln = Pr and Nd; $n = 4$ for Gd and Er) that has a $\{Cu_2(\mu\text{-}OMe)_2\}$ core with two peripheral Ln units linked through bhp ligands. Cu_2Ln_2 complexes $[Cu_2Ln_2(fhp)_8(NO_3)_2(MeOH)_2]$ (Ln = Pr, Gd, Yb) of 6-fluoro-2-pyridone (Hfhp) [84] have a fhp-bridged $\{Pr_2O_2\}$ core, similar to that of $[Cu_2La_2(chp)_8(Hchp)_2(NO_3)_2]$.

A cluster compound, $[Cu_6Na(mhp)_{12}]NO_3$, can be used as the precursor for Cu–Ln compounds of 6-methyl-2-pyridone (Hmhp) [85]. $[Cu_2Ln_2(OMe)_2(mhp)_4(NO_3)_4(Hmhp)_2(MeOH)_4]$ (Ln = La, Ce, Nd, Gd, Dy, Yb, Er) and $[Cu_2Sm_2(OMe)_2(mhp)_4(NO_3)_4(MeOH)_6]$ have been obtained by the reaction of this precursor with Ln^{III} nitrates [86]. They have a $\{Cu_2(\mu\text{-}OMe)_2\}$ core with two peripheral Ln units connected through mhp ligands. A similar reaction in CH_2Cl_2 gave an extraordinary compound of formula $[Cu_{12}La_8(OH)_{24}(NO_3)_{22}(Hmhp)_{13}(H_2O)_6](NO_3)_2\cdot 2Hmhp\cdot CH_2Cl_2$.

$[Ni_2Er_2(chp)_6(NO_3)_4(CH_3CN)_2]$ was prepared by the reaction of $[Ni_4(OMe)_4(chp)_4(MeOH)_7]$ with Er^{III} nitrate in acetonitrile [87]. It has a $\{Er_2(\mu\text{-}O(chp))_2\}$ core to which two peripheral Ni units are connected by chp ligands. A $Co_2^{II}Dy_2^{III}$ complex $(NEt_4)_2[Co_2Dy_2(OH)(chp)_6(NO_3)_5]$ was obtained by the reaction between $(NEt_4)_2[Co(chp)_4]$ and Dy^{III} nitrate. It has a central $\{Dy_2O_3\}$ core bridged by an oxo ion and two chp ligands. The two peripheral Co sites connected to the central core are quite distinct; one Co site is of six-coordination whereas the other site is tetrahedral.

2.6. d–f Complexes with oxamidates, oxamides and related ligands

In 1980, one of the present authors used *N*,*N*′-di(3-aminopropyl)oxamidatocopper(II) Cu(apod) (**16**) and *N*,*N*′-di(3-aminoethyl)oxamidatocopper(II) Cu(aeod) (**17**) as bidentate ligands to a second M^{II} ion to provide oxamidato-bridged tetranuclear CuM_3 complexes [88]. This was applied for preparing CuLn, Cu_2Ln, Cu_3Ln and Cu_4Ln complexes with apod and aeod ligands [89–94]. Dinuclear $[Cu(aeod)Ln(phen)_2(ClO_4)](ClO_4)_2$ were obtained when phen is used as the end-cap ligand. Trinuclear $[Gd\{Cu(dmpod)\}_2(H_2O)_4](NO_3)_3 \cdot 2H_2O$, derived from *N*,*N*′-bis(3-amino-2,2-dimethylpropyl)oxamidatocopper(II) Cu(dmpod), has a bent CuGdCu core where the central Gd is eight-coordinated by two Cu(dmpod) molecules in a *cis* position and four water molecules (Fig. 17). The Cu–Gd distance separated by the oxamidate group is 5.68 Å and the Cu–Cu distance is 7.694 Å.



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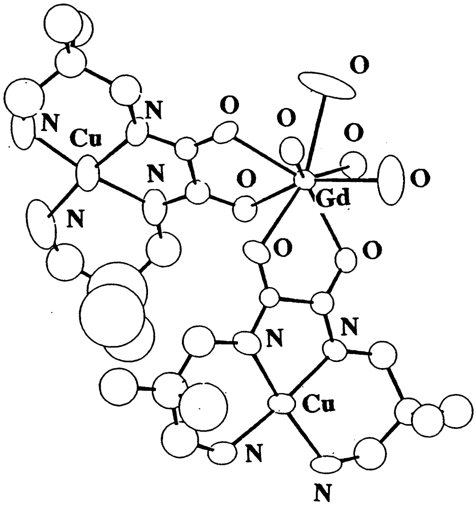


Fig. 17. Structure of $[Gd\{Cu(dmpod)\}_2(H_2O)_4](NO_3)_3 \cdot 2H_2O$.

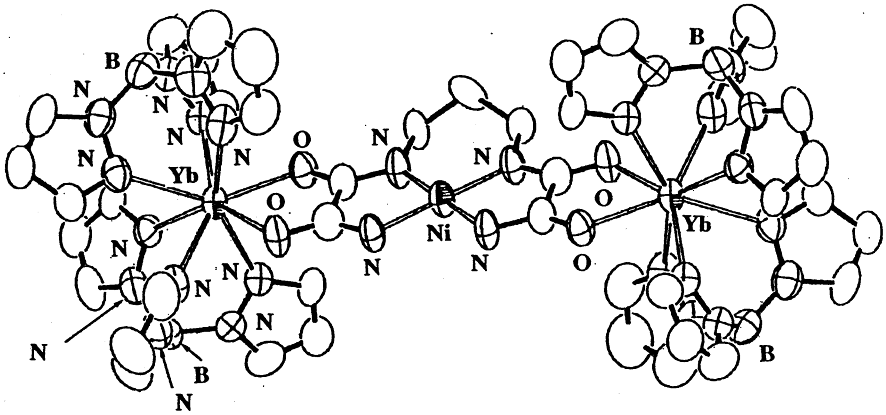
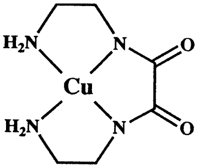


Fig. 18. Structure of Ni(tdod){Yb(htpb)$_2$}$_2$.



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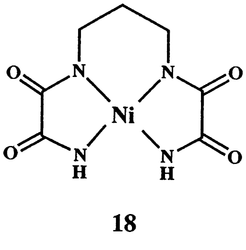
A series of tetranuclear Ln{Cu(aeod)}$_3$(ClO$_4$)$_3$(H$_2$O)$_{0-3}$ and pentanuclear Ln{Cu(apod)}$_4$X$_3$·nH$_2$O (Ln = Dy, Ho, Gd; X = ClO$_4^-$, PF$_6^-$) has been obtained [93,94]. X-ray crystallographic studies for the Cu$_4$Dy and Cu$_4$Ho complexes indicate a pseudo-square-antiprismatic environment about the Ln with eight oxygen atoms from four Cu(apod) molecules.

Trimethylenedi(oxamidato)nickelate(II) [Ni(tdod)]$^{2-}$ (**18**) and ethylenedi(oxamidato)nickelate(II) [Ni(edod)]$^{2-}$ (**19**) were used for providing Ni(L){Ln(htpb)$_2$}$_2$ (L = tdod or edod; htpb$^-$ = hydrotri(pyrazol-1-yl)borate; Ln = Eu, Tb, Yb) [95] of a linear Ln$^{\text{III}}$–Ni$^{\text{II}}$–Ln$^{\text{III}}$ core structure extended by the oxamidate group (Fig. 18). The Yb is eight-coordinate with six nitrogen atoms from two htpb ligands and two oxygen atoms from the oxamidate bridge.

3d–4f Complexes extended by an oxamato bridge have been extensively studied by Kahn with a view to the development of magnetic materials. They are discussed in the following section.



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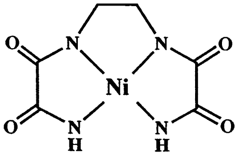

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3. Physicochemical properties

3.1. Magnetic properties

The first magnetic study of d–f complexes was carried out by Bencini et al. for $Gd\{Cu(acpen)\}_2(H_2O)_3(ClO_4)_3 \cdot 2Cu(acpen)$ and $Gd\{Cu(salen)\}_2(H_2O)(ClO_4)_3 \cdot 2Cu(salen) \cdot 0.5C_2H_5NO_2$ [5] consisting of a trinuclear Cu_2Gd unit and two isolated Cu complexes. A gradual increase in the $\chi_M T$ value with decreasing temperature suggested a ferromagnetic spin-exchange interaction between the adjacent Cu^{II} and Gd^{III} ions in the trinuclear core. The spin Hamiltonian for the trinuclear Cu^1–Gd^2–Cu^3 is given as $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J'S_1 \cdot S_3$ (Hamiltonian $H = -2\Sigma J_{ij} S_i S_j$ is used throughout this manuscript), where J is the exchange integral between the adjacent Cu^{II} and Gd^{III} ions and J' is that between the terminal Cu^{II} ions. Best-fits were carried out for the data, subtracted by the amount for two paramagnetic Cu^{II} from the net magnetic susceptibility, to obtain $J = +2.66$ cm^{-1} and $J' = -2.10$ cm^{-1} for the former complex and $J = +3.7$ cm^{-1} and $J' = -6.12$ cm^{-1} for the latter complex.

In order to avoid the ambiguities arising from the presence of the mononuclear Cu^{II} complexes in the above cases, cryomagnetic studies have been done for discrete dinuclear and trinuclear complexes containing Cu^{II} and Gd^{III} ions. The trinuclear complex, $Gd\{Cu(saltn)\}_2(H_2O)(NO_3)_3 \cdot 2C_2H_5NO_2$, showed a ferromagnetic interaction between the adjacent Cu and Gd ions ($J = +0.61$ cm^{-1}) and an antiferromagnetic interaction between the terminal Cu ions ($J' = -1.8$ cm^{-1}) [6]. This has $S_T = 9/2$ ground state and shows a long-range magnetic ordering at 245 mK [96]. Magnetic simulations for dinuclear $Gd(hfa)_3\{Cu(salen)(Meim)\}$ based on the magnetic susceptibility equation for $Cu^{II}(S = 1/2)$–$Gd^{III}(S = 7/2)$ gave a positive exchange integral of $J = +0.7$ cm^{-1} ($g_{Cu} = 2.10$ and $g_{Gd} = 2.00$) [7]. These and other studies for complexes containing Gd^{III} and Cu^{II} [10,11,97–99] have clarified that the magnetic interaction between the metal ions is substantially ferromagnetic.

To justify the observed ferromagnetic coupling between the adjacent Cu and Gd centers, Gatteschi proposed a partial delocalization of Cu^{II} unpaired electron to the empty 6s orbital of Gd^{III}. In this mechanism, the polarized spin on the 6s orbital is aligned in parallel with the electrons on the 4f orbital due to Fund's rule.

Kahn et al. have proposed an alternative mechanism that involves an interaction between the 3d–4f ground configuration (GC) and the metal–metal charge-transfer configuration (CTC) (Fig. 19) [100]. In the GC the two spin states, $S = 3$ and $S = 4$, are degenerate because the transfer integral β_{4f-3d} is essentially zero. The CTC is associated with an electron-transfer from the singly occupied orbital centered on Cu to an empty orbital centered on Gd. Two excited states, $S = 3$ and $S = 4$, arise and the latter is lower in energy owing to Hund's rule. The GT–CTC interaction stabilizes the $S = 3$ and $S = 4$ low-lying pairs by $-\beta^2_{5d-3d}/(U' + \Delta/2)$ and $-\beta^2_{5d-3d}/(U' - \Delta/2)$, respectively, so that the $S = 4$ state becomes lower in energy that the $S = 3$ state.

Such a ferromagnetic interaction has been recognized for a $Gd^{III}Ni^{II}$ complex $[NiGd(mosaldmtn)(NO_3)_3(H_2O)_2]$ ($J = +1.8$ cm^{-1}) [34], a $Gd^{III}V^{IV}(O)$ complex $VOGd(mosaldmen)(NO_3)_3$ ($J = +0.65$ cm^{-1}) [35], and a $Gd^{III}Fe^{III}$ complex $FeGd(vantren)(NO_3)_3{\cdot}2H_2O$ [55].

Magnetostructural studies have been made for some di(μ-phenoxo) CuGd complexes (Table 1), and a good correlation was established between the exchange integral and the dihedral angle defined by the $\{O_1CuO_2\}$ and $\{O_1GdO_2\}$ planes [37].

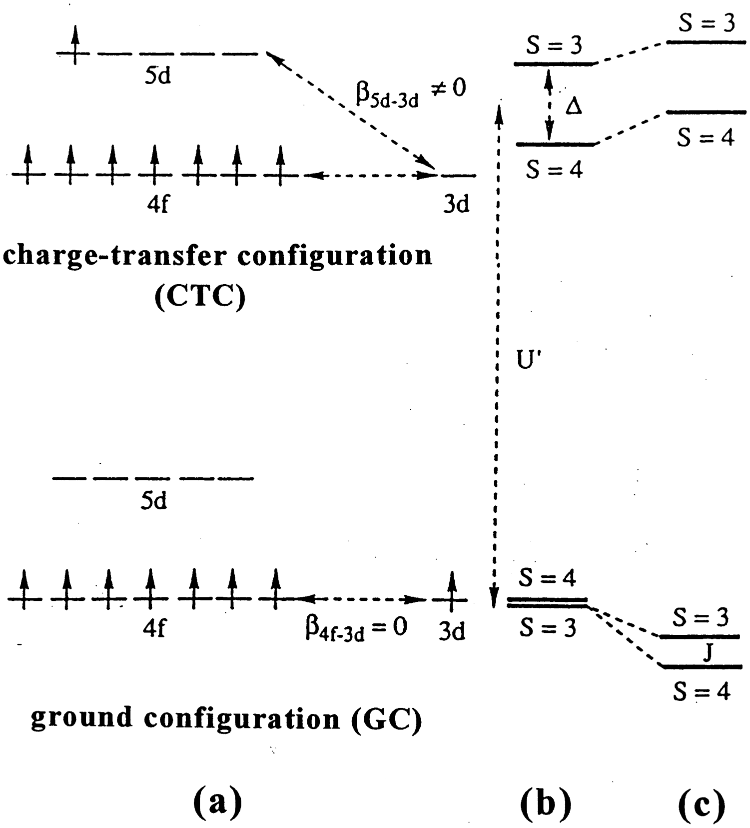


Fig. 19. A mechanism for ferromagnetic Cu^{II}–Gd^{III} interaction: (a) ground configuration (GC) and charge configuration (CTC); (b) spin states of GC and CTC without interaction between the two configurations; (c) spin states of GC and CTC in the presence of interaction between the two configurations.

Table 1
A correlation between the exchange integral and the dihedral angle ρ defined by OCuO and OGdO planes in some Cu^{II}–Gd^{III} complexes

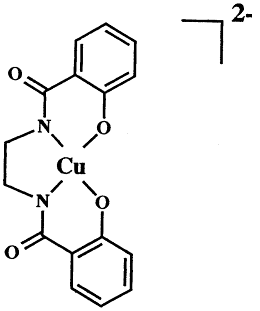
	J (cm^{-1})	ρ (°)	References
$Cu(salen)(Meim)Gd(hfa)_3$	1.4	39.6	[7]
$CuGd(mosaldmtn)(mmc)(thd)_2$ [a]	4.2	19.1	[40]
$CuGd(mosaldmtn)(acetone)(NO_3)_3$	4.8	16.6	[35]
$Cu(mosalim)_2(MeOH)Gd(NO_3)_3$	6.8	12.5	[35]
$CuGd(mosaldmen)(acetone)(NO_3)_3$	7.2	12.9	[34]
$CuGd(mosaldmtn)Cl_3(H_2O)_6$	10.1	1.2	[39]

[a] mmc = monomethyl carbonate, thd = 2,2,6,6-tetramethylheptane-3,5-donate.

The ferromagnetic interaction between Cu^{II} and Gd^{III} ions generally becomes stronger when the dihedral angle becomes smaller.

A ferromagnetic interaction between the adjacent Cu and Gd centers can occur through oxamidato bridge in spite of a large Cu–Gd separation (~ 7.7 Å) [92]. Magnetic studies ware carried out for pentanuclear $Gd\{Cu(apod)\}_4X_3 \cdot nH_2O$ ($X = ClO_4^-$, PF_6^-) which has the $S_T = 11/2$ ground state. This is a case of spin frustration. The preferred ground state among $S_T = 11/2$–$3/2$ for this system has been discussed as a function of the $J_{CuCu}/J_{GdCu}(\alpha)$ ratio.

A series of Ln_2Cu_3 complexes (Ln = Y, Pr–Yb) were derived from *N*,*N′*-ethylenedi(salicylamidato)cuprate(II) $Cu(esam)^{2-}$ (**20**) [101] and a ferromagnetic ordering is reported for $Gd_2\{Cu(esam)\}_3 \cdot 6H_2O \cdot 4DMF$.



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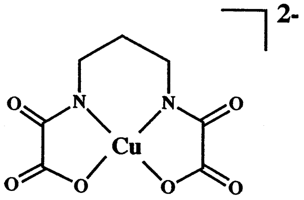
In 1988, Kahn reported a molecular-based magnet by assembling bimetallic $\{MnCu(pba)\}_n$ chains derived from 1,3-propylenebis(oxamato)-copper(II) $[Cu(pba)]^{2-}$ (**21**) [102]. Analogous bimetallic chain compounds having Ln ion as the simple metal component were extensively studied by Kahn, with the aim to develop new magnetic materials [103–106]. Three types of compounds have been derived from $[Cu(pba)]^{2-}$ [105]. One type is $Ln_2(ox)\{Cu(pba)\}_3Cu(H_2O)_5 \cdot 20H_2O$ (Ln_2Cu_3Cu) obtained from an aqueous solution of $Na_2[Cu(pba)] \cdot 6H_2O$ and hydrated $LnCl_3$. The oxalate group in the product arises from the hydrolysis of the pba ligand. The structure of the Gd_2Cu_3Cu complex has a puckered ladder structure with infinite {–Gd–Cu(pba)–}$_n$ side pieces and Cu(pba) rungs joining two Gd atoms; the ladders are associated across oxalato groups combining two Gd centers to provide a 2D layer (Fig. 20). Each Gd has a nine-coordinate polyhedra with six oxygens from three bridging Cu(pba) complexes, two oxygens from a bridging ox group and a water molecule. The $[Cu(H_2O)_5]^{2+}$ cation is interspersed between the layers. This type can be obtained for Ln = La–Gd.



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The second type of formula $Ln_2\{Cu(pba)\}_3 \cdot 23H_2O$ (Ln_2Cu_3; Ln = La–Gd), prepared by a more exotic method [105,106], consists of discrete and infinite tube-like motifs with a pseudo-four-fold symmetry, resulting from the condensation of the two ladder motifs found for the first type (Fig. 21). The third type, obtained for Ln = Tb–Yb and Y in exactly the same way as that for the first type, has the same formula as the second type (Ln_2Cu_3) but the ladder motif found for the first type. Notably the $\chi_M T$ value for the Nd_2Cu_3 complex continuously decreased with decreasing temperature and approached zero at low temperature [107]. This was explained by an antiferromagnetic interaction between the local Kramer's doublet for Nd^{III} and that for Cu^{II} to provide a non-magnetic ground state. Based on specific heat studies, the La_2Cu_3Cu and Gd_2Cu_3Cu complexes showed magnetic ordering at (T_c =) 1.12 and 1.05 K, respectively [108]. Similarly, a long-range

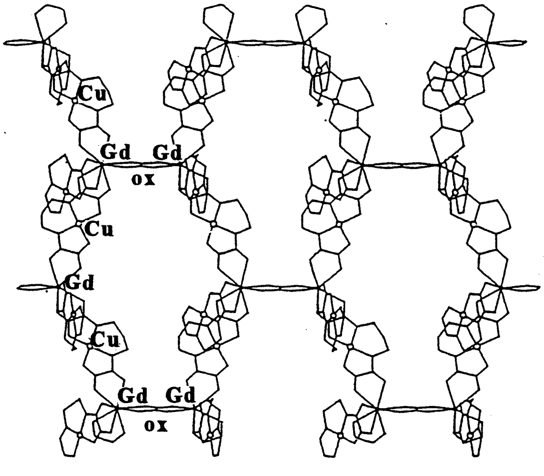


Fig. 20. Structure of $Gd_2(ox)\{Cu(pba)\}_3Cu(H_2O)_5 \cdot 20H_2O$.

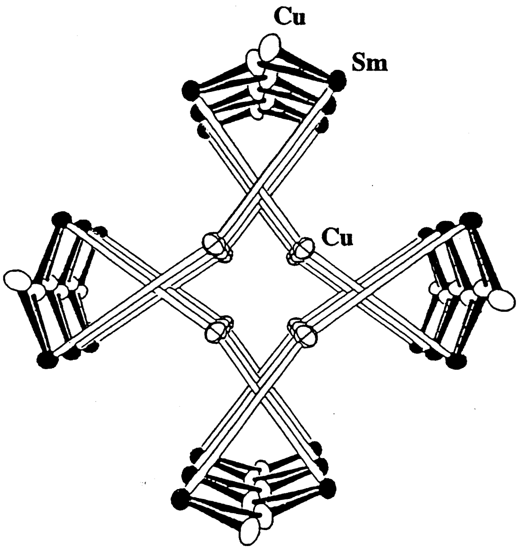
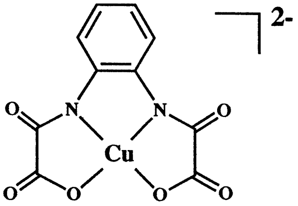


Fig. 21. Structure of $Ln_2\{Cu(pba)\}_3 \cdot 23H_2O$.

magnetic ordering was confirmed for $Gd_2\{Cu(opba)\}_3 \cdot 6DMSO \cdot 4H_2O$ ($T_c = 1.78$ K) [109].

The precursor *o*-phenylenebis(oxamato)cuprate(II) $Cu(opba)^{2-}$ (**22**) reacts with heavier Ln ions to afford $Ln_2\{Cu(opba)\}_3 \cdot xDMF \cdot yH_2O$ (Ln = Tb–Lu and Y) that consist of a ladder-type motif like that in Fig. 20 [110,111]. The nature of the Ln–Cu magnetic interaction in each compound was investigated in comparison with the corresponding Ln_2Zn_3 complexes [112]. The Ln^{III}–Cu^{II} interaction is ferromagnetic for Ln = Tb and Dy, might be ferromagnetic for Tm, but not ferromagnetic for Ho, Er and Yb.



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3.2. Molecular recognition

The emergence of heteronucleating compartmental ligands has enabled studies of 3d–4f complexes in solution. The visible spectra of the CuLn complexes with csalen and csalpn ligands are highly dependent upon the nature of solvent used (DMSO, DMF or py) [14]. The complexes show a distinct d–d band due to the Cu^{II} in the visible region, and the band maximum shifts to lower energy in the order of solvent: py ≪ DMF < DMSO (Fig. 22). This can be explained by 'selective solvation' on the CuLn core as schematically shown in Fig. 23. That is, the solvation preferentially occurs at the Cu center in pyridine whereas at the Ln center in DMSO or DMF. In the latter case, the strong association of DMSO (or DMF) molecules with the Ln center gives rise to an essentially planar geometry about the Cu.

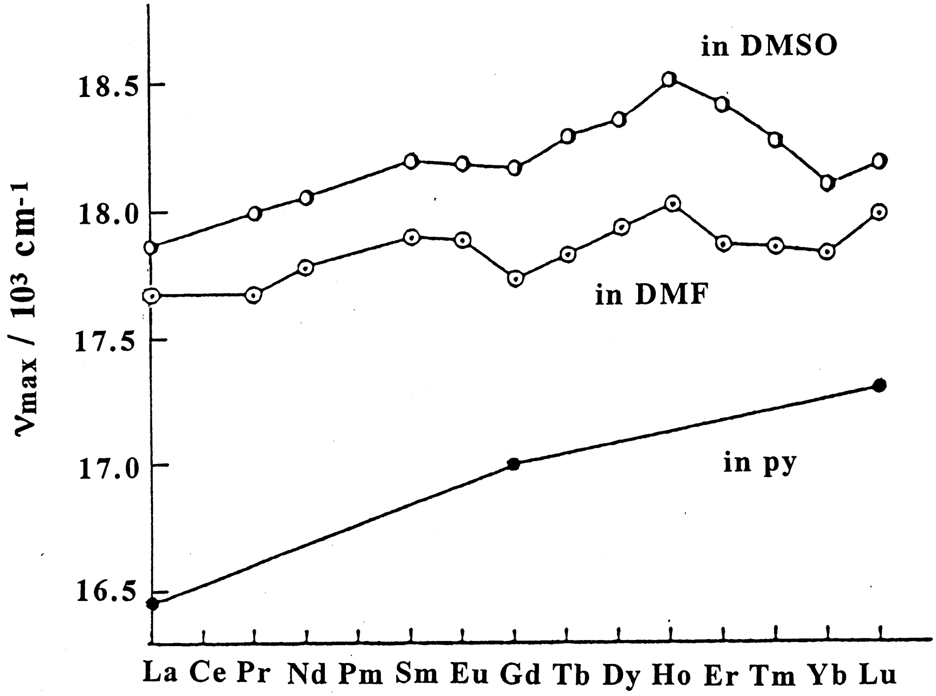


Fig. 22. Cu d–d maximum of $CuLn(csalen)(H_2O)_4$ in DMSO, DMF and py.

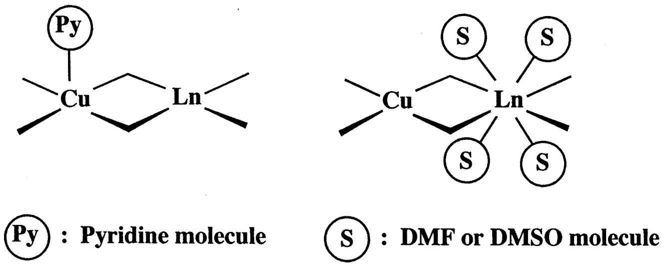


Fig. 23. Schematic pictures of selective solvation on CuLn core.

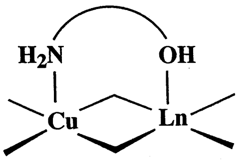


Fig. 24. Specific binding of aminoalcohols on CuLn core.

The selective solvation of the d–f complexes has been extended to 'specific binding' of substrates, having a nitrogen and an oxygen donor, onto the CuLn center (Fig. 24) [113]. In a DMF solution, an aminoalcohol is bound to the dinuclear core through the donation of the amino nitrogen to the Cu and the donation of the alcohol oxygen to the Ln. This is indicated by a pronounced red shift of the Cu d–d and a prominent circular dichroism induced to the visible band when optically active (*R*)-2-amino-1-butanol was employed. Such specific binding of aminoalcohols has been commonly observed for CuLn complexes with csaldien^{4-} [97] and CoLn complexes with csalen^{4-} [15]. It was shown that glycols are associated with the Ln center and amino acidates are also associated with the Ln center solely with the carboxylate site. The $Co^{II}Ln^{III}$ (Ln = Y, La) complexes of csalen react with 3,5-di-*t*-butyl-*o*-benzoquinone (DBQ), through a bridge over the CoLn core, providing a $Co^{III}Ln^{III}$(DBSQ) species (DBSQ = 3,5-di-*t*-butyl-*o*-semiquinone) [16]. EPR studies of the products, however, indicate that the DBSQ is bidentately bonded to the Ln center.

3.3. Photophysical properties

The neighboring effect of the d metal ion upon the fluorescence of Eu^{III} and Tb^{III} has been extensively studied in our laboratories. Fluorescence of the metal ions was drastically quenched on adding transition metal complexes of quadridentate Schiff bases [114–116], but this was not observed with simple metal salts as the additives. It is supposed that dinuclear $M^{II}Eu^{III}$ ($M^{II}Tb^{III}$) complex formation is responsible for radiation-less energy loss from excited Eu^{III} to M^{II}. The significance of a $M^{II}Eu^{III}$ pair in fluorescence quenching was proven by a study using $Eu(H_2csalen)(NO_3)(H_2O)_5$ and $MEu(csalen)(NO_3)(H_2O)_{4-6}$ (M^{II} = Cu, Ni, VO) [16,17]. In the solid state the mononuclear Eu complex shows significant fluorescent bands due to $^7F_0 \rightarrow {}^7F_J$ transitions at 580, 593, 615, 653 and ~700 nm (excited at 394 nm), whereas they are almost quenched in the dinuclear complexes (see Fig. 25). The same result was obtained in DMF solution by different excitations (342, 394 and 464 nm).

Attention has been focussed on the development of segmental ligands that have metal-binding sites coded for the selective complexation of d and f metal ions, for the design of new Ln-containing photophysical material. Piguet used a segmental ligand L^1 (see Fig. 26) for providing triple-helicated d–f complexes by a self-assembling process [117–119]. The ligand L^1 has the tridentate 2,6-bis(benzimidazol-6-yl)pyridine unit and the bidentate 2-(benzimidazol-6-yl)pyridine unit and reacts with Ln^{III} (La–Lu) and M^{II} (Zn or Fe) ions to afford $[LnM(L^1)_3]^{5+}$. The M center is surrounded by the three bidentate units in a facial octahedral manner, controlling a helical arrangement of the remaining tridentate units and leading to the facial pseudo-tricapped polyhedra about the Ln center (Fig. 26). The $[LnFe(L^1)_3]^{5+}$ complexes exhibit spin-crossover phenomena based on high-spin/low-spin transi-

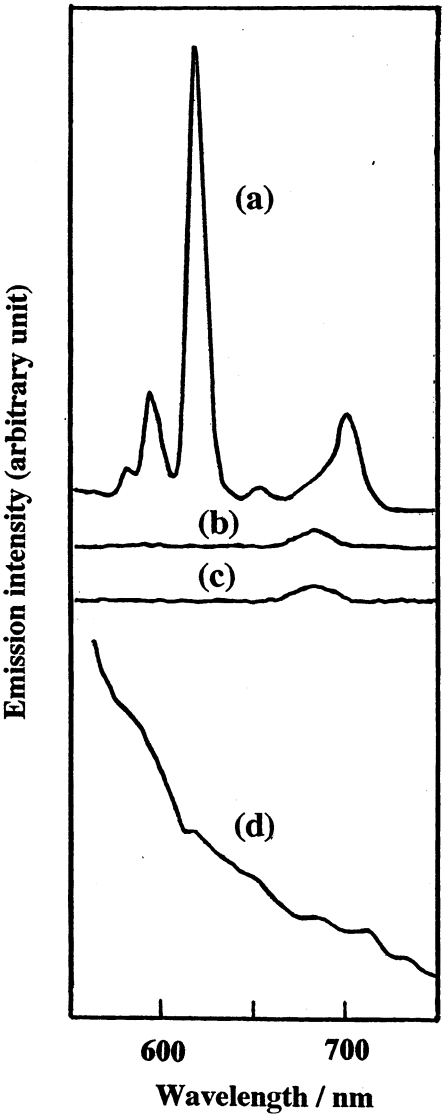


Fig. 25. Fluorescence spectra of (a) mononuclear Eu^{III}, (b) dinuclear $Cu^{II}Eu^{III}$, (c) $Ni^{II}Eu^{III}$ and (d) $V^{IV}(O)Eu^{III}$ complexes in solid state (excited at 394 nm). Slit widths (nm) of excitation and emission sides: 2 and 2 for (a) and 10 and 5 for (b), (c) and (d). Ordinate scale is 64 × .

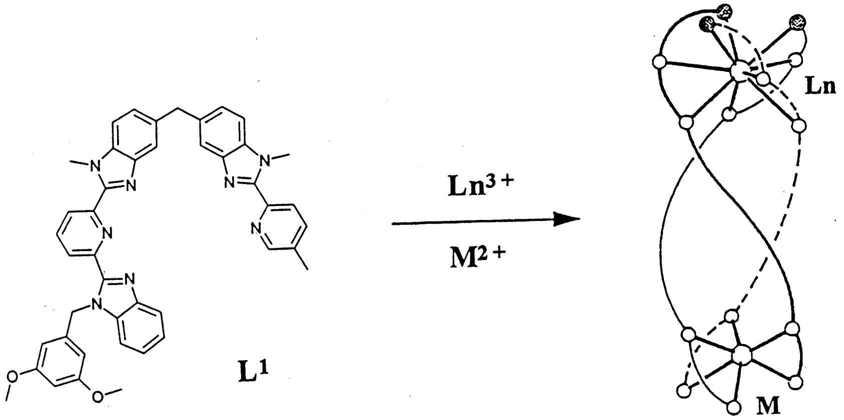
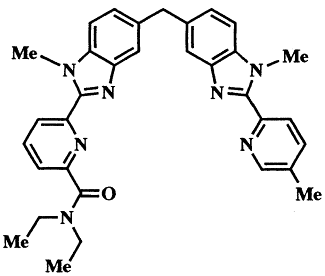


Fig. 26. Self-assembly of L^1 to provide [LnM(L^1)$_3$]$^{5+}$.

tions of Fe^{II}. The EuZn complex is only weakly luminescent as a result of the closely packed arrangement of the ligands.

The L^2 ligand (**23**) having an *N*,*N*-diethylcarboxamide group instead of the terminal benzimidazole group of L^1 has been developed [119–124] since carboxamide groups have a high affinity for Ln^{III} ion and favor resonant L$^2 \rightarrow$ Ln^{III} (Eu, Tb) energy transfer. The X-ray crystallographic results for the [EuZn(L^2)$_3$]$^{5+}$ complex indicate a helical structure with an Eu–Zn interatomic separation of 8.96 Å. The EuZn complex is strongly luminescent both in the solid state and in solution and shows emission bands associated with $^5D_0$–^7F_j transitions. The quantum yield in acetonitrile is enhanced by a factor of 10^3–10^4 relative to that of the [EuZn(L^1)$_3$]$^{5+}$ complex. The Fe^{II} of [LnFe(L^2)$_3$]$^{5+}$ (Ln = La, Nd, Eu, Gd, Tb, Yb, Lu, Y, Sc) sustains a thermally induced low-spin/high-spin transition around room temperature in acetonitrile [122]. The mole fraction of high-spin Fe^{II} at 333 K for the LnFe (Ln = La, Y, Lu, Sc) complexes ranged from 0.38 to 0.50, and decreased with decreasing temperature to zero at 230 K. Photophysical studies for the EuFe complex indicate complete quenching of the Eu emission probably due to the energy transfer from the Eu^{III} to the Fe^{II}.



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4. Conclusions

The Chemistry of d–f mixed-metal complexes has made remarkable progress in the past 15 years, though the types of complexes are still limited. Initially, interest lay in the magnetic interaction between d and f metal ions and the extension to molecular-based magnetic materials. The magnetic spin-exchange interaction between d and f metal ions is generally weak because the 4f orbitals are shielded by the outer filled 5s and 5p orbitals. The magnetic interaction between Gd^{III} and Cu^{II} (or other 3d metal ions) is certainly ferromagnetic, but the magnetic interaction in d–f systems with Ln^{III} other than Gd^{III} has not been clarified. Attempts to provide magnetic materials based on d–f assemblies have not yet been successful, but the d–f mixed-metal assemblies studied so far are restricted to those of one- or two-dimensional networks. A fairly high T_c might be possible based on a d–f assembly when the d and f metal ions are ideally arranged in a three-dimensional network. Characteristics typical of d–f complexes are limited, but new and important feature must be found in the progress of this field. Of particular importance will be the interplay of hard f metal ion and soft (or moderate) d metal ion in a d–f heteronuclear system, as indicated by the binding of aminoalcohols on a d–f dinuclear core. The idea of the interplay of d and f metal ions can be extended to the design of functional bimetallic systems, using the f metal ion as the substrate binding site and the d metal ion as the reaction site.

Another significance of d–f complexes is the potential use as precursors for d–f mixed-metal oxides [28,31,125,126]. For example, Perovskite-type solids $LaMO_3$ (Mn, Co, Ni) were obtained in high purity by the thermal decomposition of $LnM(csalen)(NO_3)(H_2O)_n$ at a low temperature (500–600°C) [125]. Similarly, superconducting $YBa_2Cu_3O_{7-\delta}$ could be readily prepared from $CuY_{1/3}Ba_{2/3}(osalen)(NO_3)_{1/3}(H_2O)_3$ [31].

Acknowledgements

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