# Synthesis, structures and magnetic properties of a series of polynuclear copper(II)-lanthanide(III) complexes assembled with carboxylate and hydroxide ligands

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Heterometallic copper(II)-lanthanide(III) complexes have been made with a variety of exclusively $O$-donor ligands including betaines (zwitterionic carboxylates) and chloroacetate, which are dinuclear CuLn, tetranuclear $Cu_2Ln_2$, pentanuclear $Cu_3Ln_2$, and octadecanuclear $Cu_{12}Ln_6$ complexes. The results show that subtle changes in both the carboxylates and acidity of the reaction solution can cause drastic changes in the structures of the products. Magnetic studies exhibit that shielding of the $Ln^{3+}$ $4f$ electrons by the outer shell electrons is very effective to preclude significant coupling interaction between the $Ln^{3+}$ $4f$ electrons and $Cu^{2+}$ $3d$ electrons in either a mono-atomic hydroxide-bridged, or a carboxylate-bridged system.

**Keywords**    Copper(II)-lanthanide(III) complex, carboxylate, hydroxide, crystal structure, magnetic properties

## Introduction

Polynuclear mixed metal complexes are of special current interest for several reasons. The nature of magnetic exchange interactions between transition and lanthanide metal ions with bridging ligands has attracted considerable interest in both theoretic study and possible applications.[1-3] This kind of compounds are also possible precursors for production of high-$T_c$ superconductors.[4,5] Recently polynuclear metal complexes have also been reported to serve as host for small molecules or ions.[6-8] Some of heterometallic compounds have been developed for new materials, such as those of magnetic bubble memories and magneto-optical devices using $SmCo_5$ and $Nd_2Fe_{14}B$,[9] the $YBa_2Cu_3O_{7-x}$ type high-$T_c$ superconduc- tors.[10]
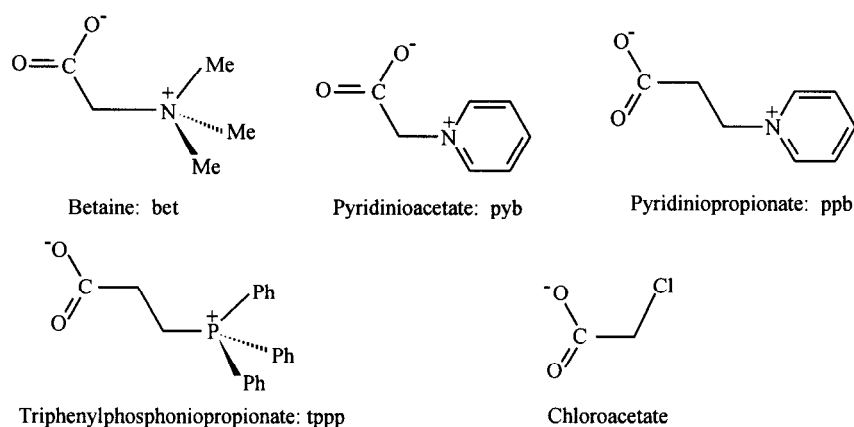
All above studies demand that the interactions of lanthanide(III) metal (designated as $Ln^{3+}$ hereafter) ions with transition metal ions be better understood, especially in order to establish a useful structural-magnetic correlation of these types of mixed-metal ions.[11] In 1985, Gatteschi *et al.* observed that when $Cu^{2+}$ and $Gd^{3+}$ were brought into close proximity the coupling between the ions was weak ferromagnetic.[1] This discovery has stimulated great attention in investigation of the interaction of $3d$-$4f$ metal ions, bearing in mind that either ferromagnetic or anti-ferromagnetic interaction between one unpaired $Cu^{2+}$ $d$ electron and rich $Ln^{3+}$ $4f$ electrons, such as $Gd^{3+}$, will yield magnetic ordering within a Cu—Ln complex, which may be a potential molecular magnet!

Obviously due to the large difference in coordination behaviors of $Cu^{2+}$ and $Ln^{3+}$ ions, in the initial work of Cu—Ln complexes, polydentate Schiff-base ligands were used to bridge these metal centres,[1-3] later pyridonate and oxamide ligands had been used.[12,13] All these ligands have in common a mixed-donor set, where it was intended that harder $O$-donors would favor binding to the oxophilic $Ln^{3+}$ centers, while the softer $N$-donors would bind to the $Cu^{2+}$ centers.[14] One question raised to us: is it possible to assemble Cu—Ln complexes with ligands bearing only a single type of donors? This is challenging since so far heterometallic complexes consolidated by a single type of donors, such as $O$-atoms, are rarely observed.

**Scheme 1**    Carboxylate ligands



Betaine: bet          Pyridinioacetate: pyb          Pyridiniopropionate: ppb

Triphenylphosphoniopropionate: tppp          Chloroacetate

In 1991, we isolated and structurally characterized an interesting monomeric $Cu^{2+}$ tetracarboxylate, namely $[Cu(betaine)_4](NO_3)_2$ (betaine = trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$, designated as bet hereafter, see Scheme 1), in which four zwitterionic carboxylate ligands act in an unsymmetric chelate mode in coordination to the $Cu^{2+}$ center.[15] We have also found that the stable $[Cu(bet)_4]^{2+}$ core can be used as a "metallo-ligand" to bind other hard metal ions, i. e. $Ca^{2+}$ and $Li^+$, to form heterometallic complexes $[LiCu(bet)_4]_n(ClO_4)_{3n}$ and $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$ (Scheme 1).[16,17] Since $Ln^{3+}$ ions are very similar to hard $Ca^{2+}$ ion in coordination chemistry, we were encouraged by these facts to believe that the monomeric $Cu^{2+}$ tetracarboxylates could also be used to bind $Ln^{3+}$ ions to form carboxylate-bridged polynuclear Cu—Ln complexes, thus providing a new synthetic route for heterometallic complexes in metal carboxylate chemistry, as well as a new ground for magnetic investigation of this kind of heterometallic complexes. Indeed, we succeeded in generating the first carboxylate-bridged Cu—Ln complexes using a betaine derivative pyridinioacetate (pyb), namely $[CuLn(pyb)_5(H_2O)_5](ClO_4)_5 \cdot nH_2O$.[18,19] Thereupon, we have also succeeded in preparation of a series of polynuclear Cu—Ln complexes containing uniquely O-donors such as betaine derivatives and chloroacetate, as shown in Scheme 2, which include dinuclear $CuLn$,[19] tetranuclear $Cu_2Ln_2$,[20,21] pentanuclear $Cu_3Ln_2$,[19,22] as well as octadecanuclear $Cu_{12}Ln_6$ complexes.[23-25] In this review, we describe systematically the synthesis, crystals structures and mag-

netic properties of these heterometallic complexes.

**Scheme 2**    Ligation of the $Cu^{2+}$ tetracarboxylate as "metallo-ligands" to bind other hard metal ions
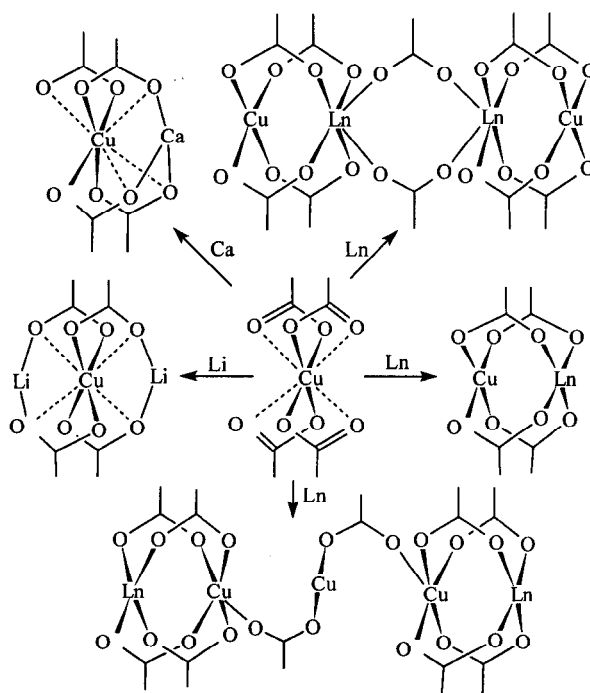


# Complexes of pyridinioacetate and pyridiniopropionate

When aqueous solutions of pyb, $Cu(NO_3)_2$, $Ln(NO_3)_3$ and $NaClO_4$ in the ratio of $6:1:2:10$ were adjusted to pH $\approx 2.5$, we obtained dinuclear complexes comprising novel discrete dinuclear $[CuLn(pyb)_5-$

$(H_2O)_5]^{5+}$ (1, $Ln^{3+}$ = $La^{3+}$, $Ce^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Dy^{3+}$, $Gd^{3+}$, $Er^{3+}$, or $Y^{3+}$) cations,[18,19] perchlorate anions and lattice water molecules. A view of the dinuclear cation is shown in Fig. 1. The $Cu^{2+}$ ion in **1** is coordinated by four carboxylate $O$-atoms at the basal plane and completed by an aqua ligand at the apical position to form a square-pyramidal geometry. The $Ln^{3+}$ ion is quadruply bridged to the $Cu^{2+}$ ion by four $\mu_2$-carboxylate groups with an intramolecular Cu···Ln distance of ca. 376 pm. Except for the four $\mu_2$-carboxylate $O$-atoms, the $Ln^{3+}$ ion is further coordinated by one monodentate carboxylate $O$-atom, and four aqua ligands to form a distorted monocapped square-antiprism.
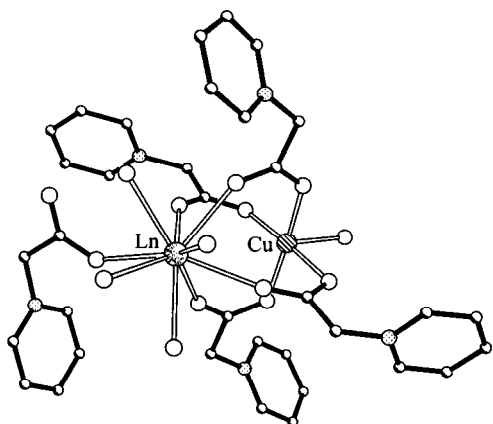


**Fig. 1**    Crystal structure of the cation in **1**. The Ln atom is speckled, the $Cu^{2+}$ atom is hatched, the N atoms are regularly dotted, and the O atoms are open circles.

Noteworthy is that when the pH of the same reaction mixture for **1·Nd** was adjusted to 3.0, a pentanuclear complex [ $Cu_3Nd_2$ ( pyb )$_{10}$ ( $NO_3$ )$_2$ ( $H_2O$ )$_8$ ] ( $ClO_4$ )$_5$·$2H_2O$ (**2**) was isolated. As shown in Fig. 2, it features a centrosymmetrical pentanuclear [ $Cu_3Nd_2$-(pyb )$_{10}$ ( $NO_3$ )$_2$ ( $H_2O$ )$_8$ ]$^{10+}$ cation, in which each $Nd^{3+}$ ion is quadruply bridged to a $Cu^{2+}$ ion by four syn-syn $\mu_2$-carboxylate groups of pyb with an intramolecular Cu···Nd separation of 365 pm. The coordination sphere of the $Nd^{3+}$ ion is further completed by a chelate nitrate group and three aqua ligands to form a monocapped square-antiprism. The $Cu^{2+}$ ion in the subunit is ligated in a distorted square-pyramid with four $O$-atoms from the quadruple $\mu_2$-carboxylate bridge at the basal plane and one $O$-atom from another carboxylate at

the apical position. A pair of the $Cu^{2+}$ atoms in two inversely related CuNd subunits is each linked to the central $Cu^{2+}$ ion by a single syn-anti $\mu_2$-carboxylate bridge, furnishing a pentanuclear cation. The central $Cu^{2+}$ atom, being located at an inversion center, is ligated by two carboxylate $O$-atoms and two aqua $O$-atoms in a slightly distorted square-planar fashion.
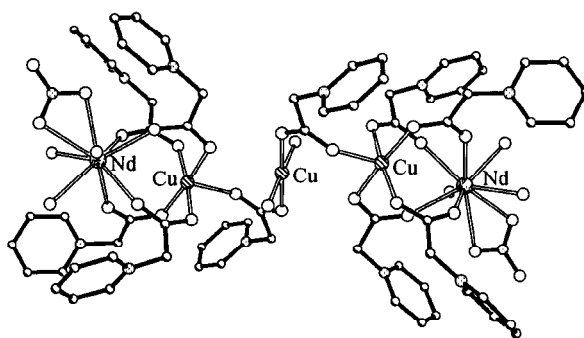


**Fig. 2**    Crystal structure of the cation in **2**. The Ln atoms are speckled, the $Cu^{2+}$ atoms are hatched, the N atoms are regularly dotted, and the O atoms are open circles.
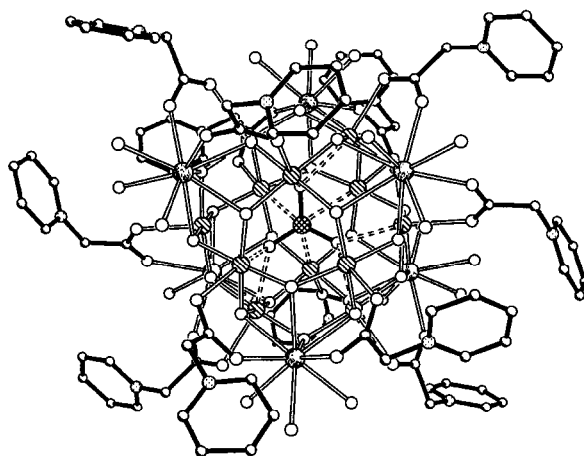


**Fig. 3**    Crystal structure of the cation in **3**. The Ln atoms are speckled, the Cu atom are hatched, the Cl atom is cross-hatched, the N atoms are regularly dotted, and the O atoms are open circles.

More interestingly, when pH values of the same reaction mixtures for **1** were adjusted to 3.5 or higher, [ $Cu_{12}Ln_6$($\mu_3$-OH)$_{24}$(pyb)$_{12}$($H_2O$)$_{18}$($ClO_4$) ] ( $ClO_4$ )$_{17}$·$nH_2O$ complexes (**3**, $Ln^{3+}$ = $Y^{3+}$, $Ce^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Gd^{3+}$, or $Er^{3+}$) were yielded,[23,24] the cation of which features a pseudocubic $O_h$ symmetry, with six $Ln^{3+}$ ions positioned at the vertices of a regular octahe-

dron and twelve $Cu^{2+}$ ions located at the midpoints of the twelve octahedral edges as shown in Fig. 3. The polyhedron of twelve $Cu^{2+}$ ions may be viewed as a cuboctahedron that is capped on the six square faces by the six $Ln^{3+}$ ions. This Cu—Ln metal framework is interconnected by twenty-four $\mu_3$-OH bridges that are each linked to one $Ln^{3+}$ ion and two $Cu^{2+}$ ions such that each $Ln(\mu_3$-OH$)_4$ fragment is square-pyramidal and each Cu-$(\mu_3$-OH$)_4$ fragment is square-planar (Fig. 4a). The encapsulated $ClO_4^-$ anion exhibits an unprecedented 12-co-

ordinate mode, in which each of the four $O$-atoms is connected to three $Cu^{2+}$ ions (Fig. 4b). The entire cation is then generated by addition of the eighteen $H_2O$ and twenty-four carboxylate $O$-atoms of the twelve pyb ligands. The external linkage of a pyb $O$-atom to each $Cu^{2+}$ ion results in an elongated octahedron. Each 9-coordinated $Ln^{3+}$ ion is connected to four $\mu_3$-OH ligands, three aqua $O$-atoms, and two carboxylate $O$-atoms from two different pyb ligands.
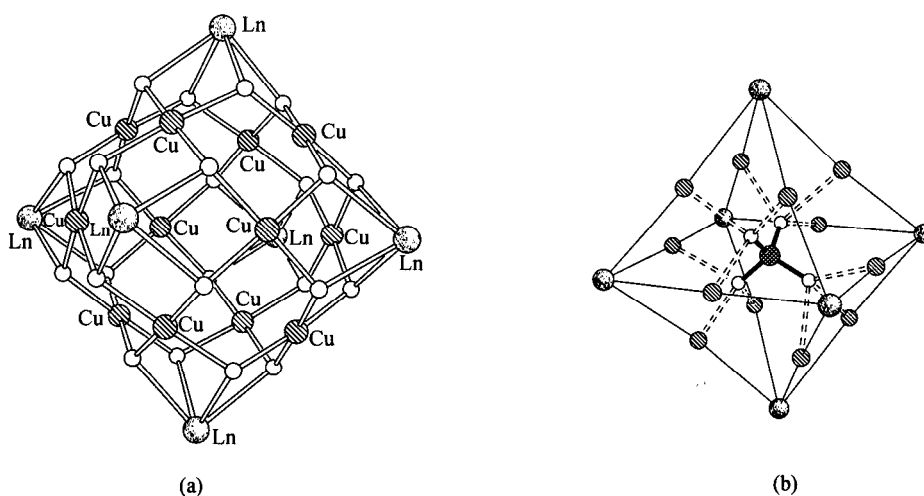


(a)                                                        (b)

**Fig. 4**  Views showing the octadecanuclear $Cu_{12}Ln_6(\mu_3$-OH$)_{24}$ cage (a) and the encapsulation of a $\mu_{12}$-$ClO_4^-$ in the octahedral $Cu_{12}Ln_6$ core (b) in **3**. The Ln atoms are speckled, the Cu atom are hatched, the Cl atom is cross-hatched, andthe O atoms are open circles.

Similar octadecanuclear cations $[Cu_{12}Ln_6(OH)_{24}$-$(prb)_{12}(H_2O)_{16}(ClO_4)]^{17+}$ (**4**, $Ln^{3+} = Gd^{3+}$ or $Sm^{3+}$) were synthesized in the same method by using an higher analogue of pyb, pyridiniopropionate (prb).[25] The crystal structures of **4** are similar to those of **3**, as illustrated in Fig. 5. The significant structural differences between **3** and **4** are given rise by the ligation modes of the carboxylate groups. In **3**, all the pyb ligands act uniquely in the $\mu_2$-carboxylate-$O$, $O'$ mode, each bridging a $Cu^{2+}$ and a $Ln^{3+}$ atoms. In contrast, only ten ppb ligands act in the $\mu_2$-bridging mode, while the other two ppb ligands act in the $\eta_2$-carboxylate-$O$, $O'$ mode each chelating a $Ln^{3+}$ ion in **4**. Meanwhile, as a pair of ppb ligands function in a chelate mode, no carboxylate $O$-atom coordinates the axial positions of two $Cu^{2+}$ atoms, resulting in the 5-coordinate environment about these two $Cu^{2+}$ atoms concomitant with shorter axial Cu—O ($ClO_4$) bonds (228 pm) as compared with those for the

6-coordinate $Cu^{2+}$ centers. In contrast, no 5-coordinate $Cu^{2+}$ center presents in **3**. Existence of the chelate ppb ligands in **4** may be rationalized on the basis that with the additional methylene group between the carboxy group and the $N$-atom as compared to pyb, the positively-charged $N$-atom of ppb has much weaker inductive effect on the carboxy group, hence ppb has a smaller O—C—O bond angle.[26] The smaller O—C—O bond angle may enhance the chelate tendency of carboxy group toward larger metal ions.[27]

In above-mentioned synthetic procedures, acidity of the reaction solution is critically important, a subtle change in acidity of the reaction solution can cause a drastic change in the structures of the products. The three types of complexes **1**, **2** and **3** are synthesized in the similar conditions with slight differences in pH values of the solutions. At low pH value (pH $\approx 2.5$), the [Cu-$(pyb)_4]^{2+}$ core can bind a $Ln^{3+}$ ion to form dinuclear $[CuLn(pyb)_4]^{5+}$ cores in **1**, which can be connected to

construct higher nuclearity complexes such as the pen-tanuclear core in **2**. At higher pH value ($pH \geq 3.5$), hydroxide anions may participate in coordination to form larger complexes, such as the octadecanuclear $Cu_{12}Ln_6$ complexes (see Scheme 3). Higher pH value can promote the formation of octadecanuclear complexes; we have observed that the yields were increased when the pH values of the reaction mixtures were increased up to ca. 6. Our observations are in accord with a very recent report[2b] that an interesting $\mu_4$-$O$-bridged tetrahedral $Gd_2Co_2$ complex with a poly-carboxylate ligand at pH ~4.5.
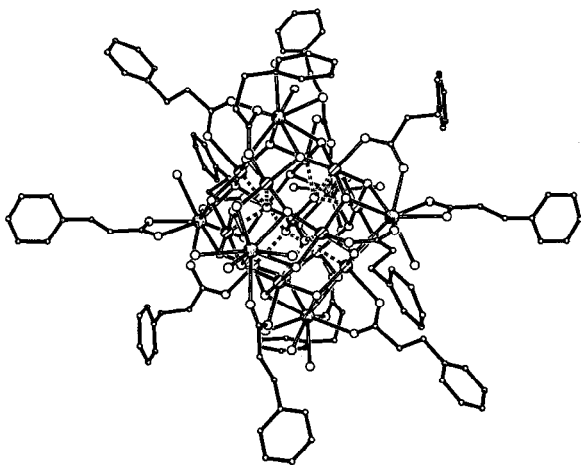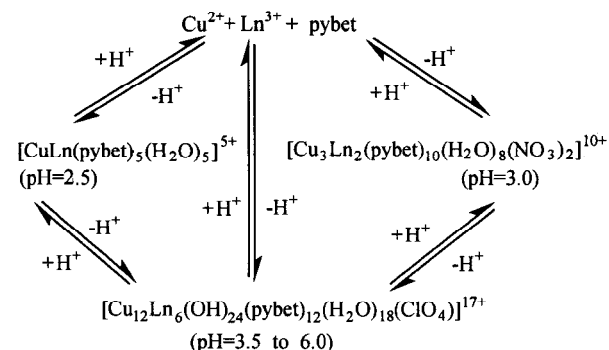


**Fig. 5**    Crystal structure of the cation in **4**. The Ln atoms are speckled, the Cu atom are hatched, the Cl atom is cross-hatched, N atoms are regularly dotted, and the O atoms are open circles.

**Scheme 3**    Assembly of the polynuclear complexes at different pH conditions



$Cu^{2+} + Ln^{3+} + pybet$

$[CuLn(pybet)_5(H_2O)_5]^{5+}$
(pH=2.5)

$[Cu_3Ln_2(pybet)_{10}(H_2O)_8(NO_3)_2]^{10+}$
(pH=3.0)

$[Cu_{12}Ln_6(OH)_{24}(pybet)_{12}(H_2O)_{18}(ClO_4)]^{17+}$
(pH=3.5 to 6.0)

# Complexes of betaine and triphenylphosphiniopropionate

Analogous to those for pyb, we obtained two types

of tetranuclear complexes $[Cu_2Ln_2(bet)_{10}(H_2O)_8]$-$(ClO_4)_{10} \cdot 2H_2O$ (**5**, $Ln^{3+} = La^{3+}$, $Ce^{3+}$ or $Gd^{3+}$) and $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (**6**, $Ln^{3+} = Gd^{3+}$ or $Sm^{3+}$).[20] The crystal structures of **5** feature a centrosymmetric tetranuclear $[Cu_2Ln_2(bet)_{10}(H_2O)_8]^{10+}$ cation, as shown in Fig. 6(a). A $Cu^{2+}$ ion is ligated by four carboxylate $O$-atoms at the basal plane and completed by an aqua ligand at the apical position to form a square-pyramid. The $Cu^{2+}$ ion is quadruply bridged to the $Ln^{3+}$ ion by four $\mu_2$-carboxylate groups of bet, giving rise a dinuclear subunit with the Cu $\cdots$ Ln distance of ca. 380 pm. A pair of inversely related $Ln^{3+}$ atoms in the adjacent dinuclear CuLn subunits are linked together by a pair of $\mu_2$-carboxylate groups of bet with an intramolecular Ln $\cdots$ Ln separation of ca. 568 pm, resulting in the formation of a tetranuclear core. Except the six carboxylate $O$-atoms, the coordination sphere of each $Ln^{3+}$ ion is completed by three aqua ligands to form a distorted monocapped square-antiprism.

The structures of **6** feature a centrosymmetric tetranuclear $[Cu_2Ln_2(bet)_{12}(ClO_4)_2]^{8+}$ cation, as shown in Fig. 6(b). In **6**, each pair of $Cu^{2+}$ and $Ln^{3+}$ atoms are bridged by four $\mu_2$-carboxylate groups of bet to form a dinuclear subunit similar to those found for **1**, and the Cu $\cdots$ Ln separation in the subunit is ca. 360 pm. The $Cu^{2+}$ ion is also coordinated in a square-pyramid with four carboxylate $O$-atoms at the basal plane, and a perchlorate $O$-atom at the apical position; in contrast, the apical position is occupied by an aqua ligand in **5**. The weaker ligation ability of the perchlorate anion at the apical position of the $Cu^{2+}$ atom, as compared to that of a water molecule, results in the markedly shorter basal Cu—O bond lengths; similar phenomenon has been observed for a number of $[Cu_2(\mu_2$-carboxylate$)_4]$ complexes.[26,28] A pair of dinuclear subunits are connected by a quadruple $\mu_2$-carboxylate bridge into a tetranuclear structure, giving rise a quadruple $\mu_2$-carboxylate-bridged dinuclear $Ln_2$ core with the an intramolecular Ln $\cdots$ Ln separation of ca. 454 pm. Similar quadruply $\mu_2$-carboxylate-bridged dinuclear structures have been well-known in homonuclear $Ln^{3+}$ carboxylates.[29] The quadruple $\mu_2$-carboxylate-bridge between the two $Ln^{3+}$ atoms not only brings the pair of $Ln^{3+}$ atoms in a much closer proximity, but also constructs a new tetranuclear cation, as compared to those of the doubly $\mu_2$-carboxylate-bridged tetranuclear cation in **5**. Moreover, this result is consis-

tent with the suggestion that in the ($\mu_2$-carboxylate)$_n$ bridged systems, the intramolecular metal-metal separation can be controlled by the number of the carboxylate

bridges.[30,31] In **6**, each $Ln^{3+}$ ion is coordinated by eight carboxylate $O$-atoms of the two quadruple $\mu_2$-carboxylate bridges, resulting in a square-antiprism geometry.
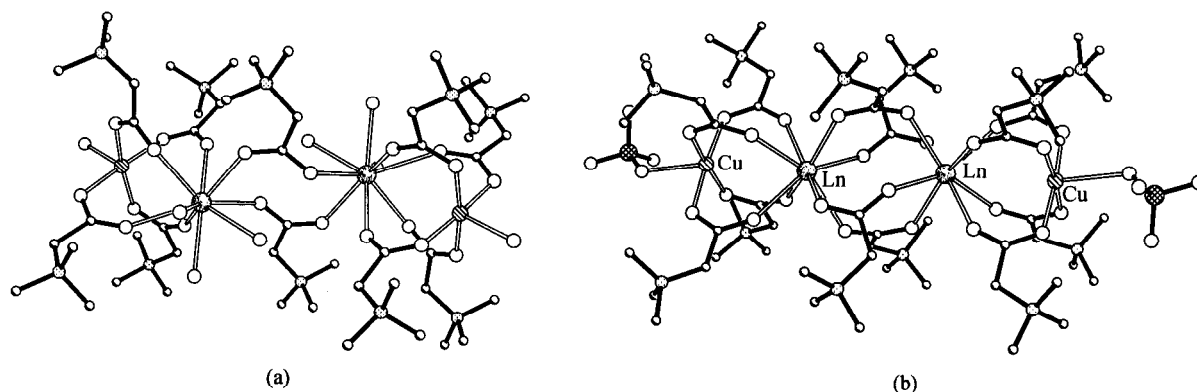


Fig. 6  Crystal structures of the tetranuclear cations in 5 (a) and 6 (b) (The Ln atoms are speckled, the Cu atom are hatched, the Cl atom is cross-hatched, N atoms are regularly dotted, and the O atoms are open circles).

With employment of triphenylphosphiniopropionate (tppp), we generated another type of tetranuclear compounds [$Cu_2Ln_2$(tppp)$_8$(H$_2$O)$_8$](ClO$_4$)$_{10}$·2H$_2$O (**7**, $Ln^{3+}$ = $Eu^{3+}$, $Nd^{3+}$ or $Ce^{3+}$).[21] The crystal structures of **7** consist of centrosymmetric tetranuclear [ $Cu_2Ln_2$-(tppp)$_8$(H$_2$O)$_8$]$^{10+}$ cations, perchlorate anions and lattice water molecules. As illustrated in Fig. 7, the tetranuclear cation is a dimer of dinuclear subunits, in which a pair of $Cu^{2+}$ and $Ln^{3+}$ atoms, being separated by ca. 352.7 pm, is linked by four $\mu_2$-carboxylato-$O$, $O'$ groups of tppp. The dinuclear subunit is structurally similar to those found for **1**, **2**, **5**, and **6**, and somewhat reminiscent of the well-known [$Cu_2$($\mu_2$-RCO$_2$)$_4$] complexes.[29] Two dinuclear subunits connected into a tetranuclear cation whose $Cu^{2+}$ atoms are separated at ca. 332 pm by a pair of such $\mu$-1,1-$O$ bridges, resulting in a centrosymmetrical $Cu_2O_2$ rhomb. The $Ln^{3+}$ ion is coordinated by four $O$-atom from the quadruple carboxylate-bridge and four aqua ligands to form a distorted square antiprism.

It may be worthy of note that the $Ln^{3+}$ ion in **1** is ligated by an extra carboxylate group other than quadruple carboxylate-bridge, and those in **5** and **6** are each ligated by two or four extra carboxylate groups into a tetranuclear structure. Compared with the other carboxylates, tppp is a much bulky ligand; its steric bulkiness probably does not permit another tppp in **7** to approach the $Ln^{3+}$ atom, thus **7** exhibits a new structural variety among the Cu-Ln carboxylates. It is also interesting that

tppp cannot duplicate the facile formation of **3** and **4** at a similar condition; this fact also suggests that the presence of the bulky tppp can enhance the stability of the kernel structure.
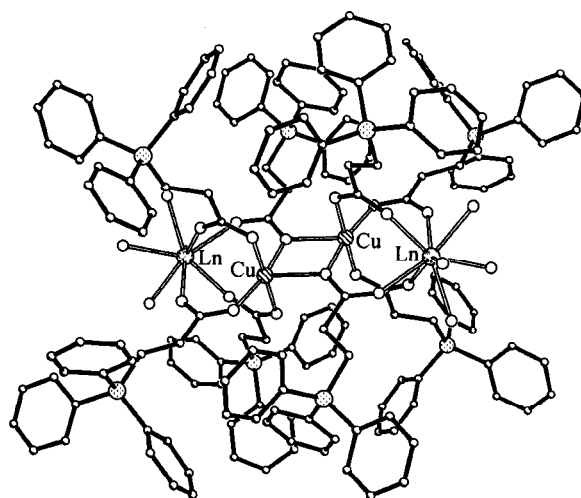


Fig. 7  Crystal structures of the tetranuclear cations in 7 (The Ln atoms are speckled, the Cu atom are hatched, the P atoms are regularly dotted, and the O atoms are open circles).

## Complexes of chloroacetate

The first heterometallic Cu—Ln complex of non-zwitterionic carboxylate, [ $Cu_3Ln_2$(ClCH$_2$CO$_2$)$_{12}$-(H$_2$O)$_8$]·2H$_2$O ($Ln^{3+}$ = $La^{3+}$, $Pr^{3+}$, $Sm^{3+}$, $Gd^{3+}$,

$Dy^{3+}$, or $Er^{3+}$) (8), was generated in 1996.[22] The pentanuclear 8 · Gd was structurally established, which features of a centrosymmetrical pentanuclear, neutral $[Cu_3Gd_2(ClCH_2CO_2)_{12}(H_2O)_8]$ molecule, as shown in Fig. 8. Each terminal $Cu^{2+}$ ion is quadruply bridged to a $Gd^{3+}$ ion by the syn-syn acetate-$O$, $O'$ ligands with the Cu···Gd distance of 356.2(1) pm, besides coordinated by four acetate $O$-atoms at the basal plane, the $Cu^{2+}$ ion further coordinated by an aqua ligand at the apical position, to form a square-pyramid. A pair of the $Gd^{3+}$ atoms in two inversely related dinuclear CuGd subunits are each linked to the central $Cu^{2+}$ ion by a single syn-anti acetate-$O$, $O'$ group, resulting in a pentanuclear molecule. The Gd···Cu(central) distance of 466.2 (1) pm is much longer than the Gd···Cu(terminal) distance. Besides five acetate $O$-atoms, the coordination sphere of each $Gd^{3+}$ ion is completed by three aqua ligands to form a distorted square-antiprism 8-coordination geometry. The central $Cu^{2+}$ atom, being located at an inversion center, is coordinated by two $O$-atoms of the bridging acetate groups and two $O$-atoms of the mon-odentate acetate groups in a slightly distorted square-planar fashion. The structure of the dinuclear CuGd subunits are different from that of 2. In 8, the central $Cu^{2+}$ ion is linked to the $Gd^{3+}$ atoms of both CuGd subunits by two syn-anti $\mu_2$-carboxylate bridges, while in 2 the central $Cu^{2+}$ ion is linked to the $Cu^{2+}$ atoms in both of CuLn subunits.



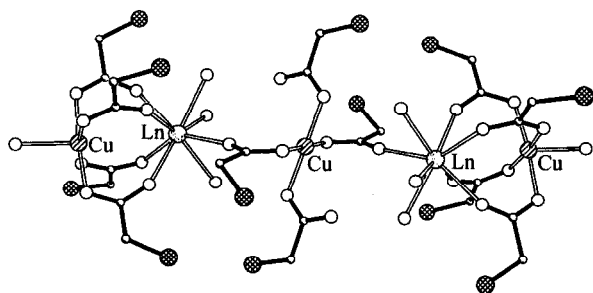**Fig. 8** Crystal structures of the tetranuclear cations in 8 (The Ln atoms are speckled, the Cu atom are hatched, the Cl atom is cross-hatched, and the O atoms are open circles).

Very recently an octadecanuclear complex of chloroacetate was reported,[32] which is synthesized at a higher pH by a similar procedure as for 3 and 4. The octadecanuclear $[Cu_{12}La_6(OH)_{24}(O_2CCH_2Cl)_{12}(H_2-O)_{16}(ClO_4)]^{11+}$ cation of this chloroacetate is struc-turally analogous to 3 and 4, capturing a perchlorate anion within the cage.

## Magnetic properties

Many of the above-mentioned complexes have been characterized by temperature-dependent magnetic susceptibility. The magnetic effective susceptibility data of the tetranuclear 5 · La and 5 · Gd were well fitted to the Curie-Weiss law ($\chi_M = C/(T - \theta)$, with $C = 0.946$ K· $cm^3 \cdot mol^{-1}$($\theta = -5.29$ K), $C = 16.0$ K· $cm^3 \cdot mol^{-1}$($\theta = -0.388$ K) for 5·La and 5·Gd, respectively. For 6· Gd, the $\mu_{eff}$ at room temperature is 11.24 $\mu_B$, which decreases slightly with decrease of temperature down to 11. 2 $\mu_B$ at 11 K, then decreases more significantly and reaches 9.5 $\mu_B$ at 2 K. These facts indicate there are only weak antiferromagnetic interactions within 5·La and 5·Gd. Similar magnetic behavior has also been found for 8·Gd. The observed susceptibility data for 8·Gd were also well fitted to the Curie-Weiss law with $C = 6.4$ K· $cm^3 \cdot mol^{-1}$, $\theta = -1.55$ K, indicating very weak antifer-romagnetic intermolecular interaction. Even in the oc-tadecanuclear 3 ($Ln^{3+} = Y^{3+}$, $Nd^{3+}$ or $Gd^{3+}$), the magnetic properties of these large clusters are dominated by the anti-ferromagnetic exchange between $Cu^{2+}$ ions. Due to the unusual complexity of the octadecanuclear complexes 3, it is almost impossible to fit the magnetic data with appreciate theoretic models at present. Nevertheless, we have found that these series of complicated complexes show weak antiferromagnetic intermolecular interaction. The magnetic data for the simplest case, namely 3·Y, is the only one can be fitted, where no $f$-electron is present.[33] The magnetic coupling constants between the $Cu^{2+}$ ions in 3·Y bridged mainly by the $\mu_3$-hydroxo groups have been fitted, giving the coupling constants $J$ the magnitude of $-20$ $cm^{-1}$. Whereas the magnetic behavior of 3·Gd is weak antiferromagnetic. In 3·Gd, $\mu_{eff}$ decreases gradually from 20.3 $\mu_B$ at 320 K, which is expected for a no-interacting complex, to 18.8 $\mu_B$ at 320 K, then decreases more drastically and reaches 9.54 at 2 K. This fact is in contrast to those found for Cu—Gd complexes of Schiff-base, pyridonate and oxam-ide, in which weak ferromagnetic interactions were reported. Although we cannot explain such difference be-tween ours and the others' results, one conclusion may be derived is that the magnetic interaction between $Cu^{2+}$

demonstrated that shielding of the $Ln^{3+}$ $4f$ electrons by the outer shell electrons is very effective to preclude significant coupling interaction between the $Ln^{3+}$ $4f$ electrons and $Cu^{2+}$ $3d$ electrons in either a monatomic hydroxide-bridged, or a carboxylate-bridged system.

## Conclusions

Upon ligation to a soft $Cu^{2+}$ ion, the two $O$-atoms of a carboxylate group become chemically different. This behavior can be used in synthesis of heterometallic Cu— Ln complexes. Subtle changes in the acidity of the reaction solution and the carboxylate ligands can cause drastic changes in the structures of the products. Magnetic studies exhibit that shielding of the $Ln^{3+}$ $4f$ electrons by the outer shell electrons is very effective to preclude significant coupling interaction between the $Ln^{3+}$ $4f$ electrons and $Cu^{2+}$ $3d$ electrons in either a mono-atomic hydroxide-bridged, or a carboxylate-bridged system. The future of magnetic study of heterometallic $3d$-$4f$ complexes may lie in the study of more complicated ions than $Cu^{2+}$ and $Gd^{3+}$, since other metal ions may be of anisotropic magnetic properties, which appears important in forming "single-molecule magnet".

## References

1. Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, A.; Dei, A.; Gatteschi, D., *J. Am. Chem. Soc.*, **107**, 8128(1985).

2. a) Andruh, M.; Ramade, I.; Codjovi, E.; Guillou, O.; Kahn, O.; Trombe, J.C., *J. Am. Chem. Soc.*, **115**, 1822(1993).
   b) Ma, B.-Q.; Gao, S.; Bai, O.; Sun, H.-L.; Xu, G.-X., *J. Chem. Soc.*, *Dalton Trans.*, 1003(2000).

3. Georges, R.; Kahn, O.; Guillou, O., *Phys. Rev. B*, **49**, 3235(1994).

4. Wang, S.; Pang, Z.; Smith, D.L., *Inorg. Chem.*, **32**, 4992(1993).

5. Blake, A. J.; Cherepamov, V. A.; Dunlop, V. A.; Grant, V.A.; Milne, V.A.; Rawson, V.A.; Winpenny, V.A., *J. Chem. Soc.*, *Dalton Trans.*, 2719(1994).

6. Cornia, A.; Caneschi, A.; Dapporto, P.; Fabretti, A. C.; Gatteschi, D.; Malavasi, W.; Sangregorio, C.; Sessoli, R., *Angew. Chem. Int. Ed.*, **38**, 1780(1999).

7. Salta, J.; Chen, Q.; Chang, Y.-D.; Zubieta, J., *Angew. Chem.*, *Int. Ed. Engl.*, **33**, 757(1994).

8. a) Schnebeck, R.-D.; Freisinger, E.; Lippert, B., *Angew. Chem. Int. Ed. Engl.*, **38**, 168(1999).

b) Stang, P.J.; Olenyuk, B., *Acc. Chem. Res.*, **30**, 502(1997).

9. Tsushima, T., in "*Physics of Magnetic Materials*", Eds. Rauluszkiewicz, J.; Szymczak, H.; Lachowiczak, H.K., World Scientific, Singapore, 1985, p. 479, 158, 283.

10. Hor, P. H.; Meng, R. L.; Wang, Y. Q.; Gao, L.; Huang, Z.J.; Bechtold, J.; Forster, K.; Chu, C. W., *Phys. Rev. Lett.*, **35**, 7238(1987).

11. *Magneto-Structural correlations in Exchange Coupled Systems*, Eds. Willet, R. D.; Gatteschi, D.; Kahn, O., Reidel.Dordrecht, The Netherlands, 1985.

12. a) Goodgame, D.M.L.; Williams, D.J.; Winpenny, R. E.P., *Polyhedron*, **8**, 1531(1989).
    b) Blake, A.J.; Milne, P.E.Y.; Winpenny, R.E.P.; Thornton, P., *Angew. Chem.*, *Int. Ed. Engl.*, **30**, 1139(1991).
    c) Blake, A.J.; Gould, R.O.; Grant, C.M.; Milne, P. E. Y.; Parson, S.; Winpenny, R. E. P., *J. Chem. Soc.*, *Dalton Trans.*, 485(1997).

13. a) Benelli, C.; Fabretti, A.C.; Giusti, A., *J. Chem. Soc.*, *Dalton Trans.*, 409(1993).
    b) Gullou, O.; Kahn, O.; Oushoom, R.L.; Boubekar, K.; Batail, P.; Guillot, M., *Angew. Chem.*, *Int. Ed. Engl.*, **31**, 626(1992).

14. Winpenny, R. E. P., *Chem. Soc. Rev.*, **27**, 447 (1998).

15. Chen, X.-M.; Mak, T. C. W., *Polyhedron*, **10**, 273 (1991).

16. Chen, X.-M.; Mak, T. C. W., *Polyhedron*, **13**, 1087 (1994).

17. Chen, X.-M.; Mak, T.C.W., *Inorg. Chem.*, **33**, 2444 (1994).

18. Wu, Y.-L.; Tong, Y.-X.; Yang, Y.-S.; Chen, X.-M., *Acta Sci. Nat. Univ. Sunyatseni*, **34** (4), 36 (1995).

19. Yang, Y.-Y.; Wu, Y.-L.; Long, L.-S.; Chen, X.-M., *J. Chem. Soc.*, *Dalton Trans.*, 2005(1999).

20. Chen, X.-M.; Wu, Y.-L.; Yang, Y.-Y.; Aubin, S. M.J.; Hendrickson, D. N., *Inorg. Chem.*, **37**, 6186 (1998).

21. Yang, Y.-Y.; Chen, X.-M.; Ng, S. W., *Aust. J. Chem.*, **52**, 983(1999).

22. a) Chen, X.-M.; Tong, M.-L.; Wu, Y.-L.; Luo, Y.-J., *J. Chem. Soc.*, *Dalton Trans.*, 2181(1996).
    b) Tong, M.-L.; Wu, Y.-L.; Chen, X.-M.; Sun, Z.; Hendrickson, D.N., *Chem. Res. Chin. Univ.*, **14**, 230 (1998).

23. Chen, X.-M.; Aubin, S.M.J.; Wu, Y.-L.; Yang, Y.-S.; Mak, T. C. W.; Hendrickson, D. N., *J. Am. Chem. Soc.*, **117**, 9600(1995).

24. Chen, X.-M.; Wu, Y.-L.; Wang, R.-J., *Sci. in China*, *Series B*, **39**, 536(1996).

25.  Chen, X.-M.; Wu, Y.-L.; Tong, Y.-X.; Huang, X.-Y., *J. Chem. Soc.*, *Dalton Trans.*, 2443(1996).

26.  Chen, X.-M.; Mak, T.C.W., *Struct. Chem.*, **4**, 247 (1993).

27.  Chow, M.-Y.; Chen, X.-M.; Mak, T.C.W., *J. Chem. Soc.*, *Dalton Trans.*, 3413(1993).

28.  Chen, X.-M.; Feng, X.-L.; Xu, Z.-T.; Zhang, X.-H.; Xue, F.; Mak, T.C.W., *Polyhedron*, **17**, 2639 (1998), and references cited therein.

29.  Chen, X.-M.; Wu, Y.-L.; Yang, Y.S., *Aust. J. Chem.*, **48**, 1643(1995).

30.  Chen, X.-M.; Tong, Y.-X.; Xu, Z.-T.; Mak, T.C.W., *J. Chem. Soc.*, *Dalton Trans.*, 4001(1995).

31.  Tong, Y.-X.; Chen, X.-M.; Ng, S.W., *Polyhedron*, **16**, 3363(1997).

32.  Cui, Y.; Chen, J.-T.; Huang, J.-S., *Inorg. Chim. Acta*, **293**, 129(1999).

33.  Unpublished result.
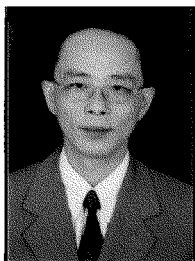
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