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# Syntheses and Structures of Transition Metal-hedp Compounds and the Template Influences (hedp = 1-Hydroxyethylidenediphosphonate)

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The chemistry of metal phosphonates has been of increasing interest during the past two decades, owing to their practical applications as ion exchangers, catalysts and sensors. Great efforts have been devoted to the metal diphosphonates, by modifying the organic tether (R) of $R(PO_3H_2)_2$, to explore new materials with large pores and interesting functions. The template effect on directing the formation of different metal diphosphonate structures, however, has not been well documented. We present here the syntheses and structures of eleven M-hedp compounds, where M = Cu, Fe, Ni; hedp = 1-hydroxyethylidenediphosphonate. The influences of templates on the final products are discussed.

Keywords: *1-hydroxyethylidenediphosphonate; copper; iron; nickel; crystal structure; template*

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## INTRODUCTION

In recent years, increasing attention has been paid to the syntheses of new inorganic/organic hybrid materials or coordination solids with open-framework structures.[1–3] The work has been motivated in order to explore a new generation of zeolite-type materials which not only mimic the properties of traditional zeolites but also have applications in such areas as chiral recognition. Several approaches have been developed to achieve this goal, among which the metal phosphonate compounds have been shown to be particularly interesting candidates.

The chemistry of metal phosphonates grew primarily out of the similarity of phosphonates of group 4 and 14 elements to the inorganic phosphates and their potential applications in ion exchange, catalysis and sensors.[4–7] Subsequent studies from several research groups have shown that the metal phosphonates usually adopt layered or pillared layered structures.[8–10] The organic part of the phosphonates plays a space-filling role between the two-dimensional layers or participates in the three-dimensional open-framework structures via strong covalent linkages. Although a few metal monophosphonates also exhibit porous structures,[11–14] more effort has been devoted to the diphosphonates due to their promising capabilities in building up open-framework structures with metal ions. By modifying the length and functionality of the organic tether (R) in $R(PO_3H_2)_2$, a number of new compounds, particularly those with open-framework structures, have been prepared,[10,15,16] Reports on the diphosphonate compounds involving organic templates, however, have not been well documented especially for the transition metal ions other than vanadium.

Traditionally, organic templates played very important roles in the synthesis of zeolites. The use of such templates still attracts significant interest in searching for new zeolite structures. For example, the M41S family was discovered by scientists at Mobil[17] through the successful use of self-assembling surfactant cations such as $(C_{16}H_{33})(CH_3)_3N^+$. More recently, organic templates have been actively used in metal phosphate chemistry,[3,18,19] and many interesting phosphate materials with open-framework or porous structures have been discovered. In the metal phosphonate area, Haushalter and Zubieta *et al.* also found that organic templates may be employed to direct the organization of layered solids of $V/O/RPO_3^{2-}$ phases.[20,21]

The potential of organic templates in directing structures and for the discovery of new materials has prompted us to carry out a systematic study of the template effect on the structures of metal diphosphonates. Our efforts have focused on searching for transition metal diphosphonates with new structure types, based on the 1-hydroxyethylidenediphosphonate [$CH_3C(OH)(PO_3)_2$, hedp] ligand, which has been selected because of its versatile coordination abilities with metal ions (scheme I).

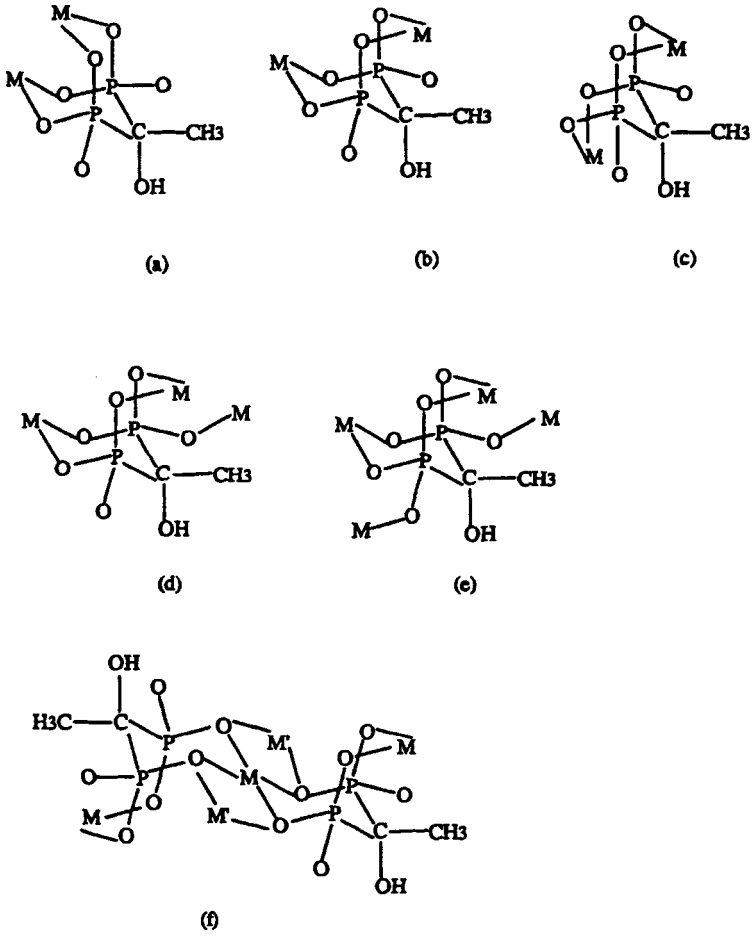
In contrast with most of the diphosphonates which favor pillared layered structures, the short length of the R tether in hedp permits formation of stable M-O-P-C-P-O six member rings with the metal ions. Although an exception has been observed in $Sn_2$(hedp),[22] where each hedp serves to bridge six Sn ions through each of the six oxygen donors, hedp is more likely to behave as a bis(bidentate) bridging ligand using its four phosphonate oxygen atoms as shown in scheme I. The coordination of the remaining two oxygen atoms of the $\{CPO_3\}$ moieties may lead to the formation of compounds with higher dimensionalities [scheme I(d)-(e)]. The additional $-CH_3$ and -OH groups attached to the organic tether of hedp provide not only a steric hindrance but also a possible hydrophobic or hydrophilic environment which could be important in the self-assembly of metal diphosphonates. This coordination chemistry of hedp is reminiscent of that of methylenediphosphonate. Several transition metal methylenediphosphonate compounds with chain, layer or framework structures have already been reported.[16,23–25]

When some of the phosphonate oxygen atoms in hedp coordinate to more than one metal ion, more complicated structures could be generated such as the case shown in scheme I(f). If the phosphonate oxygen atoms are partially protonated, the ability of hedp to build up higher dimensional structures is substantially lowered. The bis-protonated $hedpH_2^{2-}$ may even behave as a terminal ligand.

So far, only a few metal-hedp complexes have been structurally characterized, including $Sn_2$(hedp)[22] with an open-framework structure, a number of one-dimensional lanthanide-$hedpH_n$ (n = 1–3)[26] compounds, and a few polynuclear compounds with metal ions such as Mo.[27] In this paper, we describe the syntheses and structures of some transition metal-hedp compounds by using different templates. The crystallographic data for these compounds are listed in Table I. The influences of the various templates on directing the final products are also discussed.

TABLE I Crystallographic data

| *Compound* | *system* | *space group* | *cell constant (Å, °)* | *ref* |
|---|---|---|---|---|
| $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$ (**1**) | monoclinic | $P2_1/n$ | $a$ = 6.2137(13), $b$ = 14.747(2), $c$= 11.1802(12) β = 105.83(2) | 28 |
| $[NH_3(CH_2)_2NH_3]Cu_2(hedp)_2 \cdot H_2O$ (**2**) | monoclinic | $P2_1/n$ | $a$ = 12.2579(10), $b$ = 5.5010(4), $c$= 16.8746(13) β = 101.188(1) | 29 |
| $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2$ (**3**) | triclinic | P-1 | $a$ = 7.4840(12), $b$ = 8.032(3), $c$ = 10.007(2) α = 111.68(2), β = 96.188(14), γ = 96.97(2) | 28 |
| $[NH_3(CH_2)_4NH_3]Cu_3(hedp)_2 \cdot 2H_2O$ (**4**) | triclinic | P-1 | $a$ = 7.0155(6), $b$ = 8.0904(9), $c$ = 9.2644(11) α = 112.611(13), β = 90.819(8), γ = 92.824(7) | 28 |
| $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$ (**5**) | trigonal | P-3 | $a$ = 11.720(2), c = 9.531(1) | 30 |
| $[NH_3(CH_2)_4NH_3][Fe_2(hedpH)_2]_2 \cdot 2H_2O$ (**6**) | monoclinic | $P2_1/c$ | $a$ = 5.5362(2), $b$ = 12.8676(5), $c$= 15.4337(5) β = 99.279(1) | 31 |
| $[NH_3(CH_2)_5NH_3][Fe_2(hedpH)_2]_2 \cdot 2H_2O$ (**7**) | monoclinic | $P2_1/c$ | $a$ = 5.541(1), $b$ = 12.726(2), $c$ = 16.137(4) β = 99.38(2) | 32 |
| $[NH_3(CH_2)_2NH_3]Fe(hedpH_2)_2 \cdot 2H_2O$ (**8**) | monoclinic | C2/c | $a$ = 24.754(5), $b$ = 5.3305(10), $c$= 16.010(3) β = 117.787(3) | 32 |
| $[NH_3(CH_2)_2NH_3]Ni(hedpH_2)_2 \cdot 2H_2O$ (**9**) | monoclinic | C2/c | $a$ = 24.7864(5), $b$ = 5.2565(1), $c$= 16.0468(2) β = 117.903(1) | 33 |
| $[NH_3(CH_2)_3NH_3]Ni(hedpH_2)_2(H_2O)$ (**10**) | triclinic | P-1 | $a$ = 10.0926(4), $b$ = 10.5621(4), $c$= 10.9212(4) α = 111.520(1), β = 110.833(1), γ = 93.630(1) | 33 |
| $[NH_3(CH_2)_4NH_3]Ni(hedpH_2)_2(H_2O)_2$ (**11**) | monoclinic | C2/c | $a$ = 16.227(17), $b$ = 12.430(13), $c$= 12.657(13) β = 121.997(10) | 33 |




SCHEME 1

## SYNTHESIS

The reactions were conducted under hydrothermal conditions at temperatures of 110 ~ 180°C in the presence of different templates including

$NH_3 \cdot H_2O$, $NH_2(CH_2)_nNH_2$ (n = 2, 3, 4, 5), $NH(C_2H_4)_2NH$, 1,4-diazabicyclo[2.2.2]octane (dabco) and $Na^+$ etc. Typically, the compound $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$ (**1**) was synthesized by heating a mixture of $Cu(NO_3)_2 \cdot 3H_2O$, 50% $hedpH_4$, $NH_4HF_2$ and $H_2O$, adjusted by $NH_3 \cdot H_2O$ to pH ≈ 3, in a Teflon-lined autoclave at 140°C for 2 d. Fluorides ($NH_4HF_2$ or LiF) were added in order to improve the crystallization. The syntheses of the other compounds except **5** were similar to that of **1**, although $FeSO_4$ and $NiSO_4$ were used as starting materials for the iron-, and nickel-hedp compounds, respectively, and a different template was involved in each reaction. The compound $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$ (**5**) was prepared in the presence of both $Na^+$ and 1,4-diazabicyclo[2.2.2]octane (dabco).

## STRUCTURAL DESCRIPTION

### Copper-hedp compounds

Compounds **1–4** were synthesized under the same conditions except different templates were used. The structures of **1** and **2** consist of anionic Cu-hedp chains which are charge-balanced by the ammonium or diprotonated ethylenediamine (Figs. 1 and 2). Compounds **3** and **4** have two-dimensional layer structures with the diprotonated amines filling the inter-layer spaces (Figs. 3 and 4).

Figure 1 shows the infinite chain structure of $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$ (**1**) with a ladder-type motif. A symmetric $Cu_3(hedp)_2(H_2O)_4^{2-}$ building block is found in this structure which contains two types of copper atoms [Fig. 1(a)]. The Cu(1) atom is in a planar environment with the four oxygen atoms from centrosymmetrically related hedp groups. The Cu(2) atom has a distorted square pyramidal coordination geometry. The hedp group forms bis(bidentate) bridges between the Cu(1) and Cu(2) atoms, using four oxygen atoms from its two $\{CPO_3\}$ moieties. One of the remaining two oxygen atoms, O(6), is further linked to the Cu(2) atom in the neighboring $Cu_3(hedp)_2(H_2O)_4^{2-}$ trimer unit. The other oxygen atom, O(3), is terminal. Therefore the sidepieces of the ladder chains are formed by the $\{Cu(2)O_5\}$ tetragonal pyramid and the $\{CPO_3\}$ tetrahedra, while the rungs of the ladder are formed by the $\{Cu(1)O_4\}$ planes [Fig. 1(b)]. The $NH_4^+$ cations stabilize

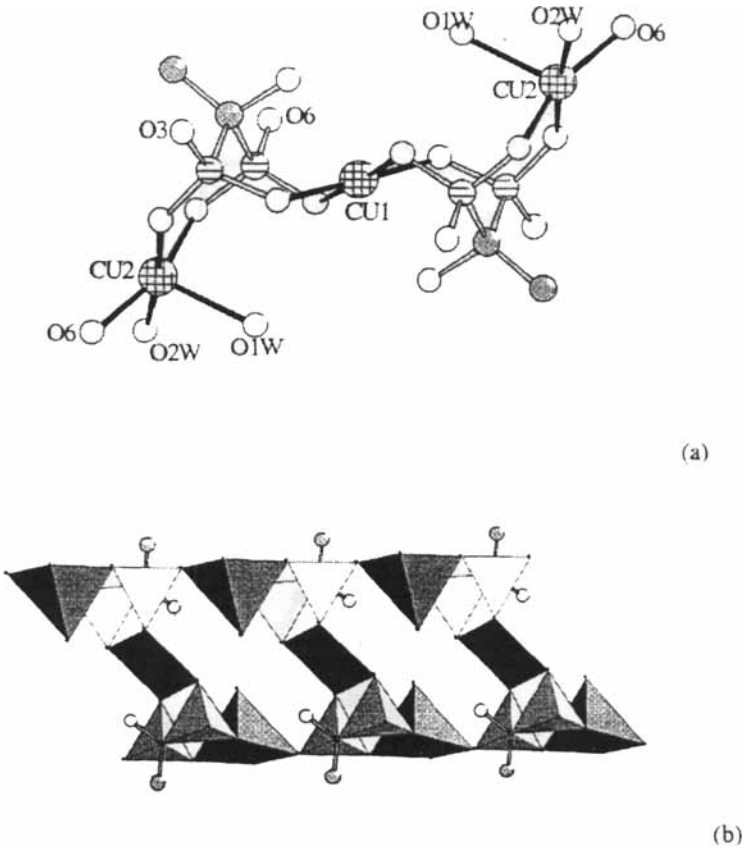



FIGURE 1 (a) The building unit of structure 1; (b) The ladder-like anionic chain of the structure 1

the lattice through extensive hydrogen bonds with the phosphonate and hydroxy oxygen atoms.

The structure of $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2$ (3), using piperazine as template, is two-dimensional with the inter-layer space occupied by the $[NH_2(C_2H_4)_2NH_2]^{2+}$ cations (Fig. 3). As in 1, the building unit of 3 is a $Cu_3(hedp)_2^{2-}$ trimer. However, the remaining two oxygen atoms of

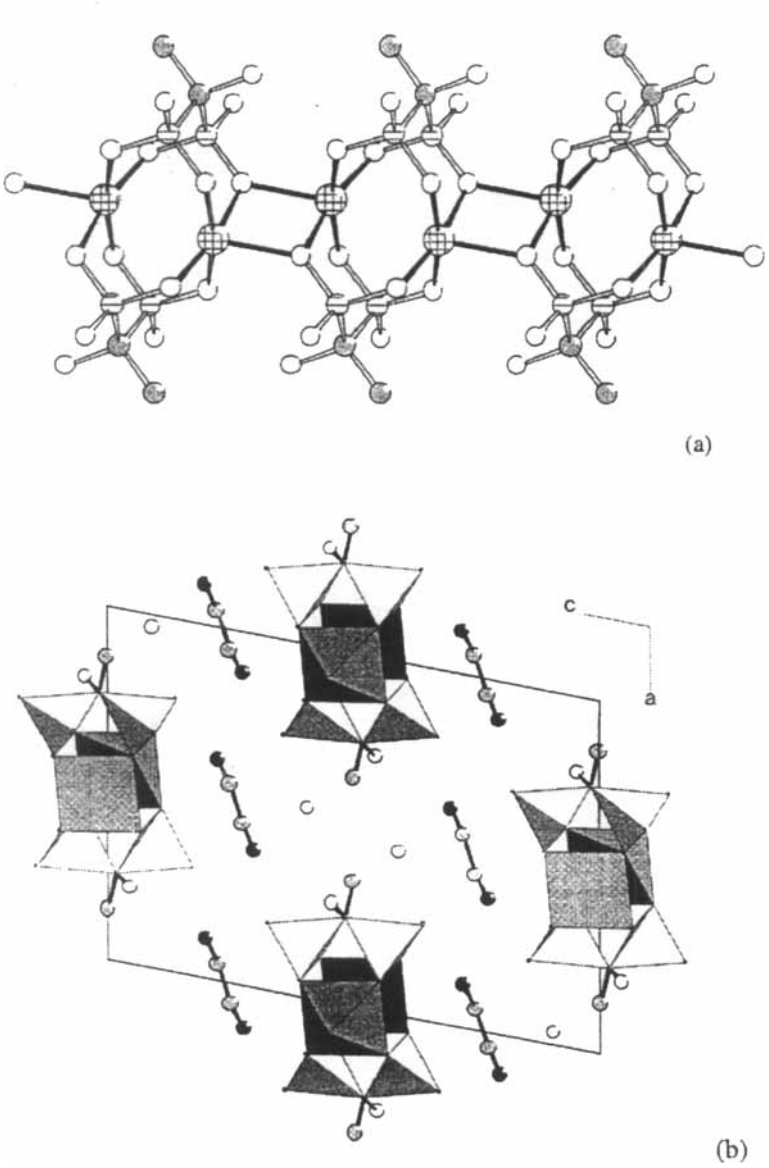
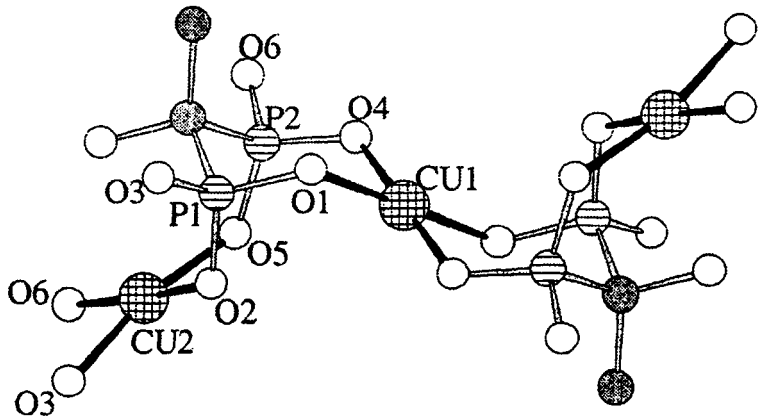
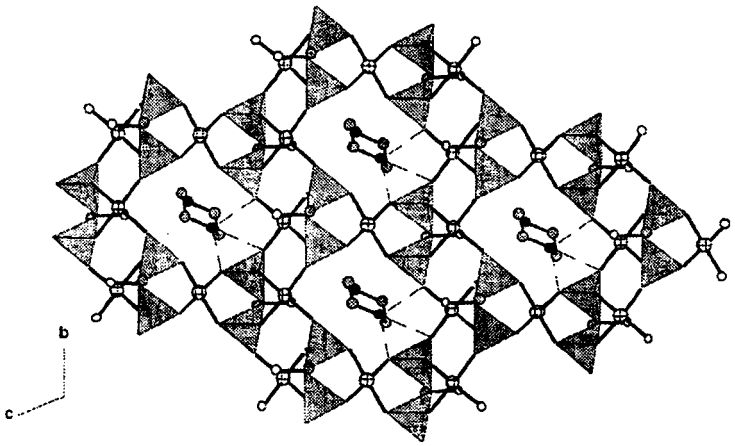



FIGURE 2 (a) The linear anionic chain of structure **2**; (b) Structure **2** packed along *b*-axis

hedp, after bridging Cu(1) and Cu(2), are both coordinated to copper atoms from neighboring trimer units. Consequently, a two-dimensional anionic layer is formed, containing 4- and 8-membered rings assembled from vertex-sharing $\{CuO_4\}$ units and $\{CPO_3\}$ tetrahedra. The replacement of piperazine by 1,4-butylenediamine as template leads to the formation of $[NH_3(CH_2)_4NH_3]Cu_3(hedp)_2{\cdot}2H_2O$ (**4**) which is isostructural to **3**.




(a)



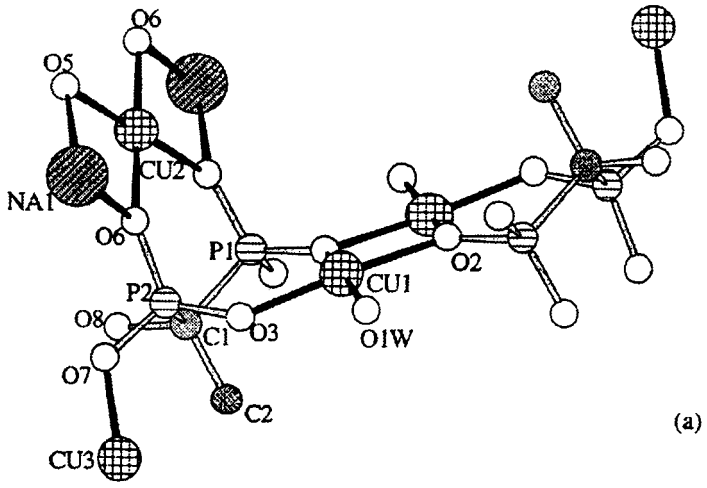

(b)

FIGURE 3 (a) The building unit of **3**; (b) One layer of structure **3** packed along *a*-axis

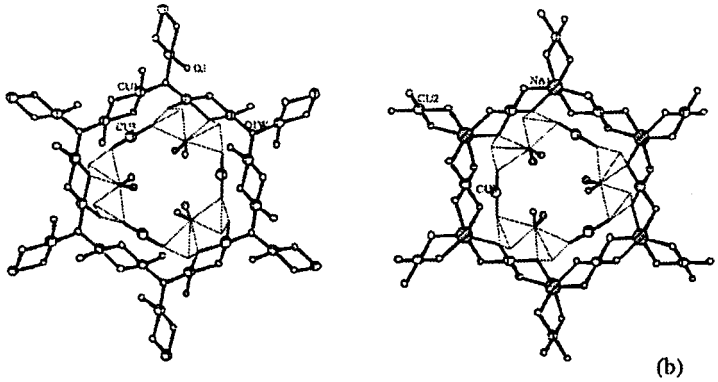
It is interesting that a linear chain is observed in the compound $[NH_3(CH_2)_2NH_3]Cu_2(hedp)_2 \cdot H_2O$ (**2**) which has a symmetrical dimer building unit $\{Cu_2(hedp)_2\}$ (Fig. 2). The hedp also behaves as a bis(chelating) bridging ligand. However, when the coordination geometries of the building units in **1** and **2** are compared carefully, the differences are significant. Scheme I shows clearly that the two six membered rings formed by hedp and metal ions are not planar. If both rings prefer a chair-like shape, a cis-bridging mode results [scheme I(a)] which has been found in the compound **2**. If one six membered ring displays a chair-like shape while the other a boat-like shape, a trans-bridging mode is formed as shown in scheme I(b). The mode shown in scheme I(c) could be energetically unfavorable because of steric hindrance. The trans-configuration seems to be most common, as evidenced by compounds **1** and **3–5**. Variations in the twist angles of these six membered rings may also cause structural differences.

The incorporation of sodium ion results in a completely different structure of $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$ (**5**). The hedp group in **5** again acts as a multidentate ligand [Fig. 4(a)]. It bridges the Cu(1) and Cu(2) atoms in a way similar to that in **1** by using its four terminal phosphonate oxygen atoms. In contrast to the previous four structures, three of these four oxygen atoms serve as $\mu_3$ bridging ligands. Therefore, each $Cu(1)O_4$ tetrahedron is edge-shared with another $Cu(1)O_4$ tetrahedron, and each $Cu(2)O_4$ plane is edge-shared with two $NaO_6$ octahedra. The remaining two oxygen atoms of $\{CPO_3\}$ coordinate to the monovalent Cu(3) atoms [Fig. 4 (a)]. This coordination pattern is shown in scheme I(f).

Consequently, two alternately arranged honeycomb layers are found in this structure. The $\{[Cu(1)_3O(8)]O_3\}$ sheet is based on an equilateral triangle unit created from three equivalent Cu(1) atoms centered about a $\mu_3$-O(8) atom. Each Cu(1) atom in this triangle unit is edge-shared with the other Cu(1) from the neighboring triangle unit, thus forming a two-dimensional $\{(Cu_3O)O_3\}$ network with 12-membered rings. The $\{Cu(2)O_4Na(1)\}$ sheet contains similar 12-ring cavities which are generated from edge-shared $Cu(2)O_4$ planes and $Na(1)O_6$ octahedra [Fig. 4(b)]. Between these two sheets are the nine-membered rings made up from the organic backbones of the hedp groups as well as Cu(3) [Fig. 4(b)]. Therefore, an interesting three-dimensional open-framework structure is established, with one-dimensional channels along the [001] direction [Fig. 4(c)].




(a)



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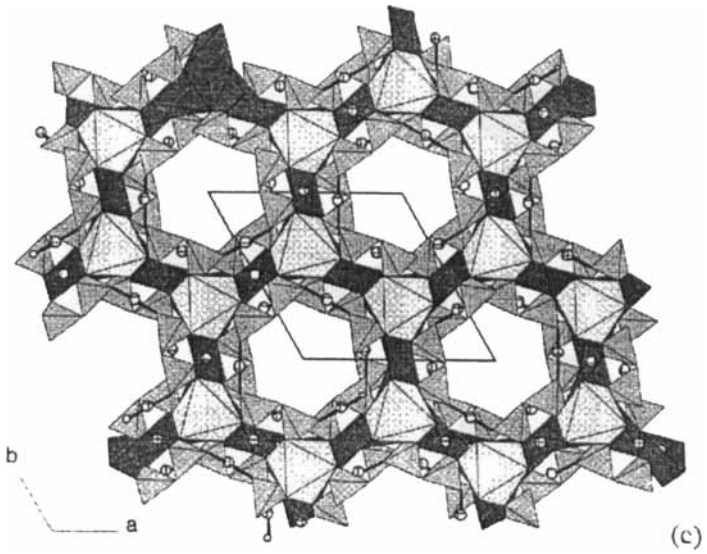



FIGURE 4 (a) Coordination geometries of hedp in **5**; (b) Fragments of $\{(Cu(1)_3O)O_3\}$ and $\{Cu(2)O_4Na(1)\}$ sheets and the nine-membered ring attached to the sheets; (c) Polyhedral representation of structure **5** packed along c-axis. All H, C2, O7 and water molecules are omitted for clarity

## Iron-hedp compounds

The structure of $[NH_3(CH_2)_4NH_3][Fe_2(hedpH)_2]_2 \cdot 2H_2O$ (**6**), where diprotonated 1,4-butylenediamine serves as charge-compensating counterions, can be best described by a supramolecular open network, built up from the strongly hydrogen-bonded covalent chains. Each chain contains a centrosymmetric dimer unit $[Fe_2(hedpH)_2]^{2-}$ [Fig. 5(a)], in which the Fe atoms adopt distorted octahedral coordination spheres that are edge-shared with each other through pairs of O(4) atoms. The $hedpH^{3-}$ ligand is again bis-chelated and bridges the Fe atoms through four oxygen atoms from the phosphonate moieties and O(7) from the hydroxy group. Between the chains there exists a very strong hydrogen bonding interaction involving the protonated O(3) and O(6) oxygens. A

three-dimensional supramolecular framework is thus constructed by the assembly of $[Fe_2(hedpH)_2]_n^{2n-}$ chains through strong hydrogen bonding, with one-dimensional channels created along the *a* axis [Fig. 5(b)]. The compound $[NH_3(CH_2)_5NH_3][Fe_2(hedpH)_2]_2 \cdot 2H_2O$ (**7**), where $[NH_3(CH_2)_4NH_3]^{2+}$ is replaced by $[NH_3(CH_2)_5NH_3]^{2+}$, exhibits a quite similar structure.

Using ethylendiamine as template, the compound $[NH_3(CH_2)_2NH_3]Fe(hedpH_2)_2 \cdot 2H_2O$ (**8**) has also been synthesized. This compound has a one-dimensional chain structure, and is isostructural with that of the corresponding nickel compound $[NH_3(CH_2)_2NH_3]Ni(hedpH_2)_2 \cdot 2H_2O$ (**9**) which is described below.

## Nickel-hedp compounds

Fig. 6 shows the structure of the compound $[NH_3(CH_2)_2NH_3]Ni(hedpH_2)_2 \cdot 2H_2O$ (**9**) which is composed of corner-sharing $\{NiO_6\}$ octahedra and $\{O_3PC\}$ tetrahedra, with the $[NH_3(CH_2)_2NH_3]^{2+}$ cations and water molecules present between the chains. The coordination geometry of each nickel atom is defined by six O atoms from four $hedpH_2^{2-}$ anions. Each $hedpH_2^{2-}$ bridges the Ni atoms using three O atoms from its two $\{PO_3H\}$ moieties. The two protonated O atoms of the $\{CPO_3\}$ moieties prevent structures with higher dimensionalities from forming, but rather contribute to extensive hydrogen bonding within and between the chains.

Compound $[NH_3(CH_2)_3NH_3]Ni(hedpH_2)_2(H_2O)$ (**10**) consists of discrete $[Ni(hedpH_2)_2(H_2O)]_2^{4-}$ dimers and $[NH_3(CH_2)_3NH_3]^{2+}$ cations. The dimer can be viewed as a fragment of the chain adopted by **9**, which is terminated by the coordination of one molecule of $H_2O$ to each Ni atom (Fig. 7). The $hedpH_2^{2-}$ moieties in the dimer serve as both terminal and bridging ligands. By using 1,4-butylenediamine instead of 1,3-propanediamine or ethylenediamine as template, a mononuclear structure compound $[NH_3(CH_2)_4NH_3]Ni(hedpH_2)_2(H_2O)_2$ (**11**) has been isolated (Fig. 8). Both $hedpH_2^{2-}$ ligands in this case act as terminal ligands. The discrete $[Ni(hedpH_2)_2(H_2O)]_2^{4-}$ dimers in **10** or $[Ni(hedpH_2)(H_2O)_2]^{2-}$ monomers in **11** are efficiently connected to each other, forming three-dimensional networks of hydrogen bonding. The cavities generated within the networks are filled by protonated 1,3-propanediamine or 1,4-butylenediamine cations.

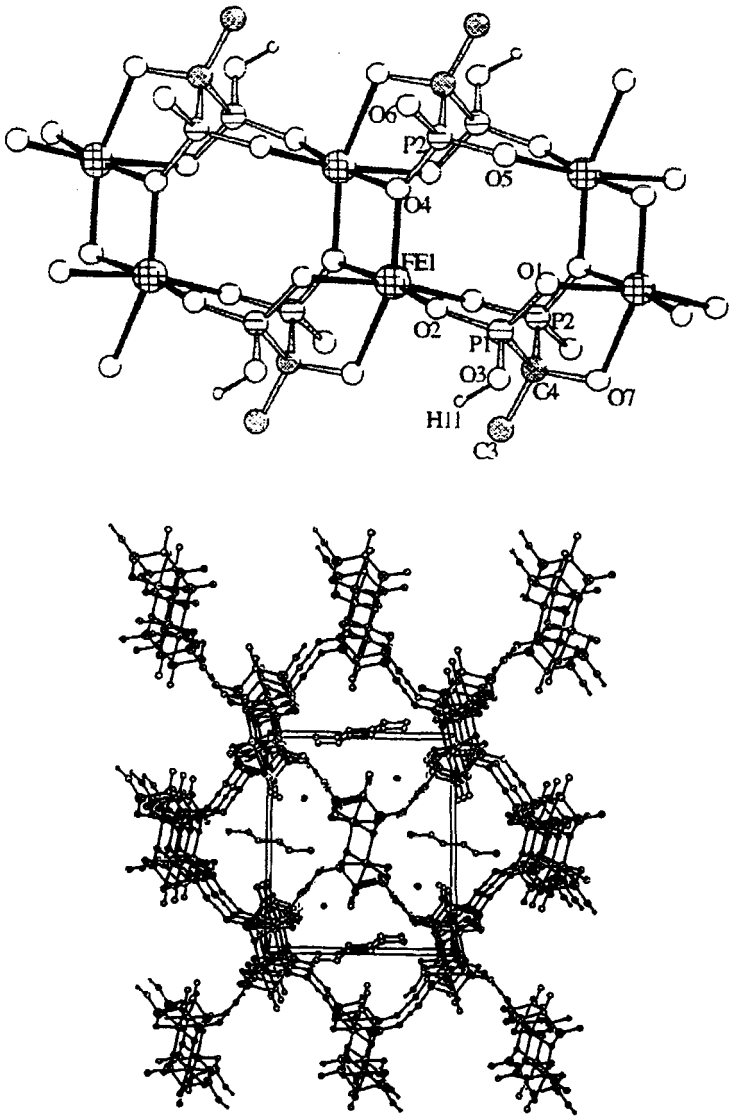



FIGURE 5 (a) A fragment of the double chain in **6**; (b) packing diagram of **6** along [100] direction

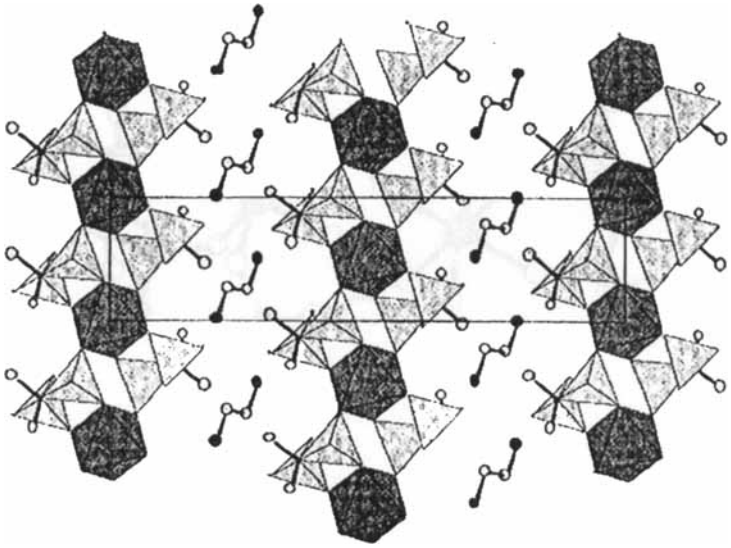


FIGURE 6 Polyhedral representation of the structure **9** packed along [001] direction

## TEMPLATE INFLUENCES

Under hydrothermal conditions, compounds **1–11** incorporating $hedpH_n$ ($n = 0 - 2$) ligands have been successfully synthesized. Their structures, described above, differ significantly and range from mononuclear to three-dimensional network. There are a number of factors that may affect the structures of the final products, such as the starting materials, the molar ratio, the temperature, pH and the templates etc. By conducting the reactions under approximately the same experimental conditions, we have found that the templates play important roles in directing the structures of the resulting metal-hedp compounds.

Generally, a template agent such as organic amine has several influences on the final products. The template effect depends on both its own properties and the nature of the anionic lattice. The properties of templates include the size, geometrical shape, hydrogen bonding ability with the other components and charge density and distribution. For the

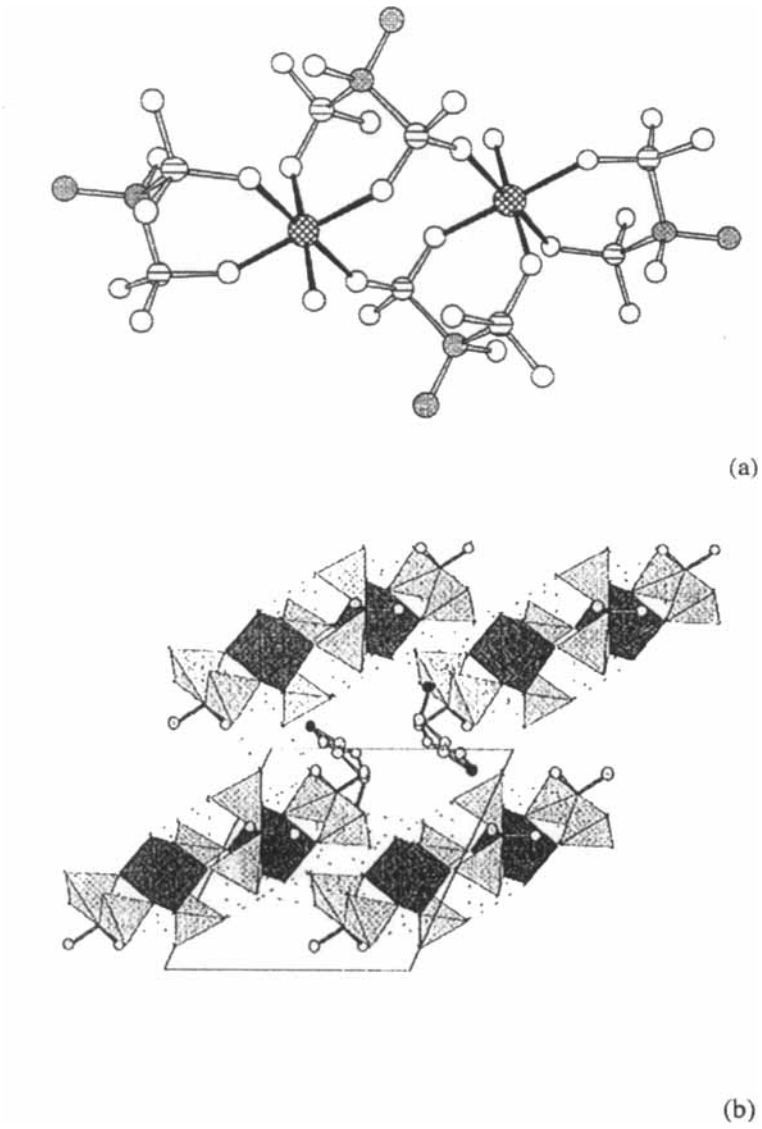
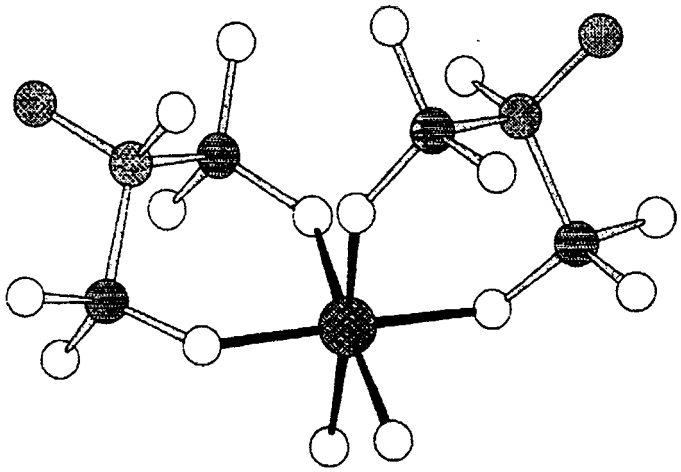



FIGURE 7 (a) The discrete dimeric anion in **10**; (b) Polyhedral representation of the structure **10** viewed along *a*-axis

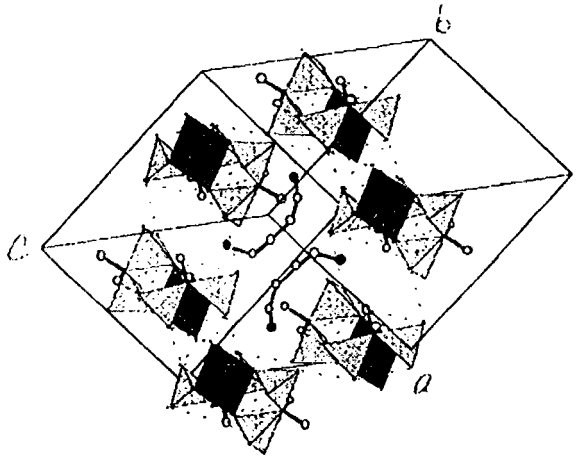
organic diamines $NH_2(CH_2)_nNH_2$ (n = 2–5) which are used as templates in this work, all can be diprotonated under acidic conditions to form diammonium counterions that charge-balance the anionic M-hedp species. Additionally, each of the two protonated terminal nitrogen atoms of the template can form extensive H-bonds with the phosphonate or hydroxy oxygen atoms, thus stabilize the lattices by holding the anionic M-hedp species together. Considering the flexibility of $NH_2(CH_2)_nNH_2$, both the size and the geometrical shape should be essential in directing the structures of the corresponding M-hedp compounds especially those with similar building units. The piperazine template, to some extent, is comparable to ethylenediamine, although it is less flexible and has a larger size.

Compounds **2–4**, prepared under similar conditions, provide good examples to discuss the effect of different templates. Compound **2** with ethylenediamine as template has a one-dimensional chain structure. The ethylenediammonium cations sit between the anionic chains [Fig. 2(b)]. And each nitrogen atom of the cation is linked to two neighboring chains via hydrogen bonds with the phosphonate and hydroxy oxygen atoms. On the other hand, compounds **3** and **4** using piperazine and 1,4-butylenediamine templates, respectively, have two-dimensional layer structures. The two compounds (**3** and **4**) are isostructural. An analogous trimer unit $Cu^{II}_3(hedp)_2$ is found in both structures, where each hedp group bridges the copper atoms in a bis(bidentate) trans-arrangement [scheme I(b)]. The remaining two phosphonate oxygens of each hedp coordinate to two Cu atoms from two neighboring trimers, thereby forming a two-dimensional layered structure. The diprotonated piperazine or 1,4-butylenediamine cations occupy the inter-layer spaces and hold the adjacent $\{Cu^{II}_3(hedp)_2\}_n^{2n-}$ layers through moderate strength hydrogen bonds between the nitrogen atoms of the amine and the phosphonate oxygen atoms. The N...O distances in **3**, for example, are 2.728 Å, 2.938 Å and 2.841 Å for N1...O1, N1...O3 and N1...O6, respectively. Keeping in mind the similarities of these three template agents except size, we may conclude that the size of the template cations is key to the structures of these three compounds. The larger cations $NH_2(C_2H_4)_2NH_2^{2+}$and $NH_3(CH_2)_4NH_3^{2+}$ favor formation of a two-dimensional anionic layer, whereas the smaller cation $NH_3(CH_2)_2NH_3^{2+}$ directs the formation of an anionic chain structure.

The failure of our efforts to synthesize a layered compound similar to those of **3** and **4** but using ethylenediamine template supports this con-



(a)




(b)

FIGURE 8 (a) The monomeric anion in **11**; (b) Polyhedral representation of the structure **11**

clusion. However, since compound **2** has a different building unit from **3** and **4**, arguments about the template influence would be more convincing if a Cu/hedp/ethylenediamine(en) compound could be synthesized with the analogous building unit $Cu^{II}_3(hedp)_2$. In fact, our studies have shown that at least one more phase can result from the Cu/hedp/en system which has a different XRD pattern from either **2** or **3**. Characterization of the structure of this phase is currently in progress. It is worth noted that the chain compound **1**, having a building unit $Cu^{II}_3(hedp)_2(H_2O)_2$ similar to **3** and **4**, was prepared in the presence of a small template $NH_3$.

For the Fe-hedp system, by using ethylenediamine, 1,4-butylenediamine or 1,5-pentamethylenediamine as template, three Fe-hedp compounds have been obtained under approximately the same experimental conditions. The compounds $[NH_3(CH_2)_4NH_3][Fe_2(hedpH)_2]_2\cdot 2H_2O$ (**6**) and $[NH_3(CH_2)_5NH_3][Fe_2(hedpH)_2]_2\cdot 2H_2O$ (**7**) are isostructural to each other. Both show a three-dimensional supramolecular open network structure which contains covalent double chains of $[Fe_2(hedpH)_2]_n^{2n-}$ linked through very strong hydrogen bonds. Compound $[NH_3(CH_2)_2NH_3]Fe(hedpH_2)_2\cdot 2H_2O$ (**8**) with ethylenediamine template, however, exhibits a linear chain structure. This result again demonstrate that the size of template is important in directing the structures. In compounds **6–8**, the larger templates $NH_2(CH_2)_4NH_2$ and $NH_2(CH_2)_5NH_2$ favor directing the formation of double chains of $[Fe_2(hedpH)_2]_n^{2n-}$.

For the Ni-hedp system, it has to be noted that compound **9**, employing ethylenediamine as template, has a one-dimensional chain structure formed by corner-sharing $\{NiO_6\}$ octahedra and $\{O_3PC\}$ tetrahedra, while compounds **10** and **11** with 1,3-propanediamine and 1,4-butylenediamine templates, exhibit discrete dimeric and monomeric structures, respectively. The fact that the 1,4-butylenediammonium cation crystallizes with a monomeric anion is contrary to the above mentioned rule. When the geometries of the templates in **9–11** are compared carefully, we found that the two nitrogen atoms in ethylenediammonium cation in **9** are arranged in a trans-manner, whereas those in 1,3-propanediammonium (**10**) [Fig. 7(b)] and 1,4-butylenediammonium (**11**) [Fig. 8(b)] are arranged in a cis-manner. The cis-arrangement of the diprotonated diamine leads to a significantly different pattern of hydrogen bonding from that of the trans-arrangement. The template influences on **9–11** may be caused by a combination of size, shape, charge distribution and

hydrogen bonding directions of the templates and, therefore, cannot be simply compared with each other. In the case of **10** and **11**, efficient hydrogen bonds are found between $[Ni(hedpH_2)_2(H_2O)]_2^{4-}$ dimers or $[Ni(hedpH_2)(H_2O)_2]^{2-}$ monomers. The mononuclear species $[Ni(hedpH_2)(H_2O)_2]^{2-}$ may create larger cavities within the hydrogen-bonding networks which can hold larger cations.

## CONCLUSIONS

In this paper we summarize the syntheses and structures of eleven transition metal-hedp compounds created using different templates. The distinct differences in the structural features between the compounds having the same metal ions are mainly attributed to the template influences in force during the hydrothermal reactions. Such influences may be related to size, shape, charge distribution and hydrogen bonds of templates. When the shape, charge distribution and hydrogen bonds of the templates are comparable, a larger template tends to direct the formation of a larger polymeric anion. In order to better understand the template influences on the transition metal-hedp compounds, a systematic investigation is demanded which should include various types of templates. From such an investigation we shall benefit to explore new transition metal diphosphonate compounds with open-framework or porous structures that are directed by templates. Finally, it has to be noted that the introduction of a second metal ion, as in the case of $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$ (**5**), may also leads to the interesting compounds with open-framework structures. Further work is in progress.



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