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Review

Hydro(solvo)thermal in situ ligand syntheses

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Contents

Abstract

Hydro(solvo)thermal in situ ligand synthesis has rapidly developed over the past several years due to its effectiveness, simplicity and environmental friendliness. More than 10 types of in situ ligand reactions have been enumerated, which include carbon–carbon bond forma-

Abbreviations: apddica, 2-(4-amino-phenyl)-1,3-dioxo-2,3-dihydro-1H-isoindole-5-carboxylate; 2,2′-biphen, 2,2′-biphenanthroline; bpdc, 2,2′-bipyridine-3,3′-dicarboxylate; bpe, 1,2-*trans*-(4-pyridyl)ethane; 2,2′-bpy, 2,2′-bipyridine; 4,4′-bpy, 4,4′-bipyridine; (*S*)-3-CNPHA, (*S*)-3-cyanophenylalanine; dpdc, diphenyl-4,4′-dicarboxylate; dppm, bis(diphenylphosphino)-methane; fum, fumarate; H_4bbh, benzene-1,2,4,5-bihydrazide; H_3bcbh, benzene-4-carboxylate-1,2-bihydrazide; 1,4-H_2BDS, benzene-1,4-disulfonic acid; H_4bta, benzene-1,2,4,5-tetracarboxylic acid; H_3btc, benzene-1,2,4-tricarboxylic acid; H_2dmap, *N*,*N*-dimethyl-aspartic acid; Hmtz, 3,5-dimethyl-1,2,4-triazole; Hobpy, 6-hydroxyl-2,2′-bipyridine; H_4odsc, 2,2′-oxydisuccinic acid; Hophen, 2-hydroxyl-1,10-phenanthroline; Hoip, 2-hydroxyisophthalate; Hptz, 3,5-dipropyl-1,2,4-triazole; 4-H_2SB, 4-sulfobenzoic acid; ip, isophthalate; ox, oxalate; pdon, 1,10-phenanthroline-5,6-dione; phen, 1,10-phenanthroline; 3-ptz, 5-(3-pyridyl)tetrazolate; 4-ptz, 5-(4-pyridyl)tetrazolate; 4-pya, 4-pyridinecarboxylate; pyz, pyrazine; quaterpy, 2,2′ ;6,2″ ;6″,2‴-quaterpyridine; tp, terephthalate; (*S*)-TPA, (*S*)-5-(3-tetrazoyl)phenylalaninato; tpbz, 1,2,4,5-tetra(4-pyridyl)benzene; tpct, 1,2,3,4-tetrakis(4-pyridyl)cyclobutane

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tion, hydroxylation, tetrazole formation, triazole formation, substitution, alkylation, ether bond formation, hydrolysis, oxidation–hydrolysis, acylation, amination and decarboxylation. Hydrothermal in situ ligand synthesis has become a powerful approach in the crystal engineering of coordination complexes and in organic synthesis, and is becoming an alternative approach in the isolation of organic isomers. In the crystal engineering of coordination complexes, in situ ligand synthesis is suitable to prepare novel coordination complexes from metal ions and organic precursors and most of these complexes are not accessible from a direct reaction of metal ions and ligands. In organic synthesis, hydrothermal in situ ligand syntheses have become very useful pathways to organic ligands, which are difficult to obtain by routine synthetic methods. In isolating organic isomers, in situ ligand synthesis is becoming an alternative route because in some special cases, only one of the several isomers of a ligand is found in crystalline complexes involving in situ ligand reactions.

Keywords: In situ ligand synthesis; Crystal engineering; Coordination complexes; Hydro(solvo)thermal; Organic synthesis

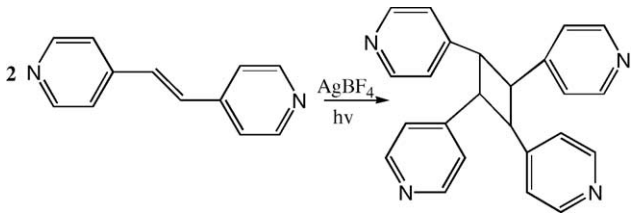
1. Introduction

Traditionally, coordination complexes are obtained by reactions of pre-synthesized or commercially available ligands with metal ions. The single crystal growth of complexes involves evaporation of solvents and diffusion procedures. Recently, in situ ligand synthesis has been developed as a new approach to the crystal engineering of complexes in which ligand precursors are used in place of ligands to react with metal directly to produce single crystals of the desired complexes.

In situ ligand synthesis is of great interest in coordination chemistry and organic chemistry for preparation of crystalline coordination complexes, and for the discovery of new organic reactions and understanding their mechanisms [1]. In situ ligand synthesis, as a new approach in crystal engineering of coordination complexes, was first proposed by Champness and Schröder in 1997, when they unexpectedly observed in situ cyclisation of 1,2-*trans*-(4-pyridyl)ethene to yield ligand 1,2,3,4-tetrakis(4-pyridyl)cyclobutane [2]. Following Champness and Schröder's success, a variety of novel coordination complexes involving in situ synthesized ligands were documented, most of which were prepared by hydro(solvo)thermal methods (occasionally also by traditional solution reactions). The in situ ligand synthesis, as an approach in the crystal engineering of complexes, has the following benefits: (1) in situ synthesis of ligands from an organic precursor removes the need to synthesize ligands that simplify the synthesis steps; (2) in situ slow formation of ligands will ensure the growth of single crystals sufficiently large to allow X-ray single-crystal structural determination; (3) it is an environmental friendly synthesis procedure. Until now, more than 10 types of hydro(solvo)thermal in situ ligand syntheses have been found, which include carbon–carbon bond formation [2–7], hydroxylation [8–11], tetrazole formation by formal cycloaddition of cyano and azide[12], triazole formation by [2 + 2 + 1] cycloaddition of cyano and amine [13], replacement of carboxyl with sulfonic group [14], alkylation [15], ether bond formation via dehydration coupling [16], hydrolysis [17–24], oxidation–hydrolysis [25,26], amination [27], acylation [28,29] and decarboxylation [9a,30].

Hydro(solvo)thermal reactions, well established for the synthesis of zeolites and typically carried out in sealed teflon bombs and in the temperature range 120–200 °C under autogenous pressure (generally 10–30 atm), exploit the self-assembly of the product from soluble precursors. The reduced viscosity of solvents under these conditions enhances the diffusion processes so that crystal growth from solution is favored. Under such non-equilibrium crystallization conditions, metastable kinetic phases, rather than the thermodynamic phase, are most likely to be isolated. In the majority of cases, crystals form at the reaction temperature and not upon cooling to room temperature. Small changes in one or more of the reaction variables of the hydrothermal parameter space such as time, temperature, pH value, stoichiometry and duration can have a profound influence on the reaction outcome [31]. Recent research has revealed that the hydro(solvo)thermal reaction is also a promising technique in preparing complexes with novel structures and special properties, especially in growing crystals of complexes involving in situ ligand synthesis [3–30]. Compared with traditional synthetic methods, hydro(solvo)thermal reactions create more chance for in situ ligand synthesis due to the relatively critical reaction conditions. Indeed, hydro(solvo)thermal method has demonstrated increasing success in providing alternative pathways to crystalline complexes with in situ synthesized ligands which are difficult to obtain by routine synthetic methods. For instance, the novel ligands 6-hydroxyl-2,2′-bipyridine (Hobpy) and 2-hydroxyl-1,10-phenanthroline (Hophen), which are quite difficult to obtain by routine synthetic methods, are easily formed under hydrothermal conditions [8]. Rigid tetradentate ligands 2,2′-biphenanthroline (2,2′-biphen) and 2,2′;6,2″;6″,2‴-quaterpyridine (quaterpy), which are not easy to obtain from 1,10-phenanthroline (phen) and 2,2′-bipyridine (2,2′-bpy), are in situ formed via dehydrogenative coupling of bipyridine-like ligands under hydrothermal conditions [3,4].

In spite of the importance of in situ ligand synthesis in the crystal engineering of complexes and in organic synthetic chemistry, there has been no review devoted to the subject. The aim of the present review is to give the reader an overview of all types of hydro(solvo)thermal in situ lig-



Scheme 1.

and syntheses to form crystalline complexes; a few non-hydro(solvo)thermal in situ ligand reactions are also covered. Although the author has tried to enumerate all types of hydro(solvo)thermal in situ ligand syntheses, it is impossible to be absolutely comprehensive due to limited knowledge. Apologies are offered in advance to those whose work may not be included.

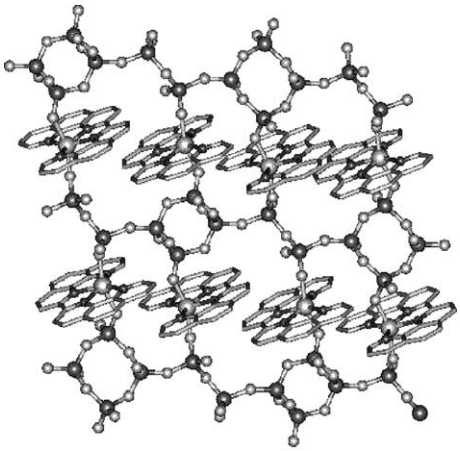


Fig. 1. View of two-dimensional framework of **2**. Generated from CIF data in Ref. [3].

2. A survey of the types of hydro(solvo)thermal in situ ligand synthesis

2.1. Carbon–carbon bond formation

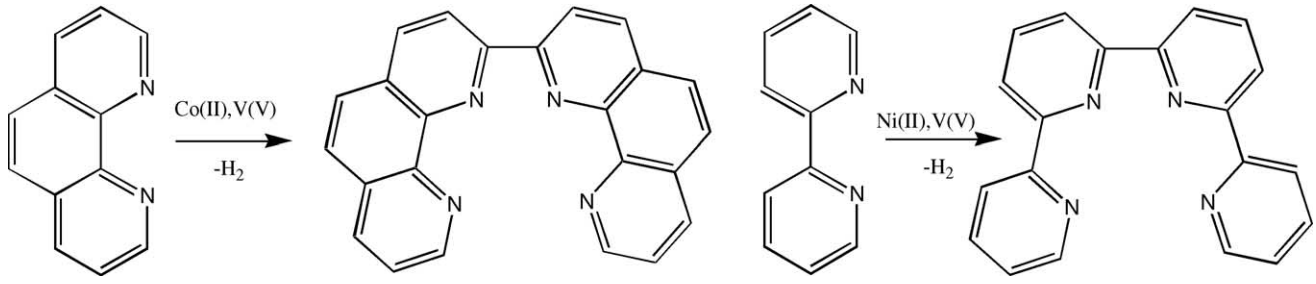
Carbon–carbon bond formation is one of the most important tools of modern organic synthesis. In situ carbon–carbon bond formation in the crystal engineering of complexes was first recognized by Champness and Schröder in 1997, when they obtained crystals of the three-dimensional (3-D) coordination polymer $\{Ag[tpct]BF_4\}_n$ (**1**) (tpct = 1,2,3,4-tetrakis(4-pyridyl)cyclobutane) from the reaction of $AgBF_4$ and 1,2-*trans*-(4-pyridyl)ethene (bpe) in $MeCN/CH_2Cl_2$ solution in the presence of light [2]. The in situ cyclisation of bpe to yield the ligand tpct is responsible for the formation of the 3-D framework of **1** (Scheme 1) [2].

This reaction is a photochemical reaction because it does not occur in the absence of a UV source. The Ag(I) ions played a key role in the light-induced process, but whether the ligand cyclisation occurs in the solid state or in solution was not clear. Interestingly, UV photolytic cyclisation of bpe in MeOH or C_6H_6 generally affords two isomers of the ligand, but in situ cyclisation of bpe in the reaction produced only single isomer of tpct ligand.

Another type of in situ ligand synthesis involving C–C bond formation is dehydrogenative coupling of bipyridine-like ligands under hydrothermal conditions (Scheme 2)[3,4].

Two solid state vanadium oxide complexes [Co(2,2′-biphen)$V_3O_{8.5}$] (**2**) and [{Ni(quaterpy)(H_2O)}$_2V_4O_{12}$] (**3**) were hydrothermally prepared via in situ ligand reactions [3,4]. Compound **2** was prepared from a mixture of NH_4VO_3, H_3BO_3, $Co(NO_3)_2{\cdot}6H_2O$, phen and H_2O (molar ratio 1:1.5:1:2:1000) at 160 °C for 120 h, while **3** from a mixture of $NiCl_2$, V_2O_5, 2,2′-bpy and H_2O (molar ratio 1:1:2:900) at 200 °C for 132 h. The structure of **2** consists of a two-dimensional neutral framework with a 4,8,10-net as shown in Fig. 1, where $[Co(2,2'\text{-biphen})]^{2+}$ units are covalently linked to $V_6O_{17}{}^{4-}$ chains. Compound **3** contains tetranuclear $V_4O_{12}{}^{4-}$ clusters decorated with $[Ni(quaterpy)(H_2O)]^{2+}$ complex fragments as shown in Fig. 2.

Though there are lots of organic–inorganic hybrid materials reported in which 2,2′-bpy or phen coordinate to metal centers, the dehydrogenative coupling of phen and 2,2′-bpy ligands under hydrothermal conditions has only been observed in the two polyoxovanadate compounds above. The in situ dehydrogenative coupling of bipyridine-like ligands in the two polyoxovanadate compounds can be rationalized by the long-term argued Gillard mechanism [32]. According to the Gillard mechanism, the coordination of metal ions to pyridine-like ligands has an effect similar to the quaternisation of the pyridine nitrogen. This will polarize the 2-



Scheme 2.

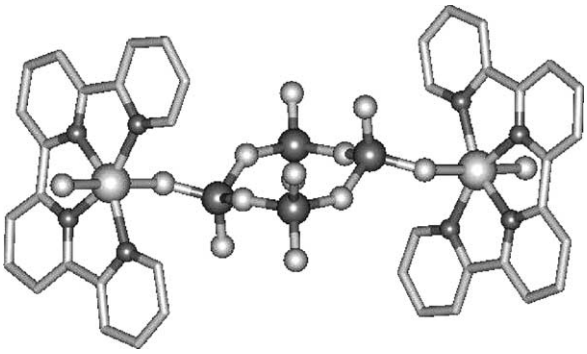
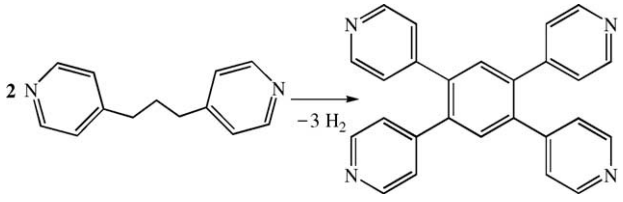


Fig. 2. View of structure of **3**. Generated from CIF data in Ref. [4].

position of pyridine and make it easier to be oxidized. In addition, high temperature and pressure and long-time reactions have also proven to be effective for the dehydrogenation of pyridine.

The third type of C–C bond formation reaction is in situ synthesis of a tetradentate dye molecule 1,2,4,5-tetra(4-pyridyl)benzene (tpbz) by dehydrogenative coupling of two 4,4′-trimethylenedipyridine units under hydrothermal conditions [5] as shown in Scheme 3.

Crystals of $[Cd_8(SC_6H_5)_{12}(tpbz)_2SO_4](HSO_4)_2(H_2O)_4$ (**4**) were prepared from a mixture of $Cd_{10}S_4(SPh)_{12}$, 4,4′-trimethylenedipyridine, Na_2SO_4 and water at 190 °C for 3 days. The dehydrogenative coupling between two 4,4′-trimethylenedipyridine units established the three-dimensional framework (Fig. 3) of **4**. High temperature and pressure may be responsible for this in situ ligand synthesis reaction. Compound **4** can be considered as lay-



Scheme 3.

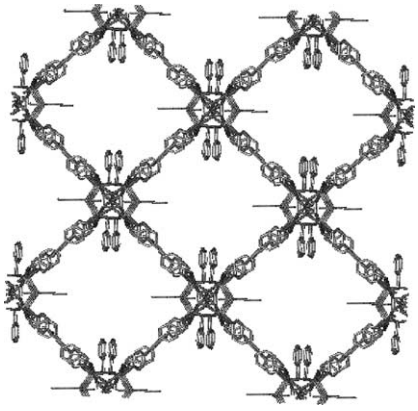


Fig. 3. View of three-dimensional framework in **4**. Generated from CIF data in Ref. [5].

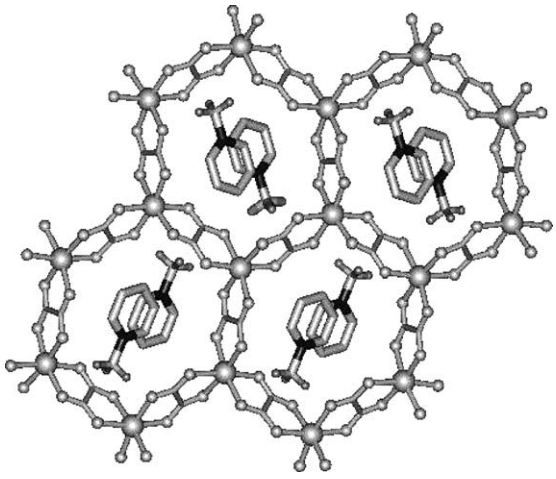
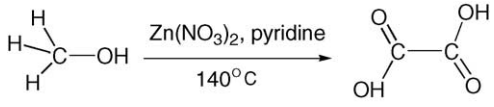


Fig. 4. View of the two-dimensional structure of **5**. Generated from CIF data in Ref. [6].

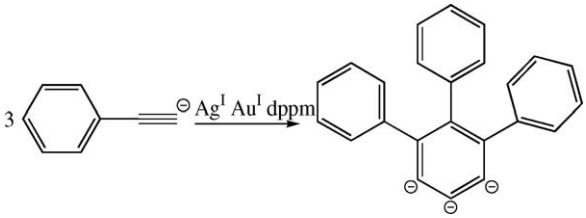
ers of $[Cd_8(SPh)_{12}]^{4+}$ clusters stacked along the *c*-axis. In the $[Cd_8(SPh)_{12}]^{4+}$ cluster, 8 cadmium ions are arranged at corners of a cube, while 12 SPh groups are distributed slightly off the center of each cubic edge. Within each layer, $[Cd_8(SPh)_{12}]^{4+}$ clusters are joined into a square pattern encircling large square pores formed by four $[Cd_8(SPh)_{12}]^{4+}$ clusters. The linkage between adjacent layers is provided by the benzene rings of tpbz.

The fourth type of C–C bond formation reaction is oxidative coupling of methanol to oxalic acid [6]. Surprisingly, when the reaction of $Zn(NO_3)_2{\cdot}6H_2O$ and pyridine was carried out in methanol at 140 °C for 5 days, colorless crystals of two-dimensional [methylpyridinium]$_2$[$Zn_2(ox)_3$] (ox = oxalate) (**5**) as shown in Fig. 4, were isolated. The oxalate ligands in **5** presumably resulted from unprecedented oxidative coupling of methanol molecules (Scheme 4) [6]. Evans and Lin [6] attempted to carry out the same reactions with zinc perchlorate in place of zinc nitrate but failed. This indicated the nitrate groups act as oxidants for oxidative coupling of methanol to oxalic acid. The insolubility of **5** under hydro(solvo)thermal condition is at least in part responsible for oxidative coupling of methanol molecules to oxalic acid. In addition to oxidative coupling of methanol to oxalic acid, in situ methylation of pyridine to methylpyridinium was also observed.

The final in situ C–C formation reaction is cyclotrimerization of arylacetylide [7] as shown in Scheme 5. Reaction of $[Au_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$[dppm = bis(diphenylphosphino)-methane] with three equivalents of $(AgC{\equiv}C\text{-}C_6H_4R\text{-}4)_n$ in dichloromethane with exclusion of light yields the heterometallic complexes $[Au_5Ag_8(\mu\text{-dppm})_4$\{1,2,3-



Scheme 4.



Scheme 5.

$C_6(C_6H_4R\text{-}4)_3\}(C{\equiv}CC_6H_4R\text{-}4)_7]^{3+}$ [R = H, (**6**) CH_3, But] (Fig. 5). The unprecedented trianion μ_5-$\{1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}^{3-}$ was derived in situ from the cyclotrimerization of arylacetylide $C{\equiv}CC_6H_4R$-4.

It is worth noting that the cyclotrimerization of substituted alkynes catalyzed by transition-metal complexes usually gives 1,3,5- and/or 1,2,4-trisubstituted benzene derivatives with high selectivity rather than 1,2,3-trisubstituted benzene derivatives. A reaction mechanism involved in the generation of intermediates such as cyclobutadiene and Dewar benzene derivatives was proposed on the basis of both experimental and theoretical evidence.

2.2. Hydroxylation

Hydroxylation is any chemical process that introduces one or more hydroxyl groups into a compound, thereby oxidizing it. In biochemistry, hydroxylation reactions are often facilitated by enzymes.

Many complexes containing phen or 2,2′-bpy have been reported. However, the hydroxylation of phen and 2,2′-bpy, until now, is only found in a few copper and molybdenum compounds [8–10]. The core of the Gillard mechanism is the nucleophilic attack of the α-carbon atom of pyridine by a hydroxide ion to form a covalent hydrate (**CH**) [32]. These complexes may provide more useful structural evidence for the Gillard mechanism and are not only important in organic heterocyclic chemistry, but also in coordination chemistry [1a,33].

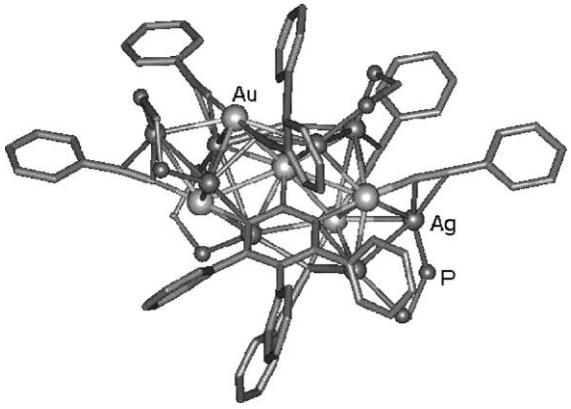


Fig. 5. View of structure of **6**. Phenyl rings of dppm are omitted. Generated from CIF data in Ref. [7].

2.2.1. Dinuclear $[Cu^I{}_2(ophen)_2]$ (7)

Hydrothermal reactions of Cu(II) salt, phen and water in the temperature range of 140–185 °C produced three supramolecular isomers of dinuclear $[Cu^I{}_2(ophen)_2]$ **7** with a hydroxylated phen ligand as shown in Fig. 6. Compound **7** crystallizes in three supramolecular isomers (α, β and γ) in which the molecular structures are virtually identical. Each Cu^I atom in **7** features a trigonal geometry, being coordinated by two nitrogen atoms from an ophen ligand and one oxygen atom from a deprotonated hydroxy group of another ophen ligand. The Cu–Cu distances in the α, β and γ forms are ca. 2.68 Å, which indicates weak Cu^I–Cu^I bonding interactions [34]. The three supramolecular isomers show remarkable differences in molecular packing arrays. There are three types of supramolecular interactions in **7**, namely C–H···O hydrogen bonding, aromatic π–π stacking and intermolecular Cu···Cu interactions, which may be responsible for the existences of the three supramolecular isomers. In **7**·α, discrete molecules are extended by C–H···O hydrogen bonds and aromatic π–π stacking interactions into a 2-D supramolecular array; in **7**·β, the C–H···O hydrogen bonds link the discrete molecules into 2-D layers, and off-set aromatic π–π stacking interactions and intermolecular Cu···Cu interactions further extend the 2-D layers into a 3-D array; in **7**·γ, two discrete molecules having intermolecular aromatic π–π interactions and Cu···Cu interactions are paired, and the molecular pairs are further interconnected via C–H···O hydrogen bonds to generate a 3-D supramolecular array.

2.2.2. Tetranuclear mixed-valence copper(I,II) complexes

Five tetranuclear mixed-valence copper(I,II) complexes namely $[Cu_4(obpy)_4(tp)]$ (**8**), $[Cu_4(ophen)_4(tp)]$ (**9**), $[Cu_4(obpy)_4(dpdc)]\cdot 2H_2O$ (**10**), $[Cu_4(obpy)_2(fum)]\cdot 6H_2O$ (**11**) and $[Cu_4(ophen)_2(fum)]$ (**12**) (tp = terephthalate, dpdc = diphenyl-4,4′-dicarboxylate, fum = fumarate) have been documented and are structurally analogous since they all consist of a pair of $[Cu_2(ophen)_2]^+$ or $[Cu_2(obpy)_2]^+$ fragments bridged by a deprotonated dicarboxylate into neutral tetranuclear dumbbell-shaped molecules (Fig. 7). The copper atoms in these complexes have a similar square-pyramidal coordination environment being surrounded by two nitrogen atoms from an ophen or obpy, a deprotonated hydroxy group from another ophen or obpy, and the adjacent copper atom (Cu–Cu ca. 2.4 Å) at the equatorial positions, and by a tp, dpdc or fum carboxylate oxygen atom at the apical position. The bond valence sum analyses and magnetic susceptibility measurements indicate that they are average mixed-valence copper(I,II) complexes which are important in metalloprotein systems due to long-distance electron transfer [35].

Complexes **7**–**12** were hydrothermally synthesized in the temperature range of 140–185 °C under autogenous pressure with a filling volume of ca. 50%. Compound **7** has three supramolecular isomers in the solid state, and the synthesiz-

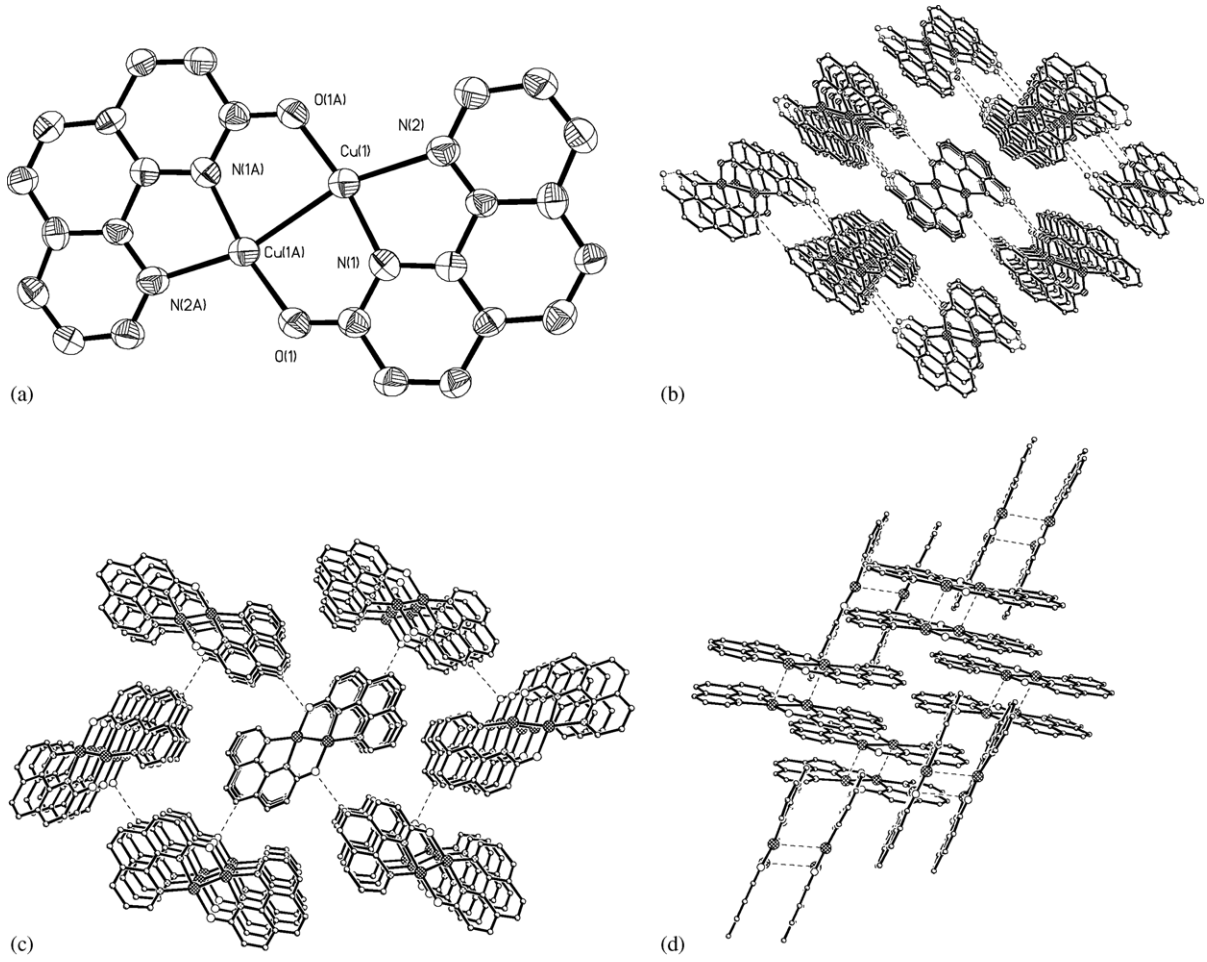


Fig. 6. View the molecular structure of **7** (a) and stacking array of its three isomers α (b), β (c) and γ (d). Generated from CIF data in Ref. [8b].

ing temperature of the three isomers from low to high is in the sequence of **1**·γ, **1**·α and **1**·β. The molecular symmetry from low to high is also in the sequence of **1**·γ, **1**·α and **1**·β. These observations are consistent with variations in entropy. From the entropy point of view, reaction at a higher temperature favors the formation of a structure of higher symmetry. In addition, complex **7** can convert into mixed-valence tetranuclear **9** by addition of an extra Cu(II) salt and tp and further hydrothermal treatment. Therefore, it may be regarded as the intermediate in the formation of **9**. Maintaining a weakly basic environment (pH 8–9) in the preparation of **7**–**12** is important for the hydroxylation of phen or bpy ligands to generate ophen or obpy.

Hydroxylation of 2,2′-bpy and phen to produce Hobpy and Hophen observed in **7**–**12** is consistent with the covalent hydrates of the Gillard mechanism and thus provides structural evidence for the Gillard mechanism. Using the Gillard mechanism, the principal steps proposed for the formation of the dinuclear copper(I) complex **7** and tetranuclear delocalized mixed-valence copper(I,II) complex **9** are shown in Scheme 6 [8b].

First, phen ligands are coordinated to copper(II) ions to form the $[Cu(phen)L_2]^{2+}$ species. This step is the prerequisite for a nucleophilic attack by hydroxide ions since the α-carbon of pyridine can only be activated by coordination of phen to a Cu^{II} ion. Secondly, the α-carbon of pyridine is attacked by a nucleophilic hydroxide to form a mononuclear covalent hydrate (**CH**), which is the core step of the Gillard mechanism. Thirdly, the deprotonation of the mononuclear covalent hydrate results in a pseudobase (**PB**) species. Then, two mononuclear **PB** species are dimerized to form a dinuclear **PB** species. Next, intramolecular electron transfer and dehydrogenation of the dinuclear **PB** species result in a neutral dinuclear copper(I) species. In this step, the role of the Cu^{II} ions as oxidant is critical in the fixation of the hydroxy group on the pyridyl ring. Intramolecular electron transfer then again generates a dinuclear Cu(I) complex **7**. Finally, one electron oxidization of the neutral dinuclear copper(I) molecule and dimerization of two dinuclear species by coordination of a tp bridge furnish a molecule of **9**, concomitant with contraction of the Cu–Cu distance.

Recently, a molybdenum complex $[Mo_2O_5(ophen)_2]$ (**13**) involving in situ hydroxylation of phen was hydrothermally synthesized from a mixture of SeO_2, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, phen and H_2O [10]. Compound **13** consists of $\{Mo_2O_5\}$ units

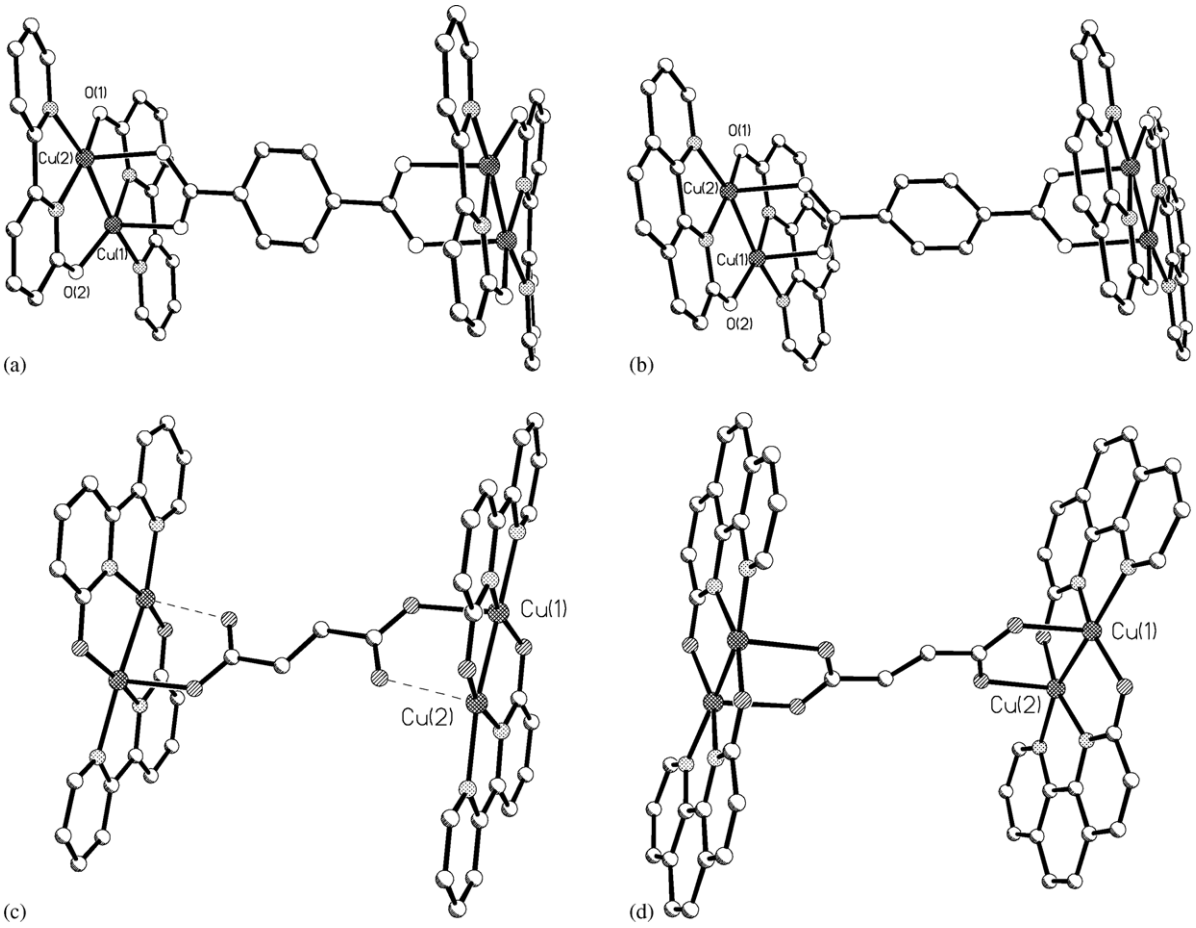
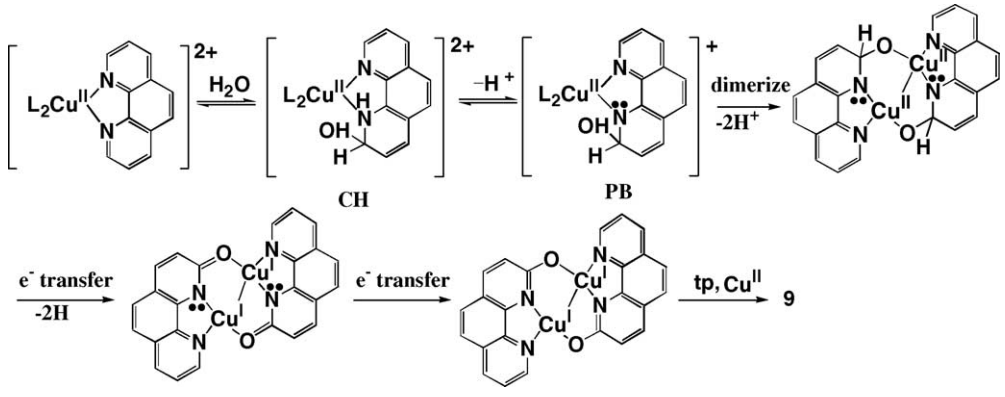


Fig. 7. View of the structures of **8** (a), **9** (b), **11** (c) and **12** (d). Generated from CIF data in Refs. [8,9].

coordinated with ophen ligands (Fig. 8). Each Mo(VI) atom in **13** possesses octahedral geometry coordinated with two nitrogen donors of an ophen group, one oxygen atom from a deprotonated pyridyl hydroxy group of another ophen ligand, two terminal oxygen atoms and one bridging oxygen atom which is linked with another Mo atom. The preparation of **13** indicates that not only copper ions but also other transition metal ions can catalyze the hydroxylation of pyridine-like ligands as predicted by the Gillard mechanism.

Another type of hydroxylation is the in situ synthesis of 2-hydroxyisophthalate (Hoip) from isophthalate (Scheme 7) [11]. The reaction of isophthalate (ip) and 4,4′-bipyridine (4,4′-bpy) with $Cu(NO_3)_2{\cdot}3H_2O$ (molar ratio 1:1:1) at 180 °C for 80 h under hydrothermal conditions generated a mixed-valence copper(I,II) complex $[Cu_2(oip)(4,4'\text{-bpy})]$ (**14**) (Fig. 9). The Cu^{II} ions possibly acted as an oxidative agent to promote the formation of the phenoxo group. Compound **14** is a two-dimensional (6,3) layer constructed



Scheme 6.

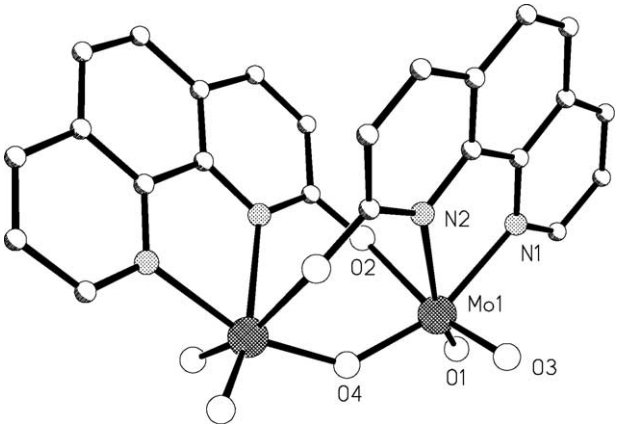
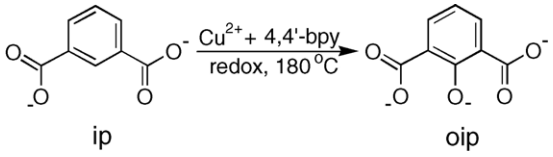


Fig. 8. View of the structures of **13**. Generated from CIF data in Ref. [10].



Scheme 7.

from the connection of $[Cu^{II}_2(oip)_2]_n^{2n+}$ 'metalloligands' and $[Cu^{I}(4,4'\text{-bpy})]_n^{n+}$ chains.

2.3. Tetrazole formation

Tetrazoles have a wide range of applications. Besides being precursors to a number of *N*-heterocycles [36], they are used in pharmaceuticals as lipophilic spacers and carboxylic acid surrogates and in photography and information recording systems [37]. Sharpless and co-worker [38] reported the metal ion assisted synthesis of tetrazoles through the formal [2 + 3] cycloaddition reactions of nitriles with azide in aqueous solution (Scheme 8).

Xiong and co-workers borrowed Sharpless' idea and prepared a series of tetrazole-based coordination polymers by the

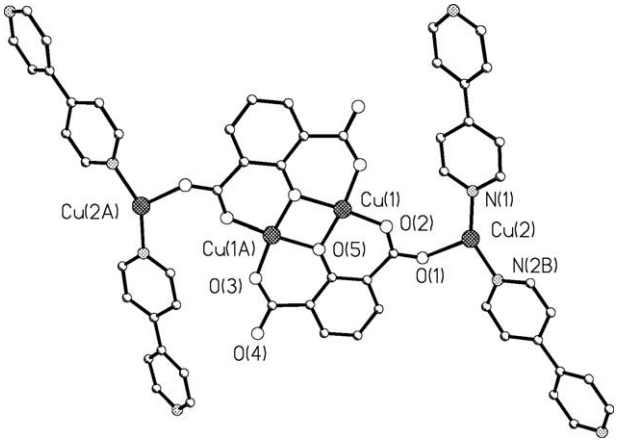
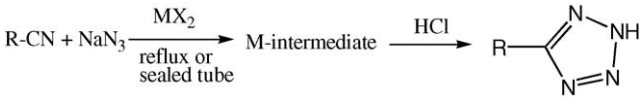


Fig. 9. View the coordination enviroment (a) of copper in **14**. Generated from CIF data in Ref. [11].

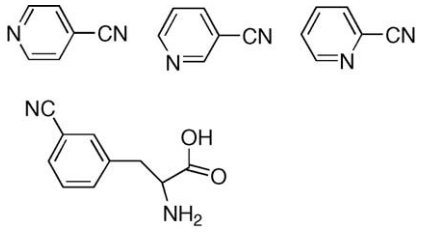


Scheme 8.

in situ synthesis of tetrazoles from various nitriles with azide [12]. This type of in situ ligand synthesis reaction is very important because the precursor nitriles are very broad. General reaction temperature is 110–160 °C and molar ratio of nitrile to azide is 1:1 or 1:1.5. Scheme 9 [12] shows some precursors for tetrazole-based ligands, which include various cyanopyridines and enantiomerically pure (*S*)-3-cyanophenylalanine [(*S*)-3-CNPHA].

Investigations of this type of hydrothermal reaction with zinc or cadmium salts were particularly fruitful and yielded a variety of coordination polymers. Complexes [Zn(OH)(3-ptz)] (**15**), $[CdN_3(3\text{-ptz})]$ (**16**), $[Cd_3(OH)_2Cl_2(4\text{-ptz})_2]$ (**17**), $[Cd(4\text{-ptz})_2(H_2O)_2]$ (**18**) [3-ptz = 5-(3-pyridyl)tetrazolate, 4-ptz = 5-(4-pyridyl)tetrazolate] were in situ synthesized from the metal salt and corresponding cyanopyridines. Compound **15** has a two-dimensional structural constructed from 3-ptz ligands and Zn–OH chains as shown in Fig. 10. Particularly interestingly, three-dimensional homochiral metal-organic polymers [Zn((*S*)-TPA)] (**19**) (Fig. 11) and [Cd((*S*)-TPA)(H_2O)] (**20**) [(*S*)-TPA = (*S*)-5-(3-tetrazoyl) phenylalaninato] were formed when chiral and enantiomerically pure (*S*)-3-CNPHA was employed in the hydrothermal reaction.

Mechanistically, this type of formal [2 + 3] cycloaddition reaction of azide and nitrile is quite complicated: several possible reaction pathways can be envisioned. Recent calculations revealed that when a proton is available, the reaction proceeds via the imidoyl azide intermediate [39a]. The transition state involves the activation of the nitrile by a proton, facilitating the attack of the azide on the carbon of the nitrile. From the imidoyl azide intermediate, simple 1,5-cyclisation occurs to give the 1*H*-tetrazole. However, when Lewis acid



Scheme 9.

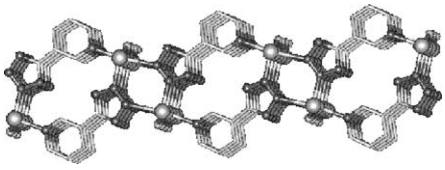


Fig. 10. Two-dimensional structure of **15**. Generated from CIF data in Ref. [12a].

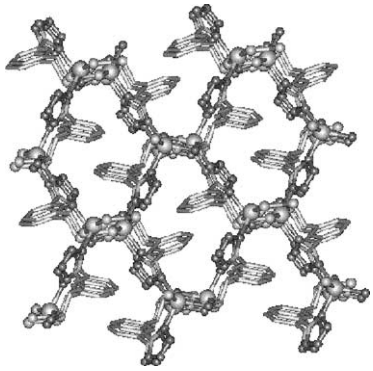


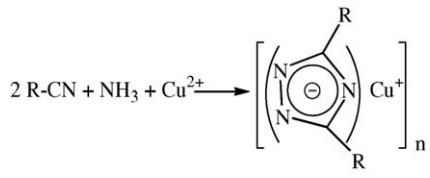
Fig. 11. Homochiral metal-organic framework of **19**. Generated from CIF data in Ref. [12c].

cations such as Zn(II) and Al(III) ions are present, the reaction energy barrier is lowered [39b]. Synthetically, this corresponds to a rate acceleration of several orders of magnitude or the temperature required to achieve a comparable rate will decrease by tens to a hundred degrees centigrade. Calculations and experimental rate studies revealed that coordination of the nitrile substrate to the Lewis acidic cations is the source of the catalysis in the formation of 1*H*-tetrazoles.

2.4. Triazole formation

Coordination complexes of 1,2,4-triazoles have been known for more than a century; however, the beginning of their systematic study dates from the late 1970s. 1,2,4-Triazole and its derivatives unite the coordination geometry of both pyrazoles and imidazoles which in combination with their strong σ-donor properties makes them very appealing for the design of polynuclear complexes and coordination polymers with interesting properties [40].

In order to extend in situ hydroxylation reaction of phen, Chen et al. carried out an analogous reaction using copper(II) nitrate, phen, ammonia, and acetonitrile, which yielded a small quantity of pale-yellow crystals of $[Cu(mtz)]_n$ (**21**) (Hmtz = 3,5-dimethyl-1,2,4-triazole). Because phen was not present in the product, a mixture of $Cu(OH)_2$ (or $Cu_2(OH)_2CO_3$) (1 mmol), aqueous ammonia (2–3 mL), and acetonitrile or butyronitrile (2–3 mL) was reacted at 160 °C for 3 days. All these reactions generated 1,2,4-triazole-based Cu^I coordination polymers **21** and $[Cu(ptz)]_n$ (**22**) (Hptz = 3,5-dipropyl-1,2,4-triazole) (Scheme 10) [13]. The aqueous ammonia and acetonitrile/butyronitrile played a solvent and reactant dual role in the in situ ligand reaction, which is key to the formation of 3,5-disubstituted 1,2,4-triazoles. Based on these observations, Chen et al. [13] suggested that the triazolates were derived from coupling of the nitriles and ammonia. The presence of Cu^I ions in the products indicates that Cu^{II} ions may act as an oxidant to assist the elimination of protons in the cycloaddition to give the final ligands. The in situ copper-mediated reactions of nitriles and ammonia provided a non-hydrazine synthetic route to 3,5-disubstituted 1,2,4-triazoles.



Scheme 10.

Compound **21** consists of 1-D helices in which the Cu^I ions are bridged by the triazolates in the imidazolate mode (Fig. 12a). Each helical chain is further connected to four adjacent antiparallel chains through interchain Cu–N coordination bonds into an unprecedented 4.8.163-D net. Compound **22** exhibits a three-connected topological 4.12^2 net, which can also be simplified to an NbO net (Fig. 12b).

2.5. Substitution

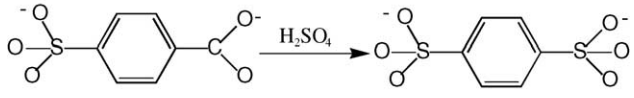
The reaction of $Eu(NO_3)_3$ (1 mmol), 4-sulfobenzoic acid (4-H_2SB) (3 mmol), ethanol (0.5 mL) and H_2SO_4 (2 mL, 5N) at 130 °C for 2 days yielded Eu_2(1,4-BDS)(4-SB)$_2$ (**23**) with a pillar-like 3-D network in which benzene-1,4-disulfonate (1,4-BDS) was in situ synthesized from 4-H_2SB by replacement of carboxyl with sulfonic group as shown in Scheme 11 and Fig. 13 [14].

The exact mechanism is not clear but Xiong et al. [14] suggested that Eu^{3+} may play an important catalytic role in the formation of 1,4-BDS, similar to that found in the preparation of 1,4-H_2BDS from the sodium salt of *p*-chlorobenzenesulfonate in the presence of $CuSO_4$.

2.6. Alkylation

The reactions of copper salts with thio-pyridine ligands are liable to result in uncharacterizable precipitates, which are insoluble in conventional solutions. But a solvothermal reaction of $CuCl_2$, KI, HS-4-C_5H_4N and EtOH in a molar ratio of 1:1:1:500 at 160 °C for 60 h afforded a large amount of yellow crystals of $[(Cu_3I_4)(EtS\text{-}4\text{-}C_5H_4NEt)]_n$ (**24**) and minor red $Cu_6(4\text{-}SC_5H_4NH)_4Cl_6$, as well as K_2SO_4. In the reaction course, EtS-4-C_5H_4NEt was in situ synthesized by an alkylation reaction [15].Compound **24** is a luminescent linear inorganic–organic hybrid coordination polymer formed by trinuclear Cu_3I_4 units with EtS-4-C_5H_4NEt attached via S–Cu coordination interaction (Fig. 14).

Based on the isolation of byproducts $Cu_6(4\text{-}SC_5H_4NH)_4Cl_6$ and K_2SO_4, as well as the existence of iodine in the filtrate, Cheng et al. [15] proposed a



Scheme 11.

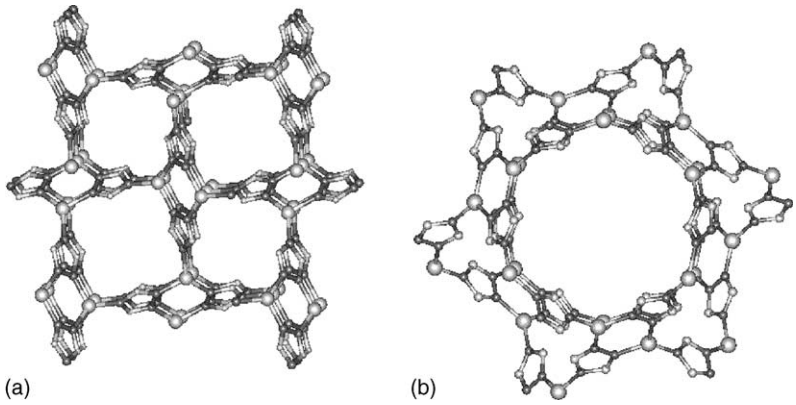


Fig. 12. View the 3-D frameworks of **21** (a) and **22** (b). Generated from CIF data in Ref. [13].

converse deduction of the synthesis of **24** in which CuI and (EtS-4-C_5H_4NEt)I are two important intermediates (Scheme 12). According to the deduction, indirect and direct alkylation reagents are ethanol and EtI, respectively.

Actually, a solvothermal in situ alkylation reaction was first observed in the preparation of **5** by Evans and Lin (see Fig. 4) [6]. It involved two in situ ligand reactions: methylation and oxidative coupling of methanol to oxalic acid. However, Evans and Lin [6] focused on explaining the mechanism of oxidative coupling of methanol to oxalic acid, and they did not explain the alkylation reaction.

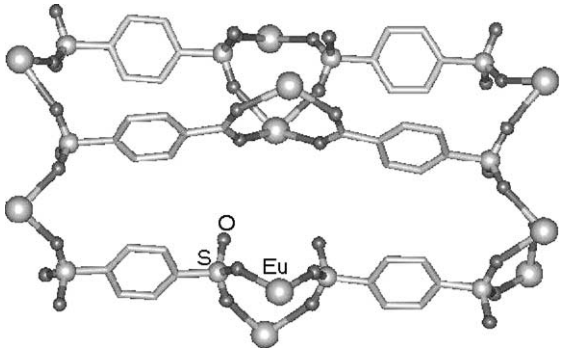


Fig. 13. Part of the structure of **23** showing in situ synthesis of 1,4-BDS. Generated from CIF data in Ref. [14].

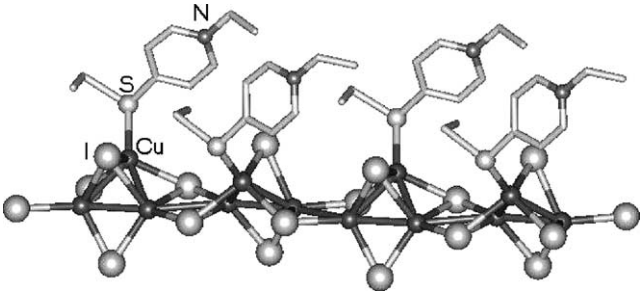


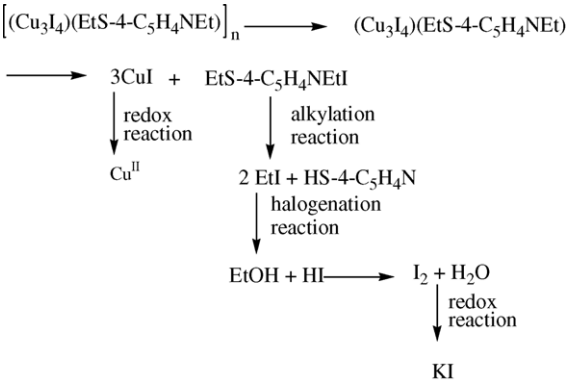
Fig. 14. The linear structure of **24** showing alkylated EtS-4-C_5H_4NEt ligand. Generated from CIF data in Ref. [15].

2.7. Ether bond formation

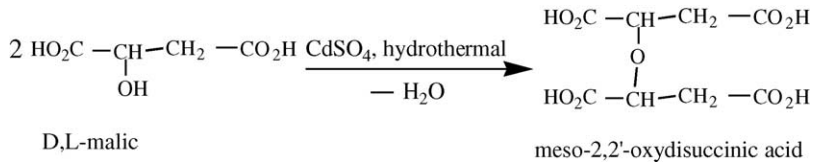
The intermolecular dehydration coupling of alcohol and diol can form ether and hexacyclic ether. However, this reaction is a chemical equilibrium and the product ether should be removed from the system in order to continue formation of the ether.

We have recently obtained a layered coordination polymer [Cd_2(*meso*-odsc)(H_2O)] (**25**) (H_4odsc = 2,2′-oxydisuccinic acid) by hydrothermal treatment of a mixture of $CdSO_4$, malic acid and NaOH (1:2:1) at pH ≈ 1 as shown in Fig. 15 and Scheme 13 [16]. The ligand *meso*-odsc was in situ formed via intermolecular dehydrative coupling of malic acid and coordinated to seven Cd(II) ions in an unprecedented fashion. Compound **25** is insoluble in water and common organic solvents. However, crystals of **25** lost transparency and became a yellow solid when treated with Na_2S aqueous solution indicating the formation of CdS and release of free *meso*-odsc ligand. The 2,2′-oxydisuccinic acid has *R*,*R*-, *S*,*S*- and *meso*-, three kinds of isomers, but only *meso*-isomer was observed in **25**.

The odsc is one important builder in detergents and cleaners because it has high binding potential for calcium or transition metal ions. Its preparation generally involves reaction of maleic anhydride (or maleic acid) with malic acid



Scheme 12.



Scheme 13.

in the presence of alkaline earth metal hydroxide under basic conditions, and the product is a mixture of three isomers [41]. Treatment of in situ synthesized **25** can result in the pure *meso*-isomer, which provides a good method to isolate isomers. Although only the *meso*-isomer as ligand in **25** was isolated, the *R*,*R*- and *S*,*S*-isomers may exist in solution because the reactants are a mixture of D- and L-malic acid.

The actual odsc formation mechanism in the reaction is not clear, but it is possibly similar to intermolecular hydration coupling of alcohol to form ether under acidic conditions. However, this reaction is a chemical equilibrium and the isolation of **25** is most probably a consequence of it being the most insoluble under the conditions employed, i.e. the kinetic product for this preparation. The mechanistic speculation is consistent with the experimental observations that no product **25** was produced when the reaction was performed at a lower reaction temperature or at higher pH.

2.8. Hydrolysis

Compared with other in situ ligand reactions, the hydro(solvo)thermal hydrolysis of cyano, ester and phosphonic ester groups is a commonly observed, easily understood and predictable reaction.

Research on the in situ hydro(solvo)thermal hydrolysis of cyano and ester groups was performed mainly in Lin's laboratory [17–20]. In order to avoid overlap with Lin's account [17], we only present these data briefly. Interest in this research lies mainly in searching for acentric solids based on infinite networks by combining unsymmetrical bridging ligands and metal centers. The slow hydro(solvo)thermal in situ hydrolysis of precursors containing cyano or ester functionalities in the presence of zinc/cadmium salt results in less soluble solids most of which are not accessible from their corresponding acids. The general synthesis procedure for these solids is exemplified by the preparation of $[Zn(4\text{-pya})_2]$ (4-pya = 4-pyridinecarboxylate) (**26**). A hydro(solvo)thermal reaction between $Zn(ClO_4)_2{\cdot}6H_2O$ and 4-cyanopyridine (1:1) in aqueous ethanol solution at 130 °C resulted in **26**. Elevated temperatures during hydro(solvo)thermal syntheses also allow in situ formation of pyridinecarboxylate ligands from a wide variety of precursors (Scheme 14) [17]. Specifically, the authors demonstrated that coordination networks based on 3-D diamondoid and 2-D grid structures can be successfully engineered with a high degree of probability and predictability to crystallize in noncentrosymmetric space groups [17].

Besides Lin's excellent work in acentric solids, a three-dimensional coordination polymer with a mixed-valence copper(I,II) dimeric unit $[Cu_2(4\text{-pya})_3]_n$ (**27**) was hydrothermally synthesized via an in situ hydrolysis reaction of Cu(II) and 4-cyanopyridine (Fig. 16) [21]. **27** is a two-fold interpenetrated three-dimensional coordination network with a cubic $[Cu_{16}(4\text{-pya})_{12}]$ building unit.

Another precursor for crystalline complexes is 1,4-dicyanobenzene, which can become terephthalic acid via hydrothermal in situ hydrolysis. A series of coordination polymers including chain-like $[M(tp)(phen)(H_2O)]_n$ (M = Co, Cu, Zn) and 3-D network structure of $[Mn(tp)(phen)]_n$ and $[Cd(tp)_{0.5}(phen)Cl]_n$ were synthesized by Hong and co-workers from various metal salts,

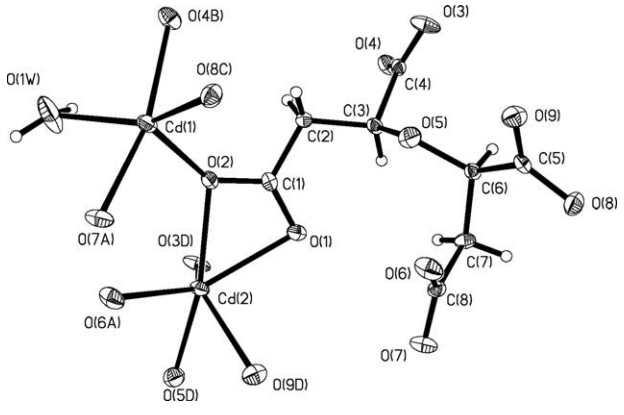
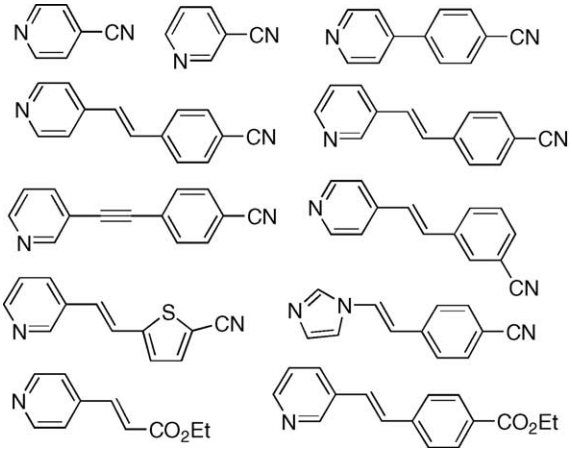


Fig. 15. View of coordination environment of Cd in **25**. Generated from CIF data in Ref. [16].



Scheme 14.

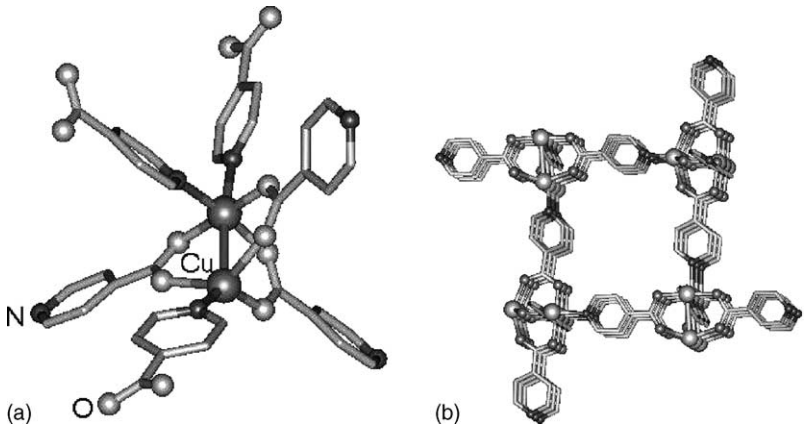


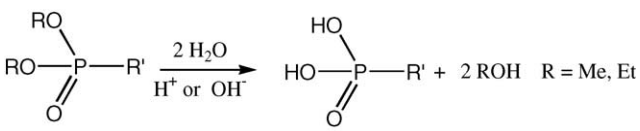
Fig. 16. Coordination environment of Cu (a) and part of 3-D structure (b) in **27**. Generated from CIF data in Ref. [21].

phen and 1,4-dicyanobenzene via the in situ hydrolysis reaction [22].

Metal phosphonates are organic–inorganic hybrid microporous solids in which the nature of the organic phosphonic acid can be designed to confer specific properties to this class of solids [42]. One problem in metal phosphonate chemistry is that many metal phosphonates from traditional methods (direct reaction of phosphonic acid with metal source by the hydrothermal method, or by refluxing appropriate solutions, or by making metal salts contact molten phosphonic acid) are formed too rapidly to allow for the growth of crystals sufficiently large for single crystal structural determination.

In order to obtain large crystals for X-ray structural analysis, a new route for metal phosphonates via the in situ hydrolysis of phosphonic ester has recently been developed by us and others (Scheme 15) [23,24]. Hix et al. prepared porous zinc phosphonate $Zn(O_3PCH_2OH)$ (**28**) by the hydrothermal treatment of zinc acetate and diethyl hydroxymethylphosphonate [23]. In the reaction, the weak acidity of the metal salt hydrolyzed diethyl hydroxymethylphosphonate ester to produce the corresponding phosphonic acid. Compound **28** has a channel structure and contains only octahedrally coordinated Zn atoms as shown in Fig. 17.

We chose trimethyl 3-phosphonopropionate as 3-phosphonopropionic acid source and hydrothermally synthesized a microporous zinc phosphonocarboxylate $Na[Zn(O_3PC_2H_4CO_2)]\cdot H_2O$ (**29**), which has a zeolite ABW open framework with channel enclosed by 22 atoms (Fig. 18) [24a]. Different from Hix's synthesis procedure, the pH in the synthesis of **29** is strongly basic to result in the hydrolysis of trialkyl phosphonocarboxylate becoming phosphonocarboxylic acid. The synthesis of metal phosphonocarboxylates via the in situ hydrolysis of dialkyl



Scheme 15.

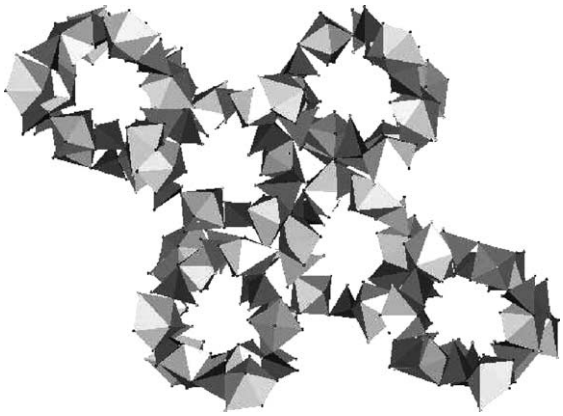


Fig. 17. View of the porous structure of **28**. Generated from CIF data in Ref. [23].

phosphonates or trialkyl phosphonocarboxylates appears to be an extremely productive adaptation of the traditional hydrothermal methods employed in the syntheses of these materials. The synthesis method has two benefits: (1) the use of the trialkyl phosphonocarboxylate rather than the phosphonocarboxylic acid removes the need to synthesize the acid because trialkyl phosphonocarboxylates are often far easier to purify than the corresponding phosphonocarboxylic acids; (2) the in situ slow formation of phosphonic acid

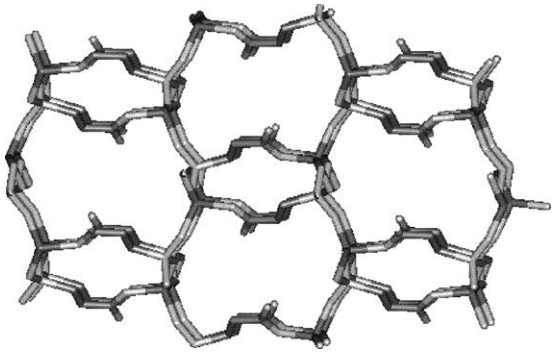


Fig. 18. View of the 3-D structure of **29**. Generated from CIF data in Ref. [24a].

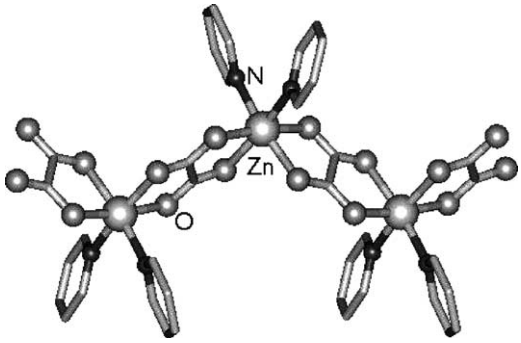


Fig. 19. View of the chain-like structure of **30**. Generated from CIF data in Ref. [25].

by hydrolysis of the corresponding phosphonic ester will ensure the growth of single crystals.

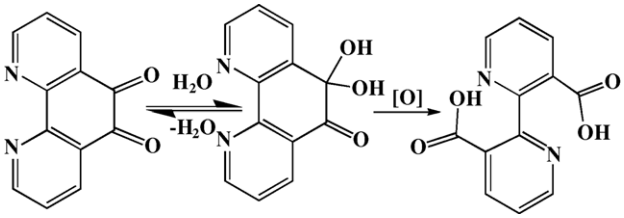
2.9. Oxidation and oxidation–hydrolysis

In order to avoid overlap, some in situ ligand reactions described in the former part of the review, which mechanistically involve an oxidation reaction or electron transfer, are not repeated. These reactions include oxidative-coupling of methanol to oxalic acid, dehydrogenative coupling of phen, 2,2′-bpy and 4,4′-trimethylenedipyridine, and hydroxylation of phen and 2,2′-bpy.

Similar to the preparation of [methylpyridinium]$_2$[$Zn_2(ox)_3$] except using ethanol in place of methanol, a solvothermal reaction of $Zn(NO_3)_2$ and pyridine in ethanol at 140 °C over 14 days resulted in the chain-like complex $[Zn(ox)(Py)_2]$ (**30**) as shown in Fig. 19 [6]. The high temperature and long time is responsible for in situ oxidation of the ethanol to oxalate ligands.

Some hydrothermal in situ ligand reactions involve not only oxidation but also a hydrolysis reaction. In our extension of the in situ synthesis of hydroxylated bipyridine-like ligands, the hydrothermal treatment of a mixture of cobalt (or nickel) acetate and 1,10-phenanthroline-5,6-dione (pdon) resulted in two chain-like coordination polymers $[Co(bpdc)(H_2O)_2]$ (**31**) and $[Ni(bpdc)(H_2O)_3]\cdot H_2O$ (**32**) [bpdc = 2,2′-bipyridine-3,3′-dicarboxylate] [25].

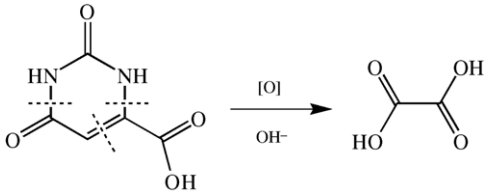
Although pdon was used as the original organic reagent in the preparation of **31** and **32**, bpdc ligand was found in the final products, which indicates an in situ transformation of pdon into bpdc during the hydrothermal treatment (Scheme 16) [25]. A possible mechanism for the in situ synthesis of bpdc is metal-assisted oxidization–hydrolysis. The ligation of the metal ion will cause some decrease of electron density on the aromatic ring of the organic ligand, hence promoting nucleophilic attack by water molecules. As a result, the hydration of the carbonyl groups of pdon furnishes an intermediate diol or even double diol. When the carbonyl carbons from sp^2 become sp^3 hybridized, the carbon–carbon bond is then oxidized and cleaved probably because of the crowdedness, resulting in the formation of bpdc.



Scheme 16.

The different coordination modes of pdon and different dihedral angles between the two pyridine rings results in simple linear chains and helical chains in **31** and **32** as shown in Fig. 20, respectively.

Another oxidation–hydrolysis reaction is the in situ oxidation–hydrolysis of orotic acid to form oxalic acid as shown in Scheme 17 and Fig. 21 [26]. A 3-D 3d-4f heterometallic coordination polymer $\{Sm_2Co(ox)_2(Hdtpc)_2(H_2O)_6\}$ (**33**) was prepared by the hydrothermal reaction of orotic acid, $Sm(NO_3)_3$ and $2CoCO_3\cdot 3Co(OH)_2$. The oxalate ligand was in situ synthesized from orotic acid. Further experiments showed that samarium ion may act as a catalyst for the formation of oxalate. The reaction mechanism remains unclear, the oxalate may be formed through an in situ metal-mediated oxidation–hydrolysis reaction of orotic acid. The hydrolysis reaction may occur at the C–N bond, whereas the oxidation reaction may happen at the C=C double bond.



Scheme 17.

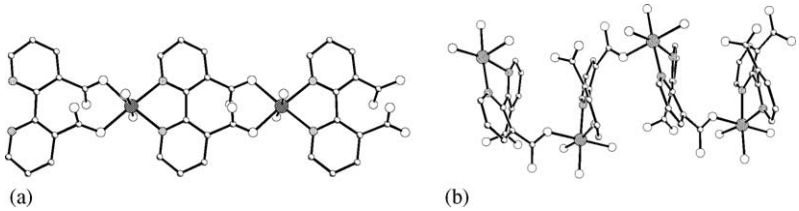


Fig. 20. View of linear chain in **31** and helical chain in **32**. Generated from CIF data in Ref. [25].

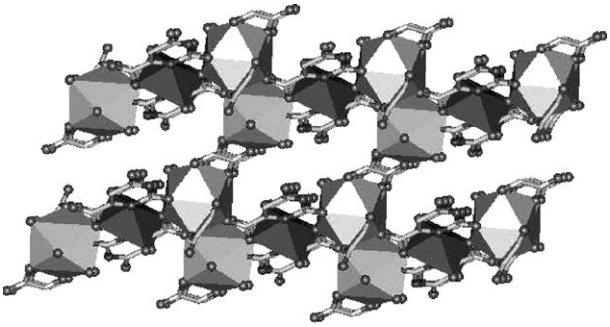


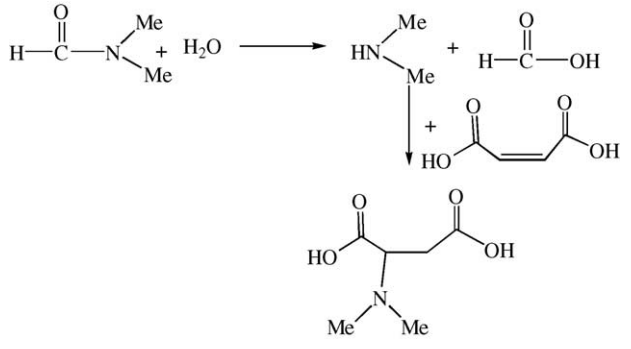
Fig. 21. View of three-dimensional structure of **33**. Generated from CIF data in Ref. [26].

2.10. Amination

The only example of hydro(solvo)thermal in situ amination reaction was observed very recently. A very spectacular octadecanuclear neutral cluster $Co_{18}O_4(dmap)_{14}$ (**34**) (H_2dmap = *N*,*N*-dimethyl-aspartic acid) was prepared by a solvothermal reaction of Co(II) salt and maleic acid in dimethylformamide (DMF) solution in which the H_2dmap was in situ synthesized via amination of maleic acid (Scheme 18) [27]. The reaction is a formal addition reaction of maleic acid and dimethylamine. The possible reaction mechanism is the slow hydrolysis of DMF at high temperature giving rise to formic acid and dimethylamine and the latter then reacts with maleic acid to generate the H_2dmap ligand. More interestingly, the Co_{18} cluster is chiral with S_6 symmetry as shown in Fig. 22.

2.11. Acylation

Recently, in situ acylation reactions of benzene-1,2,4,5-tetracarboxylic acid (H_4bta) and benzene-1,2,4-tricarboxylic acid (H_3btc) have been found in the formation of the crystalline coordination polymers $[Co(\mu_4\text{-}H_2bbh)(H_2O)_2]_n$ (**35**) $[Co(\mu_3\text{-}H_2bbh)(phen)]$ (**36**) $[Co(\mu_3\text{-}Hbcbh)(2,2'\text{-bpy})]$ (**37**) and $[Ni_{0.5}(apddica)(H_2O)]$ (**38**) (H_4bbh = benzene-1,2,4,5-bihydrazide, H_3bcbh = benzene-4-carboxylate-1,2-bihydrazide, Hapddica = 2-(4-amino-phenyl)-1,3-dioxo-2,3-dihydro-1H-isoindole-5-carboxylic acid) (Scheme 19) [28,29].



Scheme 18.

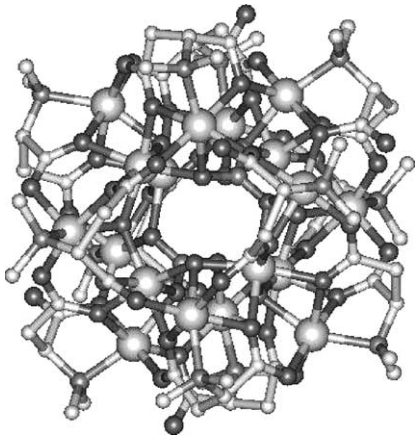


Fig. 22. View of octadecanuclear structure of **34**. Generated from CIF data in Ref. [27].

The hydrothermal reaction of $CoCl_2$, H_4bta, $N_2H_4{\cdot}H_2O$ generated a three-dimensional coordination polymer **35** (Fig. 23a) while in the presence of phen, the above reac-

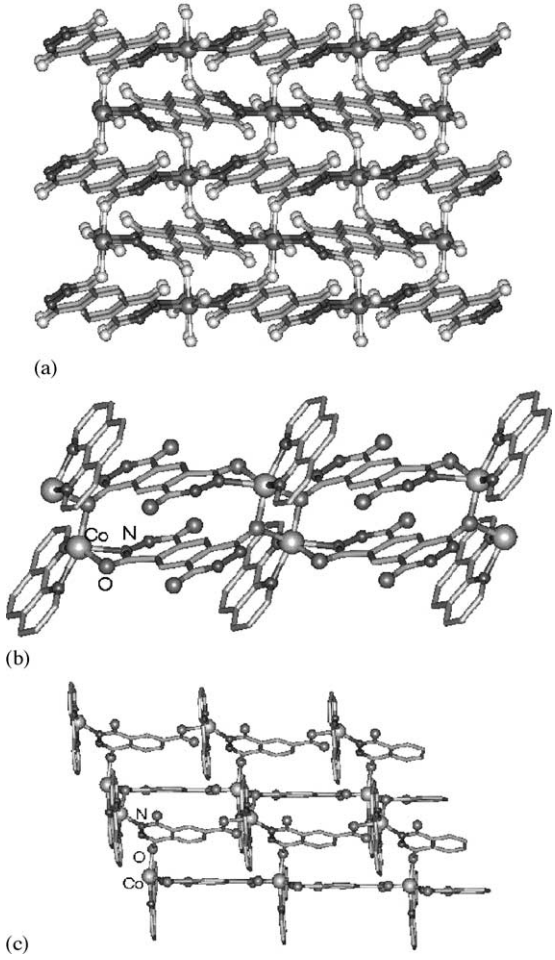
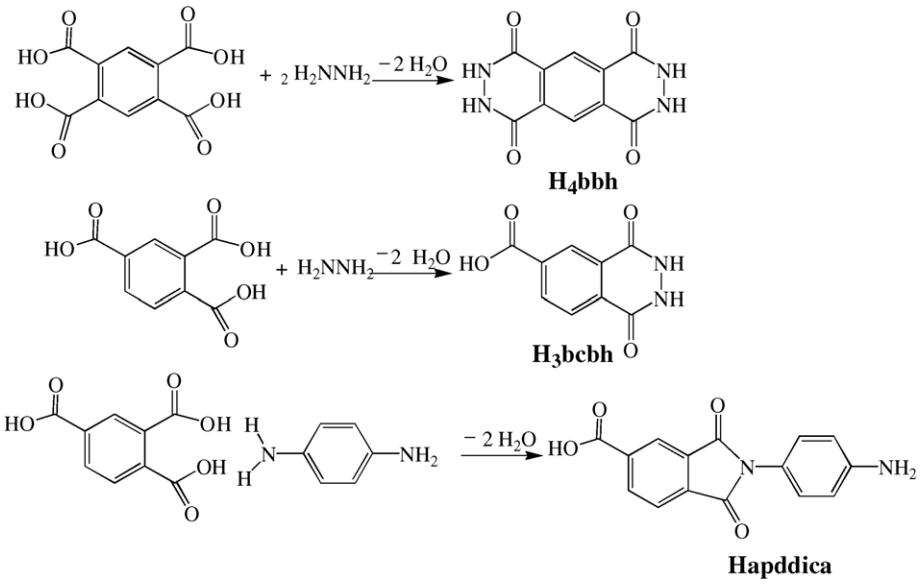


Fig. 23. View of the structures of **35** (a), **36** (b), and **37** (c). Generated from CIF data in Ref. [28].



Scheme 19.

tion resulted in 1-D **36** (Fig. 23b). Similar reaction of $CoCl_2$, H_3btc, $N_2H_4{\cdot}H_2O$ and 2,2′-bpy formed a 2-D **37** (Fig. 23c). The doubly deprotoned ligands H_4bta and H_3btc were formed via an in situ acylation reaction of H_4bta and H_3btc with $N_2H_4{\cdot}H_2O$. Interestingly, the H_4bbh ligand has eight potential donor atoms and it can lose one to four protons when it coordinates to metal ions, which will result in various coordination modes.

The acylation reactions of H_4bta and H_3btc depend on the choice of proper synthesis conditions, in which the pH value is vital, and the required reaction temperature is commonly 170–200 °C. The steric effect in the acylation reactions is also important because analogues of **35**–**37** using other aromatic multicarboxylic acids or substituting phenyl hydrazine could not be prepared.

The 2-D double-layers network of **38** (Fig. 24) was prepared by Wang et al. from a hydrothermal reaction of H_3btc, *p*-phenylenediamine, $Ni(CH_3CO_2)_2$ and Na_2SiO_3 in which ligand Hapddica was in situ synthesized via acylation of H_3btc and *p*-phenylenediamine [29]. In **38**, each apddica ligand uses one carboxylate-O and one amino-N coordinate to two Ni(II) centers which reaction results in a novel 2-D double-layer network.

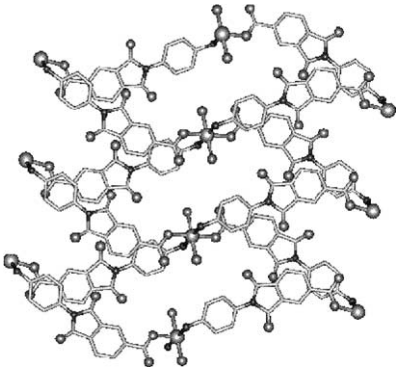


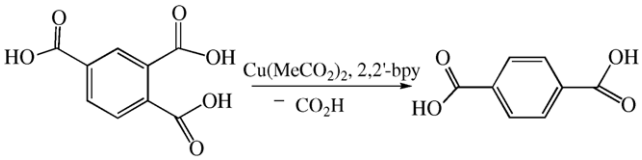
Fig. 24. View of the double-layered structure of **38**. Generated from CIF data in Ref. [29].

2.12. Decarboxylation

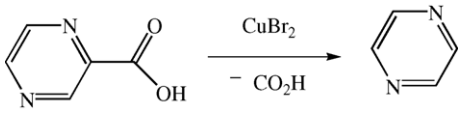
The first example of hydrothermal decarboxylation was observed by Lu and co-workers in the preparation of the mixed-valence copper(I,II) complex $[Cu_4(obpy)_4(tp)]_n$ [9a]. Although the starting material is a mixture of copper(II) acetate, H_3btc, 2,2′-bpy·2HCl, $NH_3{\cdot}H_2O$ and water, X-ray single crystal structural analysis clearly revealed that not only 2,2′-bpy was hydroxylated into Hobpy, but also the H_3btc ligand was in situ converted into tp by loss of a carboxyl group (Scheme 20) [9a].

Another decarboxylation reaction has been found in our hydrothermal preparation of coordination polymers of $[CuX(pyz)]_n$ **39** (pyz = pyrazine; X = Cl, Br). Compound **39** was hydrothermally prepared from a mixture of $CuBr_2$ and 2-pyrazinecarboxylic acid [30].

Surprisingly, the carboxyl group of 2-pyazinecarboxlate was in situ eliminated to yield the pyrazine ligand as shown in Scheme 21 [30]. The aromatic carboxyl group is difficult to eliminate even under hydrothermal conditions and relatively high reaction temperatures without catalysis. In the two reactions, in the presence of Cu(II) ions, both btc



Scheme 20.



Scheme 21.

and 2-pyrazinecarboxylate ligands lost their carboxyl group, while they did not lose a carboxyl group in the presence of other transition metal ions. This indicates that Cu(II) ions play a unique catalytic role in the decarboxylation procedure. In addition, our further experiments have shown that a higher reaction temperature favors decarboxylation of 2-pyrazinecarboxylate.

3. Isolation of in situ synthesized uncommon ligands and their applications

Hydrothermal in situ ligand synthesis is important not only in the crystal engineering of coordination complexes but also in synthetic organic chemistry. Thus, hydrothermal in situ ligand synthesis has become a powerful means to prepare organic ligands that are difficult to obtain by routine synthetic methods. The ligand Hophen which is quite difficult to obtain by routine synthetic methods, can quantitatively form via simple treatment of $[Cu_2(ophen)_2]$ **7** with $(NH_4)_2S$ [43a]. Compound **7** can easily be obtained in high yield via a hydrothermal in situ reaction as described above [8b]. Besides the Hophen ligand, derivatives of triazoles and tetrazole are also quantitatively accessible via simple treatment of corresponding complexes with HCl acid [12]. In addition, in some special cases, only one of the several isomers of the ligand is found in the crystalline complexes formed during the in situ ligand synthesis reaction; this provides an alternative route for isolation of organic isomers. For example, the 2,2′-oxydisuccinic acid has *R*,*R*-, *S*,*S*- and *meso*-, three kinds of isomers, but only the *meso*-isomer was observed in **25** [16]. The free *meso*-ligand is accessible via simple treatment of **25** with aqueous Na_2S solution. Another example is the in situ cyclisation of bpe producing only a single isomer of tetrapyridyl ligand in **1** [2].

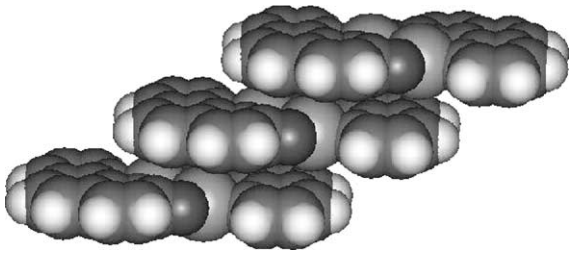


Fig. 25. View of the stacking array of **40**. Generated from CIF data in Ref. [43a].

A series of interesting complexes $[Ag_2(ophen)_2]$ (**40**), $[Hg(ophen)_2]$ (**41**), $[Cd_3Cl(ophen)_5]$ (**42**), $[Zn_4O(ophen)_4(OAc)_2]$ (**43**) has been prepared by using the isolated Hophen ligand [43]. Crystalline **40** was synthesized by the reaction of $AgNO_3$ in MeCN with Hophen in CH_2Cl_2 via the liquid diffusion method. Compound **40** is isostructural with **7**·α (see Fig. 7a and Fig. 25) [43a]. The intramolecular Ag(I)–Ag(I) distance is 2.801(1) Å indicating a very strong Ag–Ag interaction. The offset face-to-face distance between adjacent molecules is ca. 3.15 Å, and the closest Ag–C contact between adjacent molecules is 3.082 Å. Compound **40** is a highly electrical conducting single component molecule material. High conductivity can be attributed to strong π–π stacking interactions and Ag–π interactions.

The solids of **41**–**43** were obtained by reactions of sodium methoxide, Hophen and metal salts in methanol solution [43b]. Complex **41** is mononuclear in which the Hg(II) ion shows a distorted tetrahedral geometry coordinated by four nitrogen atoms from two ophen ligands. Complex **42** is a trinuclear molecule in which each Cd(II) exhibits a distorted octahedral geometry and the ophen ligands exhibit two different bridging modes (Fig. 26a). Complex **43** is a tetranuclear molecule in which each Zn(II) has a distorted square-

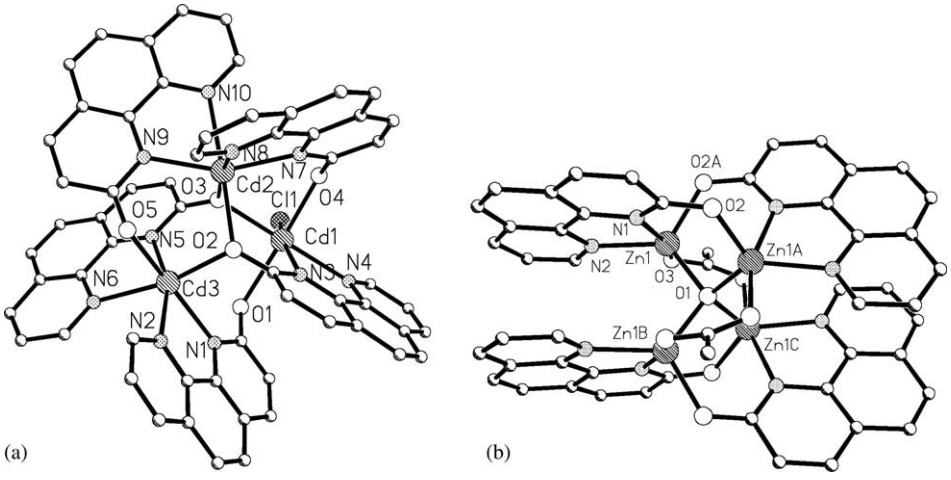
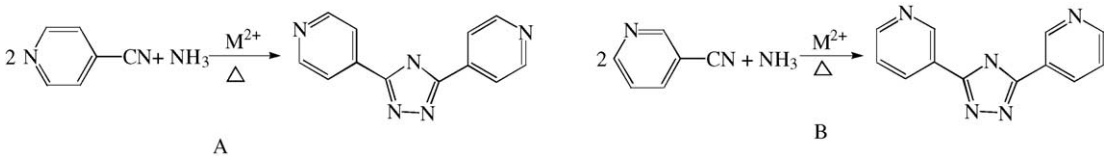


Fig. 26. View of the structures of **42** (a) and **43** (b). Generated from CIF data in Ref. [43b].

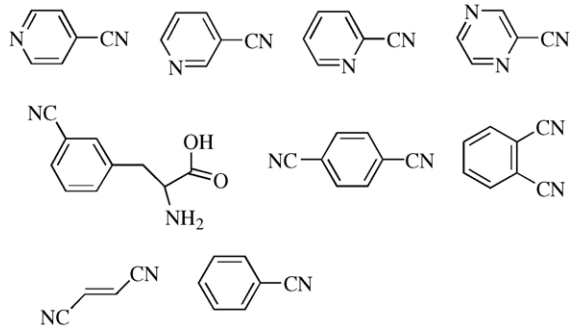


Scheme 23.

pyramidal geometry coordinated by one μ_4-oxo, two ophen nitrogen atoms, one ophen oxygen atom from another ophen, and one acetate oxygen atom (Fig. 26b). All the complexes display photoluminescent properties in the blue/green region. Molecular orbital calculations showed that the photoluminescent properties are ligand-based and can be tuned upon ligation to different metal ions.

4. Rationalization of some in situ ligand synthesis reactions

Considering a variety of hydrothermal parameters such as time, temperature, pH value, stoichiometry and duration, there is difficulty in rationalizing all hydro(solvo)thermal in situ ligand synthesis reactions [31]. However, at least a few types of in situ ligand reaction can be rationalized; these include hydrolysis of ester, cyano and phosphonate ester groups, [2 + 3] cycloaddition of CN groups and azide, [2 + 2 + 1] cycloaddition of nitrile and ammonia, and amination reactions. The ligands can be in situ synthesized by judicious selection of starting materials via corresponding in situ ligand reactions. For example, the hydrothermal in situ hydrolyses of ester, cyano and phosphonate ester groups to become the corresponding carboxylic acids and phosphonic acids are not particular about hydrothermal parameters such metal ions, pH value, stoichiometry and temperature universal, and almost all reagents containing ester, cyano or phosphonate ester groups can be used as precursors for the corresponding carboxylic acid or phosphonic acid [17–24]. However, in order to get single crystals, it is preferable to react at a lower temperature and for a longer time. Tetrazole derivatives can also be rationally synthesized via in situ

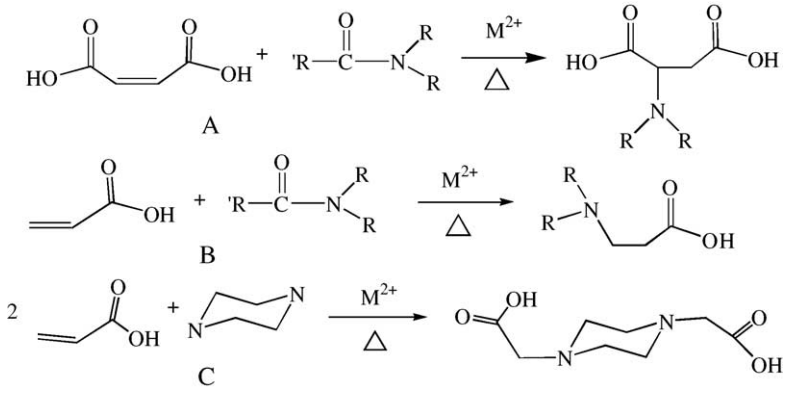


Scheme 22.

[2 + 3] cycloaddition of CN-containing reagents and azide in the 110–160 °C temperature range with molar ratio of nitrile to azide 1:1–1.5. Scheme 22 shows some CN-containing precursors for tetrazoles or bi-tetrazole [12].

Reaction of acetonitrile or butyronitrile with ammonia in the presence of Cu(II) can result in an in situ [2 + 2 + 1] cycloaddition reaction to form 3,5-dimethyl-1,2,4-triazole and 3,5-dipropyl-1,2,4-triazole [13]. This type of in situ [2 + 2 + 1] of nitrile and ammonia cycloaddition to form 3,5-substituted 1,2,4-triazoles can also be used to synthesize new ligands in the presence of Cu(II) ions, and Scheme 23 shows two possible in situ [2 + 2 + 1] cycloaddition reactions of cyanopyridines and azide to form the corresponding 1,2,4-triazole derivatives.

The [2 + 3] cycloaddition of CN and azide to form tetrazoles and [2 + 2 + 1] cycloaddition of CN and ammonia to form triazoles are examples of two types of very useful in situ ligand reactions because so many CN-containing reagents can be chosen as precursors. On the basis of the Gillard mech-



Scheme 24.

anism coordination of the *N*-heterocycle pyridine to the metal ion will activate the carbon adjacent to nitrogen and make it easy to occur hydroxylation or dehydrogenation. Thus, according to the Gillard mechanism [32], we predict that various derivatives of pyridine, 2,2′-bpy and phen are good starting materials for hydroxylation and dehydrogenative coupling reactions.

Another type of predictable in situ ligand reaction is amination, which is also very important due to the availability of many precursors. Considering the in situ reaction of maleic acid in DMF solution to form *N*,*N*-dimethyl-aspartic acid which derives from amination of maleic acid and dimethylamine, other alkene-carboxylates can react with secondary amine/diamine in similar in situ reactions. Scheme 24 shows some possible in situ amination reactions to form amino acid ligands [27].

Other in situ ligand synthesis reactions such as substitution of sulfonate for carboxylate, decarboxylation of arylcarboxylate, intermolecular dehydration coupling and alkylation cannot be rationalized at present. Thus, systematic investigation of the reaction variables should be undertaken to provide mechanistic information.

5. Conclusions

The synthesis of crystalline complexes via in situ ligand reactions has been a rapidly developing area of crystal engineering due to its simplicity, effectiveness, environmentally friendliness and the ease of growing large single crystals [2–30]. The hydro(solvo)thermal method has been demonstrated to be a very promising technique to prepare complexes involving in situ synthesized ligands. Such in situ ligand syntheses are important not only in coordination chemistry but also in organic chemistry. The in situ ligand syntheses are useful to prepare complexes, which are not available from a direct reaction of metal salt and ligands [2–30]. For example, most metal pyridinecarboxylate complexes synthesized via in situ hydrolysis of cyano and ester are not directly accessible from the reaction of metal salt and pyridinecarboxylic acid [17]. In organic synthesis, hydrothermal in situ ligand synthesis has provided powerful pathways to organic ligands that are difficult to obtain by routine synthetic methods [3–5,43]. For example, the novel ligand Hophen which is quite difficult to obtain by routine synthetic methods, can be quantitatively obtained via the simple treatment of complex $[Cu_2(ophen)_2]$ with $(NH_4)_2S$ [43a]. A variety of novel complexes showing interesting optical and electronic properties have been prepared by reaction of metal salts with the isolated Hophen ligand. Furthermore, although some organic ligands exist as several isomers, only one of these isomers may arise from the in situ synthesis of the metal complex, which provides a alternative way to isolate the ligand isomers [2,25]. For example, although 2,2′-oxydisuccinic acid has three isomers, only the *meso*-isomer is included in crystalline **25** [25]. Ligand tpct has two isomers, but in situ [2 + 2] cyclisation of bpe in **1** produced only single isomer [2].

To sum up, great success has been made in the crystal engineering of complexes involving in situ synthesized ligands over the past several years. More than 10 types of in situ ligand reaction have been found and fifty crystalline complexes involving in situ ligand synthesis have been prepared. Attempts to isolate some uncommon organic ligands from in situ synthesized complexes, for example 2,2′-biphen, quaterpy, tpct and H_2dmap, have not yet been performed [3-5,27]. Therefore, in the future, while we focus on discovering new types of hydro(solvo)thermal in situ ligand syntheses, we should extend research in discovered in situ ligand reaction types including syntheses of more complex, mechanistic studies, the isolation of uncommon ligands and searching for new applications.

Acknowledgements

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References

[1] (a) E.C. Constable, Metals and Ligand Reactivity, VCH, Weinheim, 1996;
(b) R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299;
(c) V.Y. Kukushkin, A.J.L. Pombeiro, Chem. Rev. 102 (2002) 1771 (and references therein).
[2] J. Blake, N.R. Champness, S.S.M. Chung, W.-S. Li, M. Schröder, Chem. Commun. (1997) 1675.
[3] C.M. Liu, S. Gao, H.-Z. Kou, Chem. Commun. (2001) 1670.
[4] D.-R. Xiao, Y. Hou, E.-B. Wang, J. Lou, Y.-G. Li, L. Xu, C.-W. Hu, Inorg. Chem. Commun. 7 (2004) 437.
[5] N. Zheng, X. Bu, P. Feng, J. Am. Chem. Soc. 124 (2002) 9688.
[6] O.R. Evans, W. Lin, Cryst. Growth Des. 1 (2001) 9.
[7] Q.-H. Wei, L.-Y. Zhang, G.-Q. Yin, L.-X. Shi, Z.-N. Chen, J. Am. Chem. Soc. 126 (2004) 9940.
[8] (a) X.-M. Zhang, M.-L. Tong, X.-M. Chen, Angew. Chem. Int. Ed. 41 (2002) 1029;
(b) X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, K.-F. Li, Y.-X. Tong, X.-M. Chen, Chem. Eur. J. 8 (2002) 3187.
[9] (a) Y. Yan, C.-D. Wu, C.-Z. Lu, Z. Anorg. Allg. Chem. 629 (2003) 1991;
(b) X. He, C.-Z. Lu, Z. Anorg. Allg. Chem. 630 (2003) 1756.
[10] D.-R. Xiao, Y. Hou, E.-B. Wang, S.-T. Wang, Y.-G. Li, G.-J. De, L. Xu, C.-W. Hu, J. Mol. Struct. 659 (2003) 13.
[11] J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C.L. Lin, X.-Y. Huang, J. Li, Chem. Commun. (2002) 1342.
[12] (a) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z.-L. Xue, Angew. Chem. Int. Ed. 41 (2002) 3800;
(b) X. Xue, X.-S. Wang, L.-Z. Wang, R.-G. Xiong, B.F. Abrahams, X.-Z. You, Z.-L. Xue, C.-M. Che, Inorg. Chem. 41 (2002) 6544;
(c) Z.-R. Qu, H. Zhao, X.-S. Wang, Y.-H. Li, Y.-M. Song, Y.-J. Liu, Q. Ye, R.-G. Xiong, B.F. Abrahams, Z.-L. Xue, X.-Z. You, Inorg. Chem. 42 (2003) 7710;
(d) X. Xue, B.F. Abrahams, R.-G. Xiong, X.-Z. You, Aust. J. Chem. 55 (2002) 495;

(e) L.-Z. Wang, X.-S. Wang, Y.-H. Li, Z.-P. Bai, R.-G. Xiong, M. Xiong, G.-W. Li, Chin. J. Inorg. Chem. 18 (2002) 1191;
(f) L.-Z. Wang, Z.-R. Qu, H. Zhao, X.-S. Wang, R.-G. Xiong, Z.-L. Xue, Inorg. Chem. 42 (2003) 3969.
[13] J.-P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, Angew. Chem. Int. Ed. 43 (2004) 206.
[14] R.-G. Xiong, J. Zhang, Z.-F. Chen, X.-Z. You, C.-M. Che, H.-K. Fun, J. Chem. Soc. Dalton Trans. (2001) 780.
[15] J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin, Y.-H. Wen, J. Am. Chem. Soc. 126 (2004) 7796.
[16] X.-M. Zhang, J.-J. Hou, H.-S. Wu, Dalton Trans. (2004) 3437.
[17] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 756.
[18] (a) O.R. Evans, R.-G. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem. Int. Ed. 38 (1999) 536;
(b) O.R. Evans, Z. Wang, R.-G. Xiong, B.M. Foxman, W. Lin, Inorg. Chem. 38 (1999) 2969;
(c) O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 2705;
(d) W. Lin, L. Ma, O. Evans, Chem. Commun. (2000) 2263;
(e) J. Zhang, W. Lin, Z.-F. Chen, R.-G. Xiong, B.F. Abrahams, H.-K. Fun, Dalton Trans. (2001) 1806.
[19] (a) W. Lin, O.R. Evans, R.-G. Xiong, Z.J. Wang, Am. Chem. Soc. 120 (1998) 13272;
(b) O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 3009;
(c) W. Lin, Z. Wang, L. Ma, J. Am. Chem. Soc. 121 (1999) 11249.
[20] (a) O.R. Evans, Z. Wang, W. Lin, Chem. Commun. (1999) 1903;
(b) O.R. Evans, W. Lin, J. Chem. Soc., Dalton Trans. (2000) 3949.
[21] M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li, S. Kitagawa, Chem. Commun. (2003) 428.
[22] D.-F. Sun, R. Cao, Y.-C. Liang, Q. Shi, W.-P. Su, M.-C. Hong, J. Chem. Soc. Dalton Trans. (2001) 2335.
[23] G.B. Hix, B.M. Kariuki, S. Kitchin, M. Tremayne, Inorg. Chem. 40 (2001) 1477.
[24] (a) X.-M. Zhang, Eur. J. Inorg. Chem. (2004) 544;
(b) X.-M. Zhang, R.-Q. Fang, H.-S. Wu, S.W. Ng, Acta Cryst. E59 (2003) m1149.
[25] X.-M. Zhang, H.-S. Wu, X.-M. Chen, Eur. J. Inorg. Chem. (2003) 2959.
[26] X. Li, R. Cao, D. Sun, Q. Shi, W. Bi, M. Hong, Inorg. Chem. Commun. 6 (2003) 815.
[27] Y.-L. Fu, et al. unpublished results.
[28] (a) X.-X. Hu, J.-Q. Xu, P. Cheng, X.-Y. Chen, X.-B. Cui, J.-F. Song, G.-D. Yang, T.-G. Wang, IInorg. Chem. 43 (2004) 2261;
(b) X.-X. Hu, C.-L. Pan, J.-Q. Xu, X.-B. Cui, G.-D. Yang, T.-G. Wang, Eur. J. Inorg. Chem. (2004) 1566.
[29] F.-C. Liu, L.-Y. Duan, Y.-G. Li, E.-B. Wang, X.-L. Wang, C.-W. Hu, L. Xu, Inorg. Chim. Acta 357 (2004) 1355.
[30] X.-M. Zhang, R.-Q. Fang, unpublished results.
[31] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem. Int. Ed. 38 (1999) 2638.
[32] R.D. Gillard, Coord. Chem. Rev. 16 (1975) 67.
[33] (a) N. Serpone, G. Ponterini, M.A. Jamieson, Coord. Chem. Rev. 50 (1983) 209;
(b) E.C. Constable, Polyhedron 2 (1983) 551.
[34] C.M. Che, Z. Mao, V.M. Miskowski, M.C. Tse, C.K. Chan, K.K. Cheung, D.L. Philips, K.H. Leung, Angew. Chem. Int. Ed. 39 (2000) 4084.
[35] (a) D.D. LeCloux, R. Davydov, S.J. Lippard, J. Am. Chem. Soc. 120 (1998) 6810;
(b) S.M.-F. Lo, S.S.-Y. Chui, L.-Y. Shek, Z.-Y. Lin, X.-X. Zhang, G.-H. Wen, I.D. Williams, J. Am. Chem. Soc. 122 (2000) 6293;
(c) G. Al-Obaidi Baranovic, J. Coyle, C.G. Coates, J.J. McGarvey, V. McKee, J. Nelson, Inorg. Chem. 37 (1998) 3567.
[36] R.N. Butler, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, vol. 4, Pergamon, Oxford, UK, 1996.
[37] (a) H. Singh, A.S. Chawla, V.K. Kapoor, D. Paul, R.K. Malhotra, Prog. Med. Chem. 17 (1980) 151;
(b) V.A. Ostrovskii, M.S. Pevzner, T.P. Kofmna, M.B. Shcherbinin, I.V. Tselinskii, Targets Heterocycl. Syst. 3 (1999) 467;
(c) M. Hiskey, D.E. Chavez, D.L. Naud, S.F. Son, H.L. Berghout, C.A. Bome, Proc. Int. Pyrotech. Semin. 27 (2000) 3.
[38] (a) Z.P. Demko, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2110;
(b) Z.P. Demko, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2113;
(c) Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945.
[39] (a) F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, J. Am. Chem. Soc. 124 (2002) 12210;
(b) F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, J. Am. Chem. Soc. 125 (2003) 9983.
[40] J.G. Haasnoot, Coord. Chem. Rev. 200–202 (2000) 131.
[41] E.N. Gutierrez, M.I. Hill, M. Santoso, D. Wu, S.R. Wu, Lever Brothers Company, USA. U.S. 5391823, 1995.
[42] (a) J. Zhu, X. Bu, P. Feng, G.D. Stucky, J. Am. Chem. Soc. 122 (2000) 11563;
(b) A. Clearfield, Chem. Mater. 10 (1998) 2801.
[43] (a) S.-L. Zheng, J.-P. Zhang, W.-T. Wong, X.-M. Chen, J. Am. Chem. Soc. 125 (2003) 6882;
(b) S.-L. Zheng, J.-P. Zhang, X.-M. Chen, Z.-L. Huang, Z.-Y. Lin, W.-T. Wong, Chem. Eur. J. 9 (2003) 3888.