

Self-assembly of tetrahedral  $M_4L_6$  clusters from a new rigid ligandCheng He,<sup>a</sup> Le-Yong Wang,<sup>b</sup> Zhe-Ming Wang,<sup>a</sup> Yuan Liu,<sup>a</sup> Chun-Sheng Liao<sup>a</sup> and Chun-Hua Yan<sup>\*a</sup><sup>a</sup> State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, Peking University-Nonius B. V. Demo Lab for X-Ray Diffraction, Peking University, Beijing 100871, China. E-mail: chyan@chem.pku.edu.cn<sup>b</sup> State Key Laboratory of Engineering Plastics and the Center for Molecular Sciences, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

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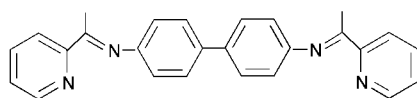
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**Self-assembled tetrahedral  $[M_4L_6]^{8+}$  ( $M = Zn^{2+}$ ,  $Cu^{2+}$ ) clusters were generated from a simply prepared conjugate imine-based ligand with two bidentate binding sites separated by a biphenyl group.**

Construction of supramolecular clusters *via* self-assembly of pre-designed ligands with appropriate metal ions is a subject of current interest because of their ability to selectively encapsulate ions and molecules within inner cavities and catalyze specific chemical transformations.<sup>1</sup> As the simplest platonic polyhedrons, tetrahedral clusters have attracted more attention because of their intrinsic beauty and interesting host-guest chemistry, as well as the fact that they illustrate some basic construction principles necessary to assemble high symmetry clusters.<sup>2-6</sup>

According to the symmetry interaction model, the general approach to construct a tetrahedral  $M_4L_6$  cluster is that four octahedral naked metal ions with three-fold symmetry are assembled with six bis-bidentate ligands of two-fold symmetry.<sup>7</sup> This synthesis strategy might also lead to the formation of  $M_2L_3$  triple helicates with the same metal/ligand ratio. Entropic considerations dictate that if the lower stoichiometry  $M_2L_3$  complex can form, it will.<sup>8</sup> Therefore, the designed ligand used in a  $M_4L_6$  tetrahedron has to be rigid and of suitable geometry.

A few bis-bidentate ligand systems constructed from catechol, hydroxamate, biester and pyrazolylpyridine binding sites have been used to build  $M_4L_6$  tetrahedrons. Imine-based ligands, the typical bidentate ligand system, have the advantage that they can be prepared by a single-step reaction from inexpensive, commercial reagents. They have been successfully used to create various supramolecular architectures.<sup>9</sup> Applying this approach, we introduce herein a new ligand L which contains two pyridylimine bidentate binding sites separated by a central spacer (Scheme 1).<sup>†</sup> It is suggested that the chosen



Scheme 1 Ligand L.

biphenyl spacer introduces enhanced rigidity into the ligand backbone to favor the formation of a  $M_4L_6$  tetrahedron, and the two phenylene rings can also sterically prevent the two binding sites from coordinating to a single metal center.

Interaction of 3 equiv. of ligand L and 2 equiv. of zinc(II) salt in methanol at room temperature for one hour led to the formation of a yellow solution from which complex  $[Zn_4L_6][ClO_4]_8$  was isolated in high yield (>80%) on addition of methanolic  $LiClO_4$ .<sup>†</sup> The ESI-MS in acetonitrile-methanol solution reveals the presence of  $[Zn_4L_6]^{8+}$  with varying numbers of associated  $[ClO_4]^-$  anions. The peaks at  $m/z$  386, 467, 580 and 751 correspond to  $[(Zn_4L_6)(ClO_4)_n]^{8-m+}$  ( $n = 1, 2, 3, 4$ ),

respectively, indicating that  $[Zn_4L_6]^{8+}$  is the most stable fragment in solution.

Recrystallization of complex 1 from acetonitrile by diethyl ether diffusion afforded X-ray quality crystals. The complex crystallized in the trigonal space group  $P3$  with three one-third of cations and associated anions in the asymmetric unit.<sup>‡</sup> The crystal structure of 1 showed that it is an idealized  $T$  symmetry tetrahedral complex (Fig. 1) in which each Zn ion occupies the

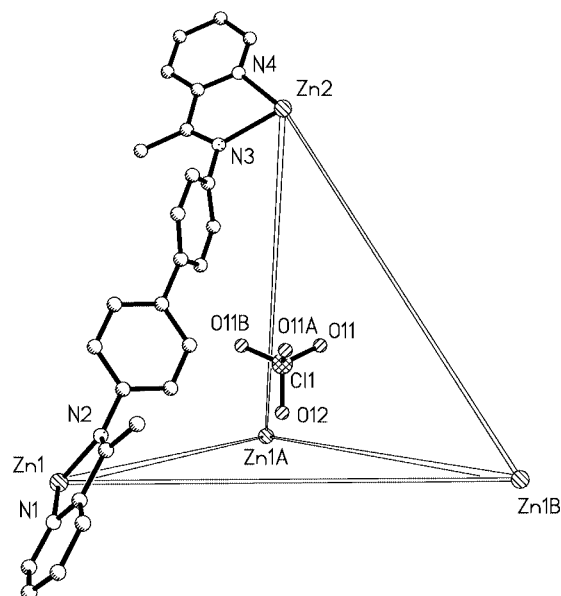
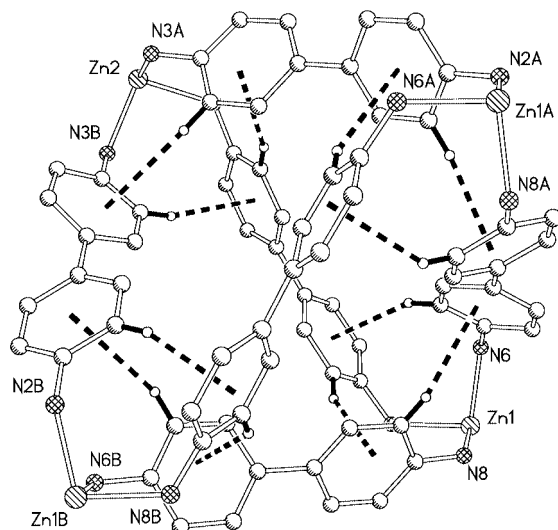


Fig. 1 Perspective view of 1, showing the tetrahedral shape of the cation and the disposition of the trapped  $ClO_4^-$  anion. Symmetry codes: A  $1 - y, x - y - 1, z$ ; B  $2 - x + y, 1 - x, z$ .

vertex with  $Zn \cdots Zn$  separations in the range of 12.62–12.81 Å, and each ligand, acting as a bridge between two metal ions, spans one edge of the tetrahedron. Each Zn ion is therefore pseudo-octahedrally coordinated by a bidentate pyridylimine binding unit arm from each of three separate ligands in a *fac* configuration, with the  $Zn-N$  distances in the range of 2.13–2.22 Å. One of the associated  $ClO_4^-$  anions is trapped in the tetrahedral cavity, and each oxygen atom of the  $ClO_4^-$  anion is directed towards the center of a triangular face of the  $Zn_4$  tetrahedron. No coordinative or hydrogen-bonding interaction exists between the tetrahedral cation and its trapped anion, it is postulated that the association should derive from a good size match between the guest and the cavity of the host, and favorable electrostatic effects. The tetrahedral cation has  $C_3$  symmetry, as shown in Fig. 1, with the  $Zn_2$ ,  $Cl_1$  and  $O_{12}$  atoms located on the three-fold axis.

It is interesting to find that there is a circular  $C-H \cdots \pi$  interaction between the three phenyl rings from different ligands



**Fig. 2** View of the C–H  $\cdots$   $\pi$  interactions within the tetrahedron, the pyridine rings, methyl groups and hydrogen atoms not involved in the interaction were omitted for clarity. Symmetry codes: A  $1 - y, x - y - 1, z$ ; B  $2 - x + y, 1 - x, z$ .

near one metal vertex (Fig. 2). The distances between the centroid of the phenyl ring and the interacting C atom are in the range of 3.49–3.91 Å, (H  $\cdots$  centroid 2.56–2.97 Å, C–H  $\cdots$  centroid 147–165°), and the inter-plane angle is from 50 to 71°. These distances are compared to those found in the crystal structure of benzene (3.78 Å and 85°), revealing the existence of C–H  $\cdots$   $\pi$  interactions.<sup>10</sup> The effect of the weak interaction between the ligands is suggested to help stabilize the tetrahedral structure.

To further investigate this new approach for assembling a tetrahedron, we treated L with Cu(II) ion using the same method as for the preparation of **1**. The dark green  $[\text{Cu}_4\text{L}_6][\text{ClO}_4]_8$  **2** was obtained by treatment of the solution containing  $\text{Cu}(\text{NO}_3)_2$  and L with  $\text{LiClO}_4$ . ESI-MS is consistent with the formulation of  $[(\text{Cu}_4\text{L}_6)(\text{ClO}_4)_n]^{(8-n)+}$  ( $n = 0, 1, 2, 3, 4$ ). The crystallographic study has revealed that the structure of **2** is analogous to the Zn complex with the same space group and similar cell parameters.† The circular C–H  $\cdots$   $\pi$  interactions also exist between the ligands within each cation. Both of the crystalline complexes were obtained in high yield and all of the crystals have the same habit and appearance. There is no evidence for a mixture of products in the solid state.

Following the established design strategy, we have introduced a new easy-to-prepare ligand to generate a  $\text{M}_4\text{L}_6$  tetrahedral cluster by placing a spacer between the bidentate binding sites. This self-assembled nano-structure shows potential for broadening the scope of further work in the self-assembly of high symmetry clusters. We are currently extending our studies to apply design rationale presented here within more sophisticated supermolecular clusters of different sizes, symmetries and stoichiometries.

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## Notes and references

† Preparation of L: 4,4'-diaminobiphenyl (1.52 g, 8.2 mmol) and 2-acetylpyridine (2.49 g, 21 mmol) were refluxed in 100 ml toluene with 0.2 g *p*-toluenesulfonic acid for 48 h. The solvent was reduced to about 20 ml and 20 ml ethanol was added. After cooling to 0 °C, the yellow precipitate (1.69 g, 4.3 mmol, yield 52.5%) was isolated, washed with

ethanol and dried under vacuum.  $\text{C}_{26}\text{H}_{22}\text{N}_4$ : Calc.: C, 80.0; N, 14.4; H, 5.7. Found: C, 79.6; N, 14.1; H, 5.6%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.70 (2H, d, py), 8.24 (2H, d, NH), 7.94 (2H, t, py), 7.73 (4H, d, Ph), 7.55 (4H, t, py), 6.96 (4H, d, Ph), 2.34 (6H, s,  $\text{CH}_3$ ).

Elemental analysis for  $[\text{Zn}_4\text{L}_6][\text{ClO}_4]_8$ :  $\text{Zn}_4\text{C}_{156}\text{N}_{24}\text{H}_{132}\text{Cl}_8\text{O}_{32}$ : Calc.: C, 55.1; N, 9.9; H, 3.9. Found: C, 54.9; N, 9.8; H, 4.0%. For  $[\text{Cu}_4\text{L}_6][\text{ClO}_4]_8$ :  $\text{Cu}_4\text{C}_{156}\text{N}_{24}\text{H}_{132}\text{Cl}_8\text{O}_{32}$ : Calc.: C, 55.2; N, 9.9; H, 3.9. Found: C, 54.8; N, 9.7; H, 4.1%.

‡ Crystallographic data for **1**:  $\text{C}_{168}\text{H}_{161.67}\text{Cl}_8\text{N}_{28}\text{O}_{36.33}\text{Zn}_4$ :  $M = 3699.33$ , trigonal, space group  $P3$ ,  $a = 29.2594(5)$ ,  $c = 19.9252(2)$  Å,  $V = 14772.8$  (4) Å<sup>3</sup>,  $T = 180$  K,  $Z = 3$ ,  $\mu(\text{Mo-K}\alpha) = 0.663$  mm<sup>-1</sup>, 122448 reflections measured, 33081 unique ( $R_{\text{int}} = 0.056$ ). Refinement of 2131 parameters with 333 restraints gave  $R1 = 0.0698$ ,  $wR2$  (all data) = 0.2033. CCDC reference number 170988.

For **2**:  $\text{C}_{169.33}\text{H}_{163.33}\text{Cl}_8\text{Cu}_4\text{N}_{26}\text{O}_{37.33}$ :  $M = 3697.69$ , trigonal, space group  $P3$ ,  $a = 29.2162(5)$ ,  $c = 19.9678(4)$  Å,  $V = 14760.7$  (5) Å<sup>3</sup>,  $T = 180$  K,  $Z = 3$ ,  $\mu(\text{Mo-K}\alpha) = 0.608$  mm<sup>-1</sup>, 132522 reflections measured, 34393 unique ( $R_{\text{int}} = 0.112$ ). Refinement of 2198 parameters with 421 restraints gave  $R1 = 0.0844$ ,  $wR2$  (all data) = 0.2365.

Intensity data were collected on a Nonius Kappa CCD diffractometer. Both structures were solved by direct methods, and refined by full-matrix least-squares on  $F^2$ , using the SHELX-97 package.<sup>11</sup> To assist the refinement, several restraints were applied in both **1** and **2**: (1) several perchlorate anions were disordered and refined as idealized tetrahedra with Cl  $\cdots$  O distances fixed at 1.43(1) Å, and O  $\cdots$  O separations fixed at 2.32(2) Å, and (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar. CCDC reference number 170989. See <http://www.rsc.org/suppdata/dt/b1/b110200a/> for crystallographic data in CIF or other electronic format.

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