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PAPER

Distinguishable Zn(II) and Pb(II) template effects on forming pendant-armed Schiff-base macrocyclic complexes including a remarkable Pb(II)–π macrocyclic complex

Cite this: DOI: 10.1039/x0xx00000x

Received 00th June 2014,
Accepted 00th 2014

DOI: 10.1039/x0xx00000x

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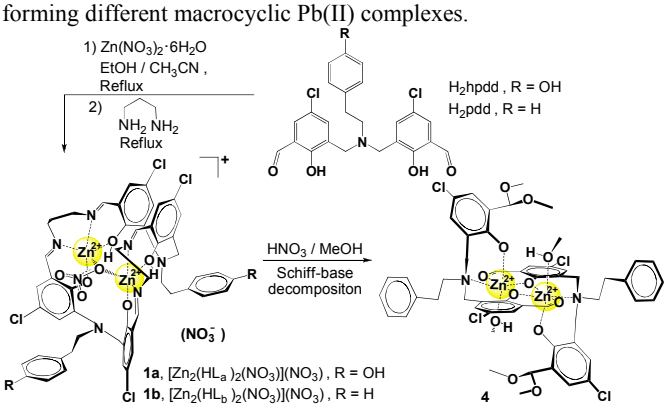
36-Membered [2+2] half-fold Schiff-base macrocyclic dinuclear Zn(II) complexes (**1a** and **1b**) and 18-membered [1+1] Schiff-base macrocyclic mononuclear Pb(II) complexes (**2** and **3**) are produced from the condensation between 1,3-propanediamine and a pair of extended dialdehydes with different functional pendant arms (H_2hpdd and H_2pdd) because of the distinguishing cationic template effects. It is very interesting to mention that a unique intramolecular Pb(II)–π macrocyclic complex **2** with an uncommon η^3-coordinated type is achieved under ambient condition and it can keep stable both in the solid state and in solution. The subtle variations of pendant-arms in the macrocyclic ligands H_2hpdd and H_2pdd yield different Pb(II) complexes, where the competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms is believed to play important roles.

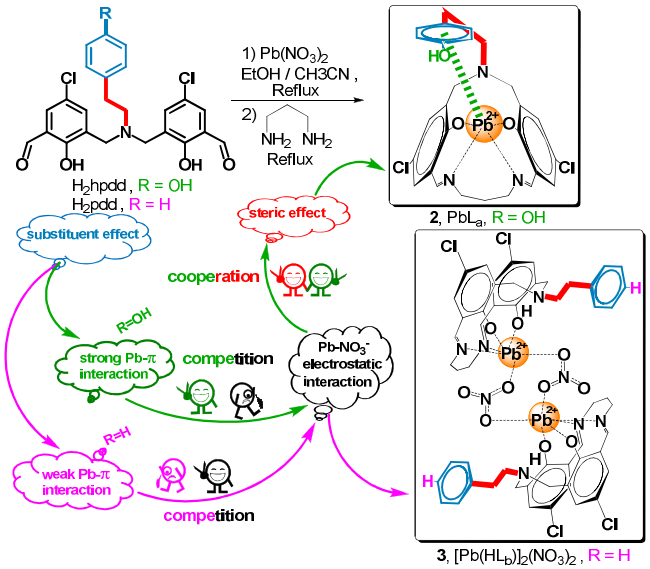
Introduction

As one of the most important fields in macrocyclic and supramolecular chemistry, Schiff-base macrocycles have been widely and deeply studied involving relative syntheses, characterizations, properties and applications.[1] But so far, it is still a challenge to synthesize a new Schiff-base macrocycle for the complexity of multiple Schiff-base condensation between the dicarbonyl compounds and diamines. During the past four decades, considerable efforts have been made to develop metal-free and metal-template[2] methods for imagined macrocycles. Commonly, the strategy of metal-template method is more effective to cyclise, and this method could control the size of Schiff-base macrocycles by different metal template ions. The reason is the final macrocyclic ligands should match the size, charge and optimal coordination geometry of the metal template ion.

Our continuous interest in the Schiff-base macrocycles[3] leads us to explore the construction of Schiff-base macrocycles with alterable size by using the same dialdehydes and diamines but different metal template ion. In this work, two flexible extended dialdehydes (H_2hpdd and H_2pdd) with different functional pendant arms (-CH_2CH_2PhOH and -CH_2CH_2Ph)[3d] as well as 1,3-propanediamine have been used to build metallomacrocycles with alterable size in the presence of suitable metal template ions. As a result, two 36-membered [2+2] half-fold macrocyclic dinuclear Zn(II) complexes **1a** and **1b** (Scheme 1) and two 18-membered [1+1] macrocyclic mononuclear Pb(II) complexes **2** and **3** (Scheme 2) are produced, respectively, because of the distinguishing Zn(II) and Pb(II) metal template effects, which are different from the formation of identical [2+2] dinuclear Zn(II) and Pb(II) macrocyclic complexes by using 2,6-difromay-4-chlorophenol as a dialdehyde precursor.[3a,4c] At the same time, it is worthwhile to mention that a unique Pb(II)–π interaction is observed under ambient condition, where the subtle variations of pendant-arms of macrocyclic ligands yield different products. The competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms are believed to play vital roles in forming different macrocyclic Pb(II) complexes.



Scheme 1. Synthetic route for the 36-membered [2+2] half-fold Schiff-base macrocyclic dinuclear Zn(II) complexes **1a** and **1b** as well as the dinuclear Zn(II) decomposition product **4**.



Scheme 2. Schematic illustration for the competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms in forming distinguishable 18-membered [1+1] macrocyclic mononuclear Pb(II) complexes.

Further pH stability investigations reveal that Pb(II) macrocyclic complexes can keep stable in the pH range of 5~8. In contrast, Zn(II) macrocyclic complexes underwent Schiff-base decomposition by adding either acid or base. As a result, a dinuclear Zn(II) decomposition complex **4** was obtained in the acidic condition (pH = 3~4) after the addition of 0.05 mol/L^{-1} HNO_3 into the methanol solution of Zn(II) macrocyclic complex **1b** (Scheme 1), where a dimethylacetalization reaction occurred for half of the aldehyde groups of pdd divalent anions.

Results and discussion

Syntheses

In the synthesis of Schiff-base macrocyclic metal complexes, metal template effects are critical. In this respect, the importance of metal template ions is reflected in directing the course of multiple Schiff-base condensation to macrocycles and increasing the yields of macrocyclic products. As is reported, all the Schiff-base condensation between 2,6-difromay-4-substituted phenol and 1,3-propanediamine in the presence of many transition-metal ions (Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Pd) produces [2+2] macrocyclic dinuclear complexes.[4] The same type of ultimate metal macrocyclic products is due to the compromise between the size, charge and coordination geometry of metal template ions together with the flexibility of macrocyclic skeleton. However, our results in this work demonstrate that the treatment of extended dialdehydes (H_2hpdd and H_2pdd) and 1,3-propanediamine in the presence of $Zn(NO_3)_2{\cdot}6H_2O$ and $Pb(NO_3)_2$ will yield distinguishable 36-membered [2+2] half-fold macrocyclic dinuclear Zn(II) complexes (Scheme 1) and 18-membered [1+1] macrocyclic mononuclear Pb(II) complexes (Scheme 2), respectively. Namely, the difference of Zn(II) and Pb(II) template effects is still expressed on forming flexible Schiff-base macrocyclic skeleton based on flexible dialdehyde and diamine.

It should be pointed out that all the Schiff-base macrocyclic Zn(II) and Pb(II) complexes in this paper are obtained in weak acidic condition with pH value about 5~6. Finally, half of the phenolic protons are removed in dinuclear Zn(II) complexes **1a** and **1b** and [1+1] Pb(II) complex **3**. However, all the phenolic protons are removed with regard to the [1+1] Pb(II)–π complex **2**. Considering that different amounts of phenolic protons are present in these macrocyclic complexes, pH stability investigations have been carried out by adding 0.05 mol/L^{-1} HNO_3 and NaOH before and after the formation of metallomacrocycles, respectively. Our results indicate that no macrocyclic compounds could be yielded if acid or base was added before the Schiff-base condensation. When complexes **1**–**3** were treated with acid or base, two Zn(II) complexes decomposed quickly accompanied by the appearance of precipitates, and a dinuclear Zn(II) complex **4** was obtained in the acidic condition after the addition of 0.05 mol/L^{-1} HNO_3 into the methanol solution of Zn(II) macrocyclic complex **1b**. However, two Pb(II) complexes are found to be stable in the pH range of 5~8, and precipitates will also be formed outside this pH range.

Interestingly, a unique Pb(II)–π macrocyclic complex is achieved under ambient condition, where the subtle variations of pendant-arms of macrocyclic ligands yield different products of **2** and **3**, as illustrated in Scheme 2. The competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms is believed to play vital roles in forming different macrocyclic Pb(II) complexes.

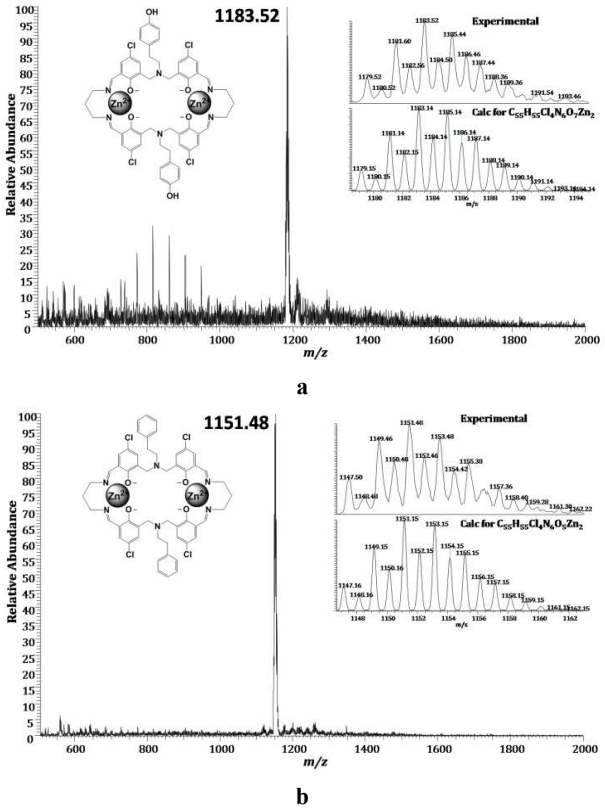


Figure 1. Positive ESI–MS of 36-membered [2+2] macrocyclic dinuclear Zn(II) complexes **1a** (**a**) and **1b** (**b**) obtained in the positive

mode, together with the experimental and calculated IDPs (Inset) corresponding to the peak at 100% abundance for comparison.

Spectral Characterizations

Relative spectral analyses are used to monitor this type of Schiff-base cyclization. From previous work,[3d] it is known that the FT-IR absorption peak of aldehyde groups is found to be 1660 and 1664 cm^{-1} in H_2hpdd and H_2pdd, respectively. In contrast, a new absorption peak is observed at 1639 and 1632 cm^{-1} in **1a** and **1b** and 1634 cm^{-1} in **2** and **3** replacing the peak of aldehyde groups, indicative of the formation of C=N Schiff-base units. From the ESI–MS spectra of **1a** and **1b**, the formation of 36-membered [2+2] macrocyclic dinuclear Zn(II) complexes can be proven by a positive peak at *m/z* = 1183.52 and 1151.48 (Figure 1), respectively, corresponding to the species of $\{[Zn_2(L_a)_2]+CH_3OH+H\}^+$ and $\{[Zn_2(L_b)_2]+CH_3OH+H\}^+$, which agrees well with the theoretic simulations.

Furthermore, ^{1}H NMR spectral characterization have been carried out to explore the variations of chemical shifts between dialdehydes precursors and their relative Zn(II) and Pb(II) macrocyclic complexes. New peaks are observed at 7.93 ppm in **1a** (CD_3OD), 7.97~8.24 ppm in **1b** (CD_3CN), and 8.18 ppm in **2** and **3** (CD_3OD), assigned as the formation of imine units. In order to further explore the Pb(II)–π interactions in solution, the comparisons among the ^{1}H NMR spectra have been carried out for H_2hpdd, H_2pdd, and their respective Pb(II) complexes **2** and **3** in CD_3OD. As displayed in Figure 2, the aromatic protons of two *p*-Cl-phenol rings in **2** and **3** are shifted to the higher field (the green ones), mainly because the deprotonation and subsequent increase of electron density are overwhelming compared with the Pb(II) ion complexation induced deshielding effects. It is noted that three pairs of protons are found to have the same δ values in **2** and **3**, i.e., 8.18 ppm (7 and 11) for the Schiff-base units and 7.08 ppm (5 and 13) and 6.97 ppm (3 and 15) for the two *p*-Cl-phenol hydrogen atoms, indicative of the formation of the same macrocyclic backbone.

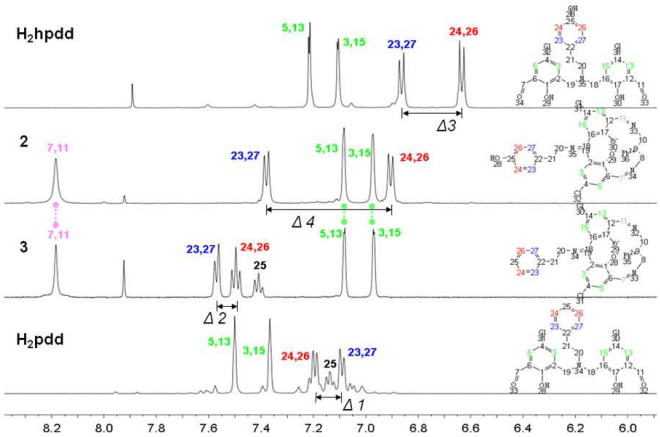


Figure 2. ^{1}H NMR spectral comparisons of extended dialdehydes and their [1+1] macrocyclic Pb(II) complexes **2** and **3** in the low field in CD_3OD, together with the assignments for the chemical shifts of protons.

However, the four aromatic protons of the pendant arms in **2** and **3** are significantly shifted to the lower field (*ca.* 0.2-0.5 ppm) after Pb(II) ion complexation, and they can be divided into two groups shown as blue (23 and 27) and red (24 and 26), respectively. Here, a parameter Δ, namely the chemical shift difference for two groups of protons, is defined. By comparing Δ1 (0.10 ppm) and Δ2 (0.07 ppm) in H_2pdd and **3** with Δ3 (0.23 ppm) and Δ4 (0.47 ppm) in H_2hpdd and **2**, as illustrated in Figure 2, it is found that two pairs of aromatic protons in the latter show distinguishable chemical environments after Pb(II) ion complexation, indicating the existence of Pb(II)–π interaction in solution. Furthermore, a large chemical shift difference of Δ4 reveals the formation of afore-mentioned η^3-coordinated mode in **2**, which means that the Pb lone-pair donates to the π^* orbital of the phenolic ring in the pendant arm, mainly the carbon atoms of C25, C26 and C27. In contrast, small Δ values observed in the former pair reveal the absence of Pb(II)–π interaction in solution. So it is concluded that the ^{1}H NMR spectral comparisons before and after metal-ion complexation provide an experimental proof on the stable existence of Pb(II)–π interactions in solution in the case of complex **2**, and a η^3-coordinated mode is detected between the phenolic ring and the Pb(II) center agreeing well with the following structural description.

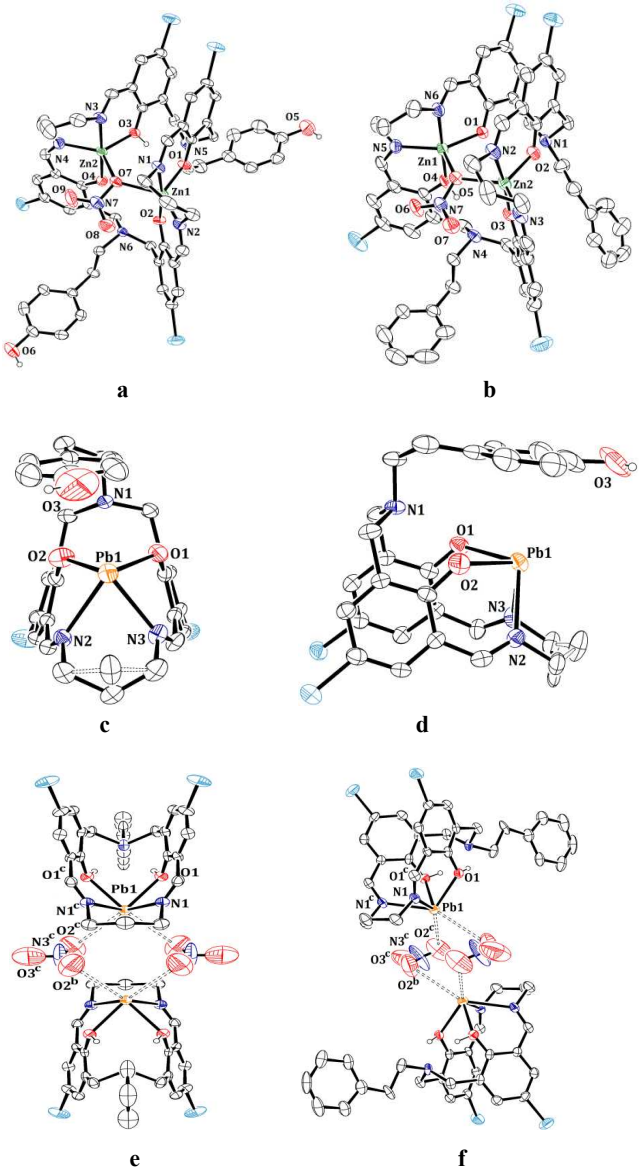


Figure 3. ORTEP drawings of Zn(II) complexes, **1a** (**a**) and **1b** (**b**), and Pb(II) complexes, **2** (**c** and **d**) and **3** (**e** and **f**), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and the phenolic protons are shown as small spheres of arbitrary radii. The counterion, solvent and hydrogen atoms except the phenolic protons are omitted for clarity,

Crystal Structures

Structures of 1a and 1b. The molecule structures of **1a** and **1b** with the atom-numbering scheme are illustrated in Figures 2a and 2b, respectively. They are both 36-membered [2+2] half-fold macrocyclic dinuclear Zn(II) complexes where the coordination configuration for each five-coordinate zinc(II) center in **1a** and **1b** is distorted trigonal bipyramidal (τ = 0.764, 0.842 and 0.981, 0.807 for Zn1 and Zn2 in **1a** and **1b**).[5] There are two nitrate counterions in the asymmetric unit for each Zn(II) complex. One serves as a μ_2 linker where one oxygen atom is found to connect two neighboring Zn(II) ions with a Zn···Zn separation of 3.809(1) Å in **1a** and 3.792(4) Å in **1b**, while the other is free of the formation of coordinative bond. The basal coordination plane of each Zn(II) ion is composed of two oxygen and two nitrogen atoms of macrocyclic ligand as well as one common oxygen atom of the nitrite anion. It is noted that the dihedral angles between the phenol rings of two pendant arms are 6.9(2)º in **1a** and 63.3(2)º in **1b**. As for the half-fold macrocyclic ligands in **1a** and **1b**, the distances between the two *ortho* carbon atoms of each phenolic hydroxyl group for the extended part are 4.983(6) Å in **1a** and 4.952(4) Å **1b**, which are longer than that in the free H_2hpdd ligand (4.333(4) Å). In contrast, the folded units have the corresponding C···C separations of 3.064(6) Å in **1a** and 2.962(4) Å in **1b**. Additionally, intramolecular π-π stacking interactions are observed between two adjacent facing 4-chlorophenol rings with the centroid-to-centroid separations of 3.480(1) Å in **1a** and 3.496(2) and 3.560(2) in **1b**.

Structures of 2 and 3. Different from the 36-membered [2+2] macrocyclic Schiff-base dinuclear compounds for Zn(II) ion template, 18-membered [1+1] macrocyclic mononuclear Pb(II) complexes **2** and **3** are produced for the same reaction when Pb(II) ion template is used. ORTEP drawings of **2** in Figures 2c-2d and **3** in Figures 2e-2f with the atom-numbering scheme are shown, where two oxygen and two nitrogen donors from the macrocyclic framework occupy half of the coordination sphere of Pb(II) ion with the Pb–O and Pb–N bond lengths in the ranges of 2.283(4)–2.330(8) Å and 2.462(5)–2.519(5) Å, respectively. However, it is worthwhile to mention that the subtle variations of pendant-arms (-CH_2CH_2PhOH *vs.* -CH_2CH_2Ph) of macrocyclic ligands yield different products because of the afore-mentioned competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms. As a result, a unique Pb(II)–π complex **2** is formed where the phenolic unit occupies the other half of the coordination sphere of central Pb(II) ion. In contrast, two NO_3^- anions act as μ_2 bridges linking adjacent two mononuclear Pb(II) units by weak Pb–O coordinative bonds, where two oxygen atoms of each NO_3^- anion are coordinated to the Pb(II) centers with the same bond length of 3.291(14) Å forming another dinuclear Pb(II) complex **3** mainly predominated by the Pb(II)–NO_3^- electrostatic interactions.

The phenolic and phenyl rings of pendant arms in the macrocyclic ligands are found to point to different directions in **2** and **3** due to the presence and absence of Pb(II)–π interactions, and the related torsion angles (two alkyl carbon and two phenyl carbon atoms in the pendant arms) are 150.6(8)º in **2** and 0.0(3)º in **3**, respectively. In addition, intramolecular π-π stacking interactions are observed between two facing 4-chlorophenol rings with the centroid-to-centroid separations of 3.767(11) Å in **2** and 3.916(11) Å in **3**, where the bite angles between the two 4-chlorophenol rings are 30.6(3)º in **2** and 34.4(3)º in **3**.

The Pb–π interactions have been systematically summarized by Tiekink and Zukerman-Schpector in 2010,[6c] where 29 known examples having at least one aryl ring are involved. They proposed two geometric parameters: one is the distance (d) between the centroid of the aryl ring and the lead center, and the other is the angle (α) defined by the vector perpendicular to the aryl ring (V_1) and the vector passing through the ring centroid to the lead atom (V_2), as described in Figure 5. They concluded that a Pb(II)–π interaction should be considered as existence commonly if d < 4.0 Å and α < 20º, and most of them fall within the ranges of 2.78 < d < 3.97 Å and 0.6 < α < 19.4º. In our case, the two values are d = 3.549(1) Å and α = 14.7(4)º, which means that the Pb(II)–π interaction does exist and it is a much weak one.

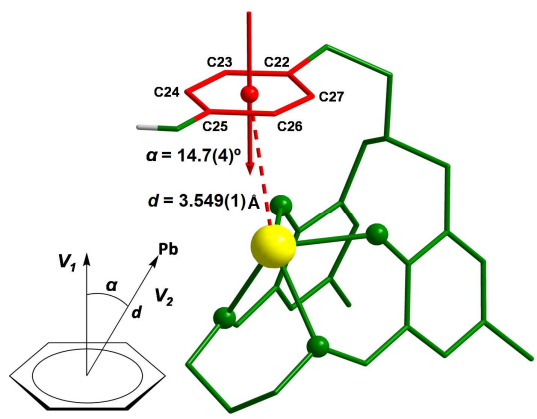


Figure 4. Illustration of the Pb(II)–π interaction in complex **2** defined by two geometric parameters.

Further investigations on six Pb–C bond lengths in complex **2** indicate that they span a wide range from 3.468(10) to 4.102(8) Å, which is not a common η^6-coordinated mode. Instead, they adopt an intramolecular η^3-coordinated type where the three Pb–C (C25–C27) bond lengths are 3.708(10), 3.468(10), and 3.578(8) Å. In contrast, the other three Pb–C (C22–C24) bond lengths are much longer in the range of 3.946(7)–4.102(8) Å. This η^3-coordinated type for the Pb(II)–π interaction observed in the solid state agrees well with the afore-mentioned ^{1}H NMR spectral results in solution.

Why we think this Pb(II)–π macrocyclic complex **2** is structurally unique? Firstly, it provides a nice small molecular model compound containing the intramolecular Pb(II)–π interaction. As a non-covalent bonding interaction, Pb–π interaction is generally recognized as a supramolecular contact. A detailed analysis for Pb(II)–π interactions by checking CCDC database shows that such a supramolecular interaction is not unusual.[6] However, most of them are related to the intermolecular Pb(II)–π interactions within the supramolecular aggregates. In contrast, very few examples of Pb(II)–π interactions are involved in the synthetic small molecules to date.[6a] Obviously, intramolecular Pb(II)–π interaction between a neutral Pb(II) center

capped by a [1+1] macrocyclic ligand and its adjunctive phenol ring in complex **2** gives such a small molecular instance for further synthetic and theoretical investigations. In addition, complex **2** is stable in solution, which can be proven by the ^{1}H NMR experiments. This phenomenon is different from the intermolecular Pb(II)–π complexes since solvation in solution usually leads to extensive disintegration of the molecular or multidimensional aggregates into the solvated components.[6b]

Secondly, study on the electron effects of the aromatic rings for Pb(II)–π interaction is realized once again by introducing different functional pendant arms. In general, Pb(II)–π interactions should be stronger and more prevalent if the electron density of the aromatic rings is increased, which may originate from the nature as donation of π electrons from the aromatic ring to vacant orbital of the Pb center.[6b] In our case, the only difference between complexes **2** and **3** is the substituted groups in the pendant arms (-CH_2CH_2PhOH *vs.* -CH_2CH_2Ph). The former arm has higher electron density, which favors to form the Pb(II)–π complex. Fortunately, the single-crystal structures of Pb(II) complexes **2** and **3** have been obtained, clearly supporting the afore-mentioned viewpoint. The Pb(II)–π macrocyclic complex **2** adopts an extraordinary η^3-coordinated type. In contrast, most of reported Pb(II)–π interactions are described as the η^6-coordinated type in literature.[6b,6c] Nevertheless, the formation of intramolecular Pb(II)–π interaction in complex **2** is greatly restricted by the spatial crowding effects of two methane units in the pendant arm and the skeleton of macrocyclic ligand. So the final η^3-coordinated type is suggested to be a cooperative result of steric effect and Pb(II)–π interaction, which could be further verified by the following ^{1}H NMR spectral and single-crystal structural investigations.

Thirdly, visual examples of Pb(II) macrocyclic complexes **2** and **3** are presented embodying the important role of anions. With regard to the factors involved in the formation of metal ion-aromatic complexes, Amma *et al.* proposed that the presence of a strong acid anion is vital in order to decrease the anion-cation binding, which will allow the appearance of metal–π interaction.[6m] Herein NO_3^- is used as a counterion and the competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions is experimentally verified, where the Pb(II)–π interaction overwhelms the Pb(II)–NO_3^- electrostatic interaction in **2** and it is just the opposite in **3**. As a result, an intramolecular Pb(II)–π complex **2** against a dimer nitrate-bridged dinuclear Pb(II) complex **3** are obtained.

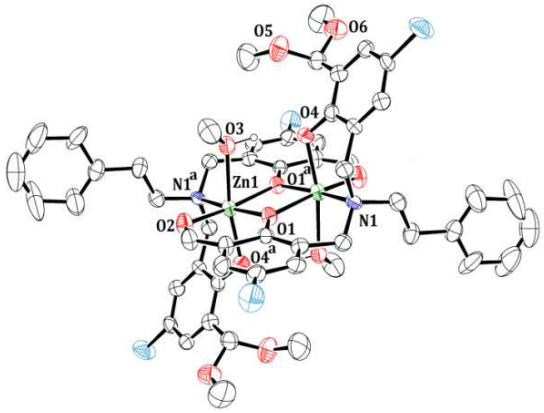


Figure 5. ORTEP drawing of Zn(II) complex **4** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and all hydrogen atoms are omitted except the protons of coordinated methanol molecules.

Structure of 4. X-ray structural analysis of dinuclear Zn(II) intermediate **4** reveals that it is only composed of two pendant-armed dialdehyde components and two Zn(II) ions, where diamine units are removed because of the protonation of nitrogen atoms (Figure 5). The coordination geometry for each Zn(II) centre is a distorted six-coordinate octahedron. However, half of the aldehyde groups underwent a dimethylacetalization reaction with solvent methanol molecules. The resultant divalent anions act as a tetradentate ligand where two phenolic oxygen atoms, one aldehyde oxygen atom and the tertiary nitrogen atom are coordinated to the central Zn(II) ions. Two μ_2 phenolic oxygen atoms from each dialdehyde unit are found to link adjacent two Zn(II) ions, and the separation between them is 3.202(2) Å. In addition, two methanol molecules are coordinated to each Zn(II) ion to fill the rest of coordination sphere. The dihedral angles between the pendant-armed phenol ring and two salicylaldehyde rings in **4** are 71.8(5) and 80.9(4)°, respectively.

Conclusion

In summary, 1,3-propanediamine is used to react with a pair of flexible extended dialdehydes with different functional pendant arms for Schiff-base macrocyclic complexes in the presence of Zn(II) and Pb(II) ion templates for comparison. As a result, 36-membered [2+2] half-fold macrocyclic dinuclear Zn(II) complexes (**1a** and **1b**) and 18-membered [1+1] macrocyclic mononuclear Pb(II) complexes (**2** and **3**) are produced, respectively, because of the distinguishing cationic template effects. FT–IR, ESI–MS and ^{1}H NMR spectral and single-crystal structural methods are used to characterize their molecular structures.

It is very interesting to mention that a remarkable intramolecular Pb(II)–π interaction is found in macrocyclic complex **2** with an uncommon η^3-coordinated type is achieved under ambient condition, and it can keep stable both in the solid state and in solution, which can be clearly verified by its X-ray single-crystal structure and ^{1}H NMR spectrum, in comparison with a similar Pb(II) macrocyclic complex **3** without the Pb(II)–π interactions. In this case, the subtle variations of pendant-arms in the macrocyclic ligands H_2hpdd and H_2pdd yield different Pb(II) complexes **2** and **3**, where the competition between Pb(II)–π and Pb(II)–NO_3^- electrostatic interactions as well as the combination of steric and electronic effects of pendant arms is believed to play vital roles. It is believed that the current study is a combination investigation on macrocyclic and organometallic chemistry and it can provide some useful information on the design, preparation and properties of new kinds of metal ion-aromatic macrocyclic complexes.

Experimental Section

Materials and Methods

Unless otherwise specified, solvent of analytical grade were purchased directly from commercial sources and used without any further purification. The extended dialdehydes H_2hpdd and H_2pdd are prepared as the reported literature.[3d]

^{1}H and ^{13}C NMR spectra spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS

($SiMe_4$) as an internal reference at room temperature. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm^{-1}) were collected on a Nicolet FT–IR 170X spectrophotometer at 25°C using KBr plates. Electrospray ionization mass spectra (ESI–MS) were recorded by a ThermoFisher Scientific LCQ Fleet mass spectrometer in a scan range of 100-2000 amu.

Preparation of Metal Complexes

Synthesis of 1a. $Zn(NO_3)_2{\cdot}6H_2O$ (0.033 g, 0.11 mmol) was dissolved in ethanol (10 mL) and added to a solution of H_2hpdd (0.048 g, 0.10 mmol) in hot ethanol (20 mL). The mixture was refluxed for 10 min, and an ethanol (10 mL) solution of 1,3-propanediamine (0.009 g, 0.1 mmol) was added. The yellow-green solution was refluxed for additional 2 h, cooled to room temperature and filtered. The filtrate was concentrated to give **1a** in a yield of 70 % (0.044 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.28~8.25 (m, 2H), 7.97 (s, 2H), 7.92 (s, 4H), 7.13~7.10 (m, 4H), 6.89~6.86 (m, 4H), 6.61 (d, J = 7.5 Hz, 4H), 3.96 (s, 8H), 3.92 (s, 8H), 3.52 (dd, J = 13.9 and 7.7 Hz, 8H), 0.92 (d, J = 6.9 Hz, 4H). *Anal.* Calc. for $C_{53}H_{50}Cl_4N_8O_{12}Zn_2$: C, 50.38; H, 3.99; N, 8.87 %. Found: C, 50.20; H, 3.90; N, 8.97 %. ESI–MS (positive mode, *m/z*): 1183.08 $[M+CH_3OH+H]^+$. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3434, 2927, 1639 (s, -CH=N), 1549, 1450, 1386, 1153, 763. Light yellow-green single crystals of the solvate complex **1a**$\cdot C_2H_5OH$ were grown from a mixture of ethanol/acetonitrile (*v/v* = 2:1) by slow evaporation in air at room temperature.

Synthesis of 1b. The synthetic process of **1b** is the same as that of **1a** except that H_2pdd (0.047 g, 0.10 mmol) was used. Yield: 0.055 g, (89 %). ^{1}H NMR (500 MHz, CD_3CN): δ 8.24 (s, 1H), 8.18 (s, 1H), 7.99 (s, 1H), 7.97 (s, 1H), 7.41 (s, 1H), 7.36 (s, 2H), 7.32 (s, 1H), 7.29 (s, 2H), 7.26 (d, J = 4.6 Hz, 4H), 7.20 (d, J = 7.6 Hz, 1H), 7.15 (s, 3H), 7.01 (d, J = 7.3 Hz, 1H), 6.93 (s, 3H), 6.89 (s, 1H), 4.60 (d, J = 12.7 Hz, 2H), 4.20 (d, J = 12.2 Hz, 2H), 4.14~4.00 (m, 4H), 3.91 (d, J = 12.9 Hz, 1H), 3.72 (dd, J = 21.2 and 8.6 Hz, 4H), 3.62~3.50 (m, 4H), 3.46 (dd, J = 12.0 and 5.9 Hz, 4H), 3.37 (d, J = 12.8 Hz, 1H), 3.22 (d, J = 11.5 Hz, 2H), 2.60 (s, 1H), 2.47 (s, 3H). *Anal*. Calc. for $C_{53}H_{50}Cl_4N_8O_{10}Zn_2$: C, 51.68; H, 4.09; N, 9.10 %. Found: C, 51.80; H, 3.93; N, 9.01 %. ESI–MS (positive mode, *m/z*): 1151.48 $[M+CH_3OH+H]^+$. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3450, 2929, 1632 (s, -CH=N), 1555, 1453, 1385, 776, 700. Light yellow-green single crystals of the solvate complex **1b**$\cdot CH_3OH$ were obtained from a mixture of methanol/acetonitrile (*v/v* = 10:1) by slow evaporation in air at room temperature.

Synthesis of 2. Anhydrous $Pb(NO_3)_2$ (0.036 g, 0.11 mmol) was dissolved in methanol (15 mL) and added to a solution of H_2hpdd (0.047 g, 0.10 mmol) in 15 mL hot methanol. After 10 min reflux, a 10 mL methanol solution of 1,3-propanediamine (0.008 g, 0.1 mmol) was added. The orange solution was refluxed for 2 h, cooled, filtered, and the volume was reduced to give the product in 40 % yield (0.029 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.15 (s, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.05 (s, 2H), 6.94 (s, 2H), 6.87 (d, J = 7.9 Hz, 2H), 4.59 (s, 8H), 4.14 (dd, J = 21.3 and 12.1 Hz, 4H), 3.91 (d, J = 12.2 Hz, 2H), 3.82 (t, J = 6.8 Hz, 2H). *Anal.* Calc. for $C_{27}H_{27}Cl_2N_3O_4Pb$: C, 44.08; H, 3.70; N, 5.71 %. Found: C, 44.20; H, 3.80; N, 5.82 %. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3451, 2933, 2863, 1634 (s, -CH=N), 1451, 1378, 1304, 760. Orange yellow crystals of complex **2** were obtained from a mixture of methanol/acetonitrile (*v/v* = 8:1) by slow evaporation in air at room temperature.

Synthesis of 3. The synthetic process of **3** is the same as that of **2** except that H_2pdd (0.046 g, 0.10 mmol) was used. Yield: 86 %, (0.065 g). Orange yellow crystals of complex **3** were obtained by slow evaporation of a mixture of methanol/acetonitrile solution (*v/v* = 1:1) in air at room temperature. ^{1}H NMR (500 MHz, CD_3OD): δ 8.17 (s, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.39 (dd, J = 11.1, 4.1 Hz, 1H), 7.07 (d, J = 2.0 Hz, 2H), 6.96 (d, J = 2.2 Hz, 2H), 4.25~4.11 (m, 4H), 3.98~3.86 (m, 4H), 3.45 (t, J = 7.0 Hz, 2H). *Anal.* Calc. for $C_{54}H_{52}Cl_4N_8O_{10}Pb_2$: C, 42.41; H, 3.43; N, 7.33 %. Found: C, 42.55; H, 3.49; N, 7.21 %. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3446, 2938, 2876, 1634 (s, -CH=N), 1545, 1446, 1378, 1305, 757.

Synthesis of 4. Dilute HNO_3 (0.05 mol/L) was added to a solution of **1b** (0.062 g, 0.049 mmol) in methanol (20 mL) till the pH value of mixture is *ca.* 3~4 at room temperature. Then the yellow green mixture was stirred for 2 h, filtered and concentrated to give complex **4** in a yield of 41 % (0.024 g). Yellow green crystals of complex **4** were obtained by slow evaporation of a mixture of methanol/acetonitrile solution (*v/v* = 8:1) in air at room temperature. ^{1}H NMR (500 MHz, CD_3OD): δ 7.91 (s, 2H), 7.25~7.20 (m, 8H), 7.17 (d, J = 7.0 Hz, 2H), 7.13 (s, 4H), 7.07 (d, J = 7.6 Hz, 4H), 5.54 (s, 2H), 3.35 (s, 6H), 2.04 (s, 4H). *Anal.* Calc. for $C_{54}H_{58}Cl_4N_2O_{12}Zn_2$: C, 54.06; H, 4.87; N, 2.34 %. Found: C, 53.98; H, 4.75; N, 2.27 %. Main FT–IR absorptions (KBr pellets, cm^{-1}): 3433, 2968, 2919, 2878, 1645 (s, -CH=O), 1544, 1456, 1210, 838, 556.

X-Ray Data Collection and Structural Determination

Single-crystal samples of five compounds were covered with glue and mounted on glass fibers and then used for data collection. Crystallographic data were collected on a Bruker SMART 1K CCD diffractometer, using graphite mono-chromated Mo Kα radiation (λ = 0.71073 Å). The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL-PC software package.[7] All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for five metal complexes is listed in Table 1, whereas selected bond distances and angles are given in Table SI1. In addition, hydrogen-bonding parameters are tabulated in Table SI2.

Acknowledgment

This work was financially supported by the Major State Basic Research Development Programs (Nos. 2013CB922101 and 2011CB933300), the National Natural Science Foundation of China (No. 21171088), and the Natural Science Foundation of Jiangsu Province (Grant BK20130054).

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† Electronic Supplementary Information (ESI) available: Selected bond distances (Å) and angles (°), hydrogen bonding parameters, FT–IR spectra and perspective view of the packing structures for related complexes. CCDC nos. 955028–955031 and 1009728 contain the supplementary crystallographic data for five complexes in this work. These data could be acquired free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: [+44]1223-336-033; or deposit @ccdc.cam.ac.uk).

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Table 1. Crystal Data and Structural Refinements forCompounds **1**-**4**.

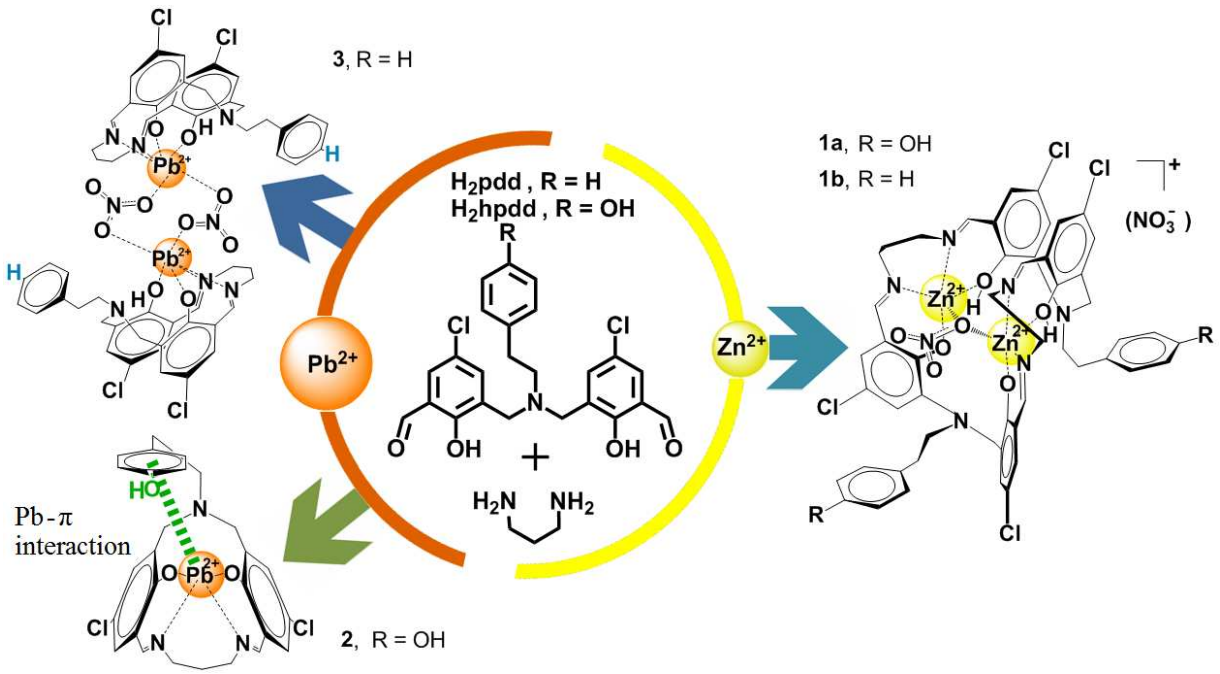
Complex	**1a**·C_2H_5OH	**1b**·CH_3OH	**2**	**3**	**4**
Empirical formula	$C_{56}H_{58}Cl_4N_8O_{13}Zn_2$	$C_{55}H_{56}Cl_4N_8O_{11}Zn_2$	$C_{27}H_{25}Cl_2N_3O_3Pb$	$C_{27}H_{26}Cl_2N_4O_5Pb$	$C_{54}H_{58}Cl_4N_2O_{12}Zn_2$
Formula weight	1323.64	1277.62	717.59	764.61	1199.60
Temperature / K	291(2)	291(2)	291(2)	291(2)	291(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal Size (mm)	0.12×0.12×0.10	0.14×0.14×0.10	0.10×0.08×0.08	0.12×0.10×0.08	0.10×0.10×0.10
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/m$	$P2_1/c$
a / Å	13.244(3)	13.689(9)	10.404(3)	20.254(8)	11.255(7)
b / Å	13.505(3)	14.944(10)	10.422(3)	10.682(3)	15.508(9)
c / Å	17.957(4)	15.540(10)	13.660(4)	13.612(4)	17.377(9)
α / °	89.565(3)	105.066(10)	98.637(5)	90	90
β / °	72.204(2)	107.277(10)	102.317(5)	98.762(8)	112.50(3)
γ / °	72.003(3)	93.069(10)	99.253(4)	90	90
V / Å^3	2895.1(11)	2901.5(3)	1401.9(7)	2910.6(16)	2802(3)
Z / D_{calcd} (g / cm^3)	2 / 1.518	2 / 1.462	2 / 1.700	4 / 1.745	2 / 1.422
F(000)	1364	1316	696	1488	1240
μ / mm^{-1}	1.084	1.076	6.240	6.023	1.108
h_{min} / h_{max}	–12 / 15	–16 / 10	–12 / 10	–24 / 18	–13 / 12
k_{min} / k_{max}	–16 / 16	–17 / 17	–12 / 11	–12 / 11	–18 / 18
l_{min} / l_{max}	–21 / 21	–13 / 18	–13 / 16	–16 / 16	–20 / 19
Data / parameters	10081 / 748	10158 / 721	4919 / 334	2696 / 194	4843 / 337
R_1, wR_2 [$I > 2\sigma(I)$]^a	R_1 = 0.0469 wR_2 = 0.1277	R_1 = 0.0794 wR_2 = 0.1966	R_1 = 0.0372 wR_2 = 0.0802	R_1 = 0.0691 wR_2 = 0.1626	R_1 = 0.0761 wR_2 = 0.1358
R_1, wR_2 (all data)^b	R_1 = 0.0763 wR_2 = 0.1397	R_1 = 0.1058 wR_2 = 0.2098	R_1 = 0.0526 wR_2 = 0.0836	R_1 = 0.0777 wR_2 = 0.1659	R_1 = 0.2268 wR_2 = 0.1776
S	1.00	0.98	0.92	1.08	0.88
Max/min $\Delta\rho$/e Å^{-3}	0.94 / –0.47	3.27 / –0.52	1.00 / –1.06	4.49 / –3.03	0.39 / –0.72

^{a} $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, ^{b} w$R_2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

Graphical Abstract

Distinguishable Zn(II) and Pb(II) template effects on forming pendant-armed Schiff-base macrocyclic complexes including a remarkable Pb(II)–π macrocyclic complex

Kun Zhang, Jiao Geng, Chao Jin and Wei Huang



36-Membered [2+2] dinuclear Zn(II) and 18-membered [1+1] mononuclear Pb(II) Schiff-base macrocyclic complexes have been described, including a unique intramolecular η^3-coordinated Pb(II)–π macrocyclic complex obtained under ambient condition.