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

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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 (H2hpdd and H2pdd) because of the distinguishable cationic template effects. It is very interesting to mention that a unique intramolecular Pb(II)–π macrocyclic complex 2 with an uncommon η3-coordination type is achieved under ambient conditions and it can remain stable both in the solid state and in solution. The subtle variations of pendant-arms in the macrocyclic ligands H2hpdd and H2pdd yield different Pb(II) complexes, where the competition between Pb(II)–π and Pb(II)–NO3− electrostatic interactions as well as the combination of steric and electronic effects of pendant arms are 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 thoroughly studied, including related syntheses, characterizations, properties and applications.1 But so far, it is still a challenge to synthesize new Schiff-base macrocycles because of the complexity of multiple Schiff-base condensation reactions between dicarbonyl compounds and diamines. During the past four decades, considerable efforts have been made to develop metal-free and metal-template2 methods for desired macrocycles. Commonly, the strategy of the metal-template method is more effective for cyclisation, and this method could control the size of Schiff-base macrocycles using 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 macrocycles3 leads us to explore their construction with alterable sizes by using the same dialdehydes and diamines but different metal template ions. In this work, two flexible extended dialdehydes (H2hpdd and H2pdd shown in Scheme 1) with different functional pendant arms (−CH2CH2PhOH and −CH2CH2Ph)3d as well as 1,3-propanediamine have been used to build metallomacrocycles with alterable sizes 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) com-

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plexes 2 and 3 (Scheme 2) are produced, because of the distinguishable 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-diformyl-4-chlorophenol as a dialdehyde precursor. At the same time, it is worthwhile to mention that a unique Pb(II)–π interaction is observed under ambient conditions, where the subtle variations of the pendant-arms of macrocyclic ligands yield different products. The competition between Pb(II)–π and Pb(II)–NO$_3$–π 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.

Further pH stability investigations revealed that Pb(II) macrocyclic complexes can remain 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 acidic conditions (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 the divalent pdd anions.

### Results and discussion

#### Syntheses

In the synthesis of Schiff-base macrocyclic metal complexes, metal template effects are critical. The importance of metal template ions is reflected in directing the sites of multiple Schiff-base condensation reactions in macrocycles and in increasing the yields of macrocyclic products. As is reported, all the Schiff-base condensation reactions between 2,6-diformyl-4-substituted phenol and 1,3-propanediamine in the presence of various transition-metal ions (Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Pd) produce [2 + 2] macrocyclic dinuclear complexes. The yield of the same types of metal macrocyclic products is due to the compromise between the size, charge and coordination geometries of metal template ions, together with the flexibility of the macrocyclic skeleton. However, our results in this work demonstrate that the treatment of extended dialdehydes (H$_2$hpdd and H$_2$pdd) and 1,3-propanediamine in the presence of Zn(NO$_3$)$_2$·6H$_2$O 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 between the Zn(II) and Pb(II) template effects is still expressed on forming flexible Schiff-base macrocyclic skeletons 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 were obtained in weak acidic conditions with pH values of about 5–6. Finally, half of the phenolic protons were removed in dinuclear Zn(II) complexes 1a and 1b and [1 + 1] Pb(II) complex 3. However, all the phenolic protons were removed with regard to the [1 + 1] Pb(II)–π complex 2. Considering that different amounts of phenolic protons were 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 metalmacrocycles, respectively. Our results indicate that no macrocyclic compounds could be yielded if acid or base was added before the Schiff-base condensation reaction. When complexes 1–3 were treated with acid or base, the two Zn(II) complexes decomposed quickly accompanied by the appearance of precipitates, and a dinuclear Zn(II) complex 4 was obtained in the acidic conditions after the addition of 0.05 mol L$^{-1}$ HNO$_3$ into the methanol solution of the Zn(II) macrocyclic complex 1b. However, the two Pb(II) complexes were found to be stable in the pH range of 5–8, and precipitates were also formed outside this pH range.

Interestingly, a unique Pb(II)–π macrocyclic complex was obtained under ambient conditions, where the subtle variations of pendant-arms of macrocyclic ligands yielded different products of 2 and 3, as illustrated in Scheme 2. The competition between Pb(II)–π and Pb(II)–NO$_3$–π 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.

#### Spectral characterizations

Relative spectral analyses are used to monitor this type of Schiff-base cyclization. From previous work, it is known that the FT-IR absorption peaks of aldehyde groups are 1660 and 1634 cm$^{-1}$ in H$_2$hpdd and H$_2$pdd, respectively. In contrast, new absorption peaks are observed at 1639 and 1632 cm$^{-1}$ in 1a and 1b and 1634 cm$^{-1}$ in 2 and 3 replacing the peaks of the aldehyde groups, indicative of the formation of C=N Schiff-base units. From the ESI-MS spectra of 1a and 1b, the for-
formation of 36-membered [2 + 2] macrocyclic dinuclear Zn(n) complexes can be proven by positive peaks at m/z = 1183.52 and 1151.48 (Fig. 1), respectively, corresponding to the species of \([\text{Zn}_{2}(\text{L}_{2})_{2} + \text{CH}_3\text{OH} + \text{H}]^+\) and \([\text{Zn}_{2}(\text{L}_{6})_{3} + \text{CH}_3\text{OH} + \text{H}]^+\), which agrees well with the theoretical simulations.

Furthermore, \(^1\text{H}\) NMR spectral characterization has been carried out to explore the variations of chemical shifts between dialdehyde precursors and their relative Zn(n) and Pb(n) macrocyclic complexes. New peaks are observed at 7.93 ppm in \(1\text{a}\) (CD\(_3\)OD), 7.97–8.24 ppm in \(1\text{b}\) (CD\(_3\)CN), and 8.18 ppm in 2 and 3 (CD\(_3\)OD), assigned as the formation of imine units. In order to further explore the Pb(n)–π interactions in solution, comparisons among the \(^1\text{H}\) NMR spectra have been carried out for H\(_2\)hpdd, H\(_2\)pdd, and their respective Pb(n) complexes 2 and 3 in CD\(_3\)OD. As displayed in Fig. 2, the aromatic protons of the two p-Cl-phenol rings in 2 and 3 are shifted to the higher field (green labels), mainly because the deprotonation and subsequent increase of electron density are overwhelming compared with the Pb(n) 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.

![Fig. 1 Positive ESI-MS of 36-membered [2 + 2] macrocyclic dinuclear Zn(n) complexes 1a (a) and 1b (b) obtained in positive mode, together with the experimental and calculated Isotopic Distribution Peaks (IDPs) (inset) corresponding to the peak at 100% abundance for comparison.](image)

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(n) 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\(_2\)pdd and 3 with Δ3 (0.23 ppm) and Δ4 (0.47 ppm) in H\(_2\)hpdd and 2, as illustrated in Fig. 2, it is found that the two pairs of aromatic protons in the latter show distinguishable chemical environments after Pb(n) ion complexation, indicating the existence of Pb(n)–π interactions in solution. Furthermore, a large chemical shift difference of Δ4 reveals the formation of the aforementioned η\(^3\)-coordination 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(n)–π interactions in solution. So it is concluded that the \(^1\text{H}\) NMR spectral comparisons before and after metal-ion complexation provide an experimental proof of the existence of stable Pb(n)–π interactions in solution in the case of complex 2, and a η\(^3\)-coordination mode is detected between the phenolic ring and the Pb(n) center, agreeing well with the following structural description.

Crystal structures

**Structures of 1a and 1b.** The molecular structures of 1a and 1b with the atom-numbering scheme are illustrated in Fig. 3a and 3b, respectively. They are both 36-membered [2 + 2] half-fold macrocyclic dinuclear Zn(n) complexes where the coordination configuration for each five-coordinate zinc(n) center in 1a and 1b is distorted trigonal bipyramidal (τ = 0.764, 0.842 and 0.89, 0.807 for Zn1 and Zn2 in 1a and 1b, respectively).\(^5\) There are two nitrate counterions in the asymmetric unit for each Zn(n) complex. One serves as a μ\(_2\) linker where one oxygen atom is found to connect to two neighboring Zn(n) ions with a Zn⋯Zn separation of 3.809(1) Å in 1a and 3.792(4) Å in
While the other is free of the formation of a coordinative bond. The basal coordination plane of each Zn(n) ion is composed of two oxygen and two nitrogen atoms of the macrocyclic ligand as well as one common oxygen atom of the nitrite anion. It is noted that the dihedral angles between the phenol carbon atoms of each pheno-ortho and two phenyl carbon atoms in the pendant arms) are 6.9(2)° in \(1a\) and 63.3(2)° in \(1b\). As for the half-fold macrocyclic ligands in \(1a\) and \(1b\), the distances between the two ortho carbon atoms of each pheno-licrylic hydroxyl group for the extended part are 4.983(6) Å in \(1b\) and 4.952(4) Å in \(1b\), which are longer than those in the free \(\text{H}_2\text{hpdd}\) 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 centroid-to-centroid separations of 3.480(1) Å in \(1a\) and 3.496(2) and 3.560(2) Å in \(1b\).

**Structures of 2 and 3.** Different from the 36-membered \([2 + 2]\) macrocyclic Schiff-base dinuclear compounds for the Zn(n) ion template, 18-membered \([1 + 1]\) macrocyclic mononuclear Pb(n) complexes 2 and 3 are produced from the same reaction when the Pb(n) ion template is used. ORTEP drawings of 2 in Fig. 3c and 3d and 3 in Fig. 3e and 3f 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 the Pb(n) 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 subtle variations in the pendant-arms (—CH₂CH₂PhOH vs. —CH₂CH₂Ph) of the macrocyclic ligands yield different products because of the aforementioned competition between Pb(n)—π and Pb(n)—NO₃ electrostatic interactions, as well as the combination of steric and electronic effects of pendant arms. As a result, a unique Pb(n)—π complex 2 is formed where the phenolic unit occupies the other half of the coordination sphere of central Pb(n) ion. In contrast, two NO₃⁻ anions act as μ₂ bridges linking two adjacent mononuclear Pb(n) units by weak Pb—O coordinative bonds, where two oxygen atoms of each NO₃⁻ anion are coordinated to the Pb(n) centers with the same bond length of 3.291(14) Å, forming another dinuclear Pb(n) complex 3 mainly predominated by the Pb(n)—NO₃ electrostatic interactions.

The phenolic and phenyl rings of pendant arms in the macrocyclic ligands are found to point in different directions in 2 and 3 due to the presence and absence of Pb(n)—π interactions, respectively, and the related torsion angles (two alkyl carbon and two phenyl carbon atoms in the pendant arms) are 150.6(8)° in 2 and 0.0(3)° in 3, respectively. In addition, intramolecular π—π stacking interactions are observed between two facing 4-chlorophenol rings with 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)° in 2 and 34.4(3)° in 3.

Pb—π interactions have been systematically summarized by Tiekink and Zukerman-Schpector in 2010, where 29 known examples having at least one aryl ring are investigated. 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 \(V₁\) and the vector passing through the ring centroid to the lead atom \(V₂\), as shown in Fig. 4. They concluded that a Pb(n)—π interaction should be considered to exist if \(d < 4.0 \text{ Å}\) and \(α < 20^\circ\), and most of them fall within the ranges of \(2.78 < d < 3.97 \text{ Å}\) and \(0.6 < α < 19.4^\circ\). In our case, the two values are \(d = 3.549(1) \text{ Å}\) and \(α = 14.7(4)^\circ\), which means that the Pb(n)—π interaction does exist and it is a very weak one.

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 η¹-coordination mode.
Instead, they adopt an intramolecular $\eta^3$-coordination 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 $\eta^3$-coordinated Pb(II)–π interaction observed in the solid state agrees well with the aforementioned $^3$H NMR spectral results in solution.

Why do 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, the Pb–π interaction is generally recognized as a supramolecular contact. A detailed analysis for Pb(II)–π interactions by checking the CCDC database shows that such a supramolecular interaction is not unusual. However, most are related to the intermolecular Pb(II)–π interactions within supramolecular aggregates. In contrast, very few examples of Pb(II)–π interactions are involved in synthetic small molecules to date. Obviously, the intramolecular Pb(II)–π interaction between a neutral Pb(II) center capped by a [1 + 1] macrocyclic ligand and its substituent phenol ring in complex 2 gives such an intramolecular instance for further synthetic and theoretical investigations. In addition, complex 2 is stable in solution, which can be proven by the $^3$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.

Secondly, the electronic effects of the aromatic rings on the Pb(II)–π interaction are 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 donation of π electrons from the aromatic ring to the vacant orbital of the Pb center. In our case, the only difference between complexes 2 and 3 is the substituted groups in the pendant arms (–CH$_2$CH$_2$PhOH vs. –CH$_2$CH$_2$Ph). The former arm has higher electron density, which favors formation of the Pb(II)–π complex. Fortunately, the single-crystal structures of Pb(II) complexes 2 and 3 have been obtained, clearly supporting the aforementioned viewpoint. The Pb(II)–π macrocyclic complex 2 adopts an extraordinary $\eta^3$-coordination type. In contrast, most of the reported Pb(II)–π interactions are described as the $\eta^6$-coordination type in the literature. Nevertheless, the formation of an intramolecular Pb(II)–π interaction in complex 2 is greatly restricted by the spatial crowding effects of the two methane units in the pendant arm and the skeleton of the macrocyclic ligand. So the final $\eta^3$-coordination type is suggested to be a cooperative result of steric effects and Pb(II)–π interactions, which can 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 demonstrating 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 interactions. 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 the opposite occurs in 3. As a result, an intramolecular Pb(II)–π complex 2 versus a dimer nitrate-bridged dinuclear Pb(II) complex 3 is obtained.

**Structure of 4.** X-ray structural analysis of the 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 the nitrogen atoms (Fig. 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 divergent 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 δ phenolic oxygen atoms from each dialdehyde unit are found to link two adjacent 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 the coordination sphere. The dihedral angles between the pendant-arm 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 as 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 distinguishable cationic template effects. FT-IR, ESI-MS and 1H 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, where an uncommon η^3-coordination is achieved under ambient conditions. The complex can remain stable both in the solid state and in solution, which can be clearly verified by its X-ray single-crystal structure and 1H 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 H2hpdd and H2pdd yield different Pb(II) complexes 2 and 3, where the competition between Pb(II)–π and Pb(II)–NO3^- electrostatic interactions, as well as the combination of steric and electronic effects of pendant arms, are believed to play vital roles. The current study is a combined investigation in 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, solvents of analytical grade were purchased directly from commercial sources and used without any further purification. The extended dialdehydes H2hpdd and H2pdd were prepared as reported in the literature.3d 1H and 13C NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS (SiMe4) 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(NO3)2·6H2O (0.033 g, 0.11 mmol) was dissolved in ethanol (10 mL) and added to a solution of H2hpdd (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 an additional 2 h, cooled to room temperature and filtered. The filtrate was concentrated to give 1a in a yield of 70% (0.044 g). 1H NMR (500 MHz, CD3OD): 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), 4.36 (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 C35H35Cl4N8O12Zn2: 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 + CH3OH + H]+. Main FT-IR absorptions (KBr pellets, cm^-1): 3434, 2927, 1639 (s, –CH==N), 1549, 1540, 1386, 1153, 763. Light yellow-green single crystals of the solvated complex 1a·C2H5OH were grown from ethanol–acetonitrile (v/v = 2:1) by slow evaporation in air at room temperature.

Synthesis of 1b. The synthesis of 1b is the same as that of 1a except that H2pdd (0.047 g, 0.10 mmol) was used. Yield: 0.055 g, (89%). 1H NMR (500 MHz, CD3CN): 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, 4H), 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 C35H35Cl4N8O12Zn2·C5H5N: 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 + CH3OH + 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 solvated complex 1b·C2H5OH were obtained from methanol–acetonitrile (v/v = 10:1) by slow evaporation in air at room temperature.

Synthesis of 2. Anhydrous Pb(NO3)2 (0.036 g, 0.11 mmol) was dissolved in methanol (15 mL) and added to a solution of H2hpdd (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). 1H NMR (500 MHz, CD3OD): 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 C23H23Cl2N2O9Pb: 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 methanol-acetonitrile (v/v = 8:1) by slow evaporation in air at room temperature.

**Synthesis of 3.** The synthesis of 3 is the same as that of 2 except that H2pdd (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 methanol-acetonitrile solution (v/v = 1:1) in air at room temperature.1H NMR (500 MHz, CD3OD): 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 C56H58Cl4N8O13Zn2: 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, C=O), 1544, 1446, 1378, 1305, 757.

**Synthesis of 4.** Dilute HNO3 (0.05 mol L−1) was added to a solution of 1b (0.062 g, 0.049 mmol) in methanol (20 mL) until the pH value of the mixture was 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 methanol-acetonitrile solution (v/v = 8:1) in air at room temperature.1H NMR (500 MHz, CD3OD): 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 C54H56Cl4N8O11Zn2: C, 42.41; 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, C=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 1 K CCD diffractometer, using graphite monochromated 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 on all data and the structures were solved by direct methods and refined by the full-matrix least-squares method on Fobs using the SHELXTL-PC software package. All non-hydrogen 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 S1. In addition, hydrogen-bonding parameters are tabulated in Table S2.†

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