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Construction of four 3d-4d/4d complexes based on salen-type schiff base ligands[†]

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Through a two-step synthetic strategy, four d¹⁰ Schiff-base complexes CdZn(DMF)(L^a)(NO₃)₂ (1), Cd[Zn(L^a)Cl]₂·H₂O (2) and [Cd(DMF)L^bS]₂·2H₂O (S = NO₃, 3; Cl, 4) (H₂L^a = N,N'-bis (3-methoxy-salicylidene)phenylene-1,2-diamine, HL^b = 2-(1*H*-benzoimidazol-2-yl)-6-methoxy-phenol) have been successfully constructed by the solvothermal reaction of Cd(NO₃)₂/CdCl₂ with Zn(L^a)/Zn(L^b)₂, and characterized by EA, IR, FAB-MS and TG, in which 1, 2 and 4 were confirmed by single crystal X-ray diffraction. The results reveal that 1 is the first 3d-4d hetero-dinuclear compound based on H₂L^a, however, 2 is a CdZn₂-type compound reported previously. 3 and 4 are the first examples of dinuclear compounds containing ligand HL^b. Moreover, luminescence and biological activities of the four compounds and two ligands H₂L^a/HL^b are investigated.

Multi-dentate Schiff bases ligands containing salen-type are capable of forming complexes with certain transition-metal ions which can exhibit unusual coordination, high thermodynamic stability, good fluorescent properties and biological activities, etc.1 Simultaneously, owing to the facile preparation, structural varieties and varied chemical properties, these multidentate Schiff-base ligands are applied widely in constructing metal-organic complexes.² The bisalen-type ligand N,N'-bis(3-methoxy-salicylidene)phenylene-1,2-diamine (H_2L^a) formed from 3-methoxysalicylaldehyde and benzene-1,2-diamine at the range of room temperature to 80 °C with one N2O2 and one O4 cavity accommodating different metal ions have been extensively investigated over the past three decades, for example, its mononuclear Cu(II), Co(II), Ni(II), Fe(II) and multinuclear Pd₂, Co₂, Zn₈, U₈, compounds^{3,4} as well as Zn₂Pb₂, Zn₂Cd, Zn_2Ni , ZnLn (Ln = La, Nd, Gd, Er, Yb *etc.*) compounds⁵ were



In addition, transition-metal complexes of the Schiff base, especially those involving 2-hydroxy-3-methoxybenzaldehyde, can themselves act as "complex ligands", which may be further coordinated through the negatively charged phenoxo groups to alkali, alkaline earth, rare earth, and d-block transition metal, resulting in the formation of new homo- and hetero-nuclear bi- and tri-metal complexes.⁹ Such μ_2 -phenoxo bridging is particularly important for the d-block homo- and hetero-metal complexes of these salen-type ligands, some of which exhibit interesting electrochemical, optical and magnetic properties *etc.* As a result, in the present paper, the Zn(II)ion was chosen as the first metal ion to coordinate with Schiff base ligands N,N'-bis(3-methoxy-salicylidene)phenylene-1,2-diamine (H_2L^a) with a relatively flexible structure and 2-(1*H*-benzo-imidazol-2-yl)-6-methoxy-phenol (HL^b) with a relatively rigid structure (Scheme 1).[‡] By using these two Schiff-base mononuclear Zn(II) complexes as precursors, four phenoxo-bridged hetero-/homometallic bi-/tri-nuclear compounds including CdZn(DMF) La(NO3)2



Scheme 1 Construction of four compounds 1-4 based on Schiff base ligands H_2L^a and HL^b .

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(1), Cd[Zn(L^a)Cl]₂· H₂O (2), [Cd(DMF)L^b(NO₃)]₂· 2H₂O (3) and [Cd (DMF)L^bCl]₂· 2H₂O (4) have been rationally designed, synthesized, and characterized by EA, IR, FAB-MS and TG, in which compound 1, 2 and 4 were further confirmed by single crystal X-ray diffraction and 2 is previously reported by Jiang and coworkers.^{5d} The luminescence properties and biological activities of these complexes 1–4 were also investigated. To the best of our knowledge, compound 1 is the first hetero-dinuclear 3d-4d compound containing H₂L^a ligand, while 3 and 4 represent the first examples of multinuclear compounds based on the HL^b ligand.

Facile condensation of salicylaldehyde and benzene-1,2-diamine according to the reported procedure¹⁰ afforded two neutral yellow condensates at the different temperatures, namely, at the range of r. t. \rightarrow 80 °C for H₂L^a and at more than 80 °C for HL^b, which have been employed as multi-dentate chelating ligands in the present work. In order to construct the heteronuclear complexes, the ligands H₂L^a/HL^b respectively react with Zn(OAc)₂· 2H₂O (1 : 1 molar ratio) in methanol, to provide the corresponding pale yellow zinc complexes ZnL^a and Zn(L^b)₂.¹¹ It is worth noting that the former compound, ZnL^a, was used to synthesize complexes **1** and **2** without being separated from the yellow parent solution. This is also true for Zn (L^b)₂, used to synthesize complexes **3** and **4**. And then ZnL^a and Zn (L^b)₂ further reacted with Cd(NO₃)₂/CdCl₂ in DMF at 70 °C and respectively gave complexes **1/2**, **3/4**, of which **2** is in agreement with a previous report^{5d} (Scheme 1, Table S1 and ESI[†]).

Complexes 1-4 were characterized by elemental analysis, FAB-MS and IR, in which the formula of compounds 1, 2 and 4 were identified by X-ray diffraction. The IR spectra of H₂L^a/HL^b and the corresponding four complexes 1-4 provide information about the metalligand bonding. Assignments are based on the typical group frequencies. A weak broad band in the region of 3250-3352 cm⁻¹ is due to a hydrogen bonded -OH group in the free Schiff base ligands H₂L^a/HL^b and is not observed in the infrared spectra of 1-4. This indicates that phenolic oxygen is deprotonated and coordinated in four complexes (Scheme 1). The strong ν (C=N) bands which occur in the range 1632-1648 cm⁻¹ for these complexes are shifted considerably toward lower frequencies compared to that of the free Schiff base ligands H₂L^a/HL^b (1650–1659 cm⁻¹), and show that the azomethine nitrogen atom is also coordinated to the metal. A weak band in the region of 468-479 cm⁻¹ for all complexes can be assigned to $\nu(M-O)$ and provides further evidence for coordination through the deprotonated phenolic oxygen atoms.

The structure of the heterobimetallic phenylene-bridged Schiff bases complex 1 was ascertained by X-ray crystallographys, and is shown in Fig. 1 with selected bond distances and angles summarized in Table S2[†]. The structure of complex **1** is very similar to that of the corresponding Zn-Ln (Ln = La, Nd, Gd and Er) Schiff base compounds of H₂L^a reported previously in the literature.^{5c} Structural analyses reveal that the relative 3d transition metal ion, zinc(II), is located in the inner N2O2 cavity and the 4d transition metal ion Cd(II) in the outer O₄ cavity of the Schiff base ligand. In compound 1, the zinc(II) ion is five-coordinate and adopts a distorted square pyramidal geometry, with the two imino nitrogen atoms and the two phenolic oxygen atoms forming the square base, while the monodentate DMF oxygen occupies the axial position. The Cd2+ ion is octa-coordinated and surrounded by four O atoms from the Schiff base, in which two are from the μ^2 -bridging phenolic groups and the other two from the methoxy groups, with the remaining four coordination sites occupied by four O atoms from two bidentate η^2 -nitrato ligands, adopting



Fig. 1 Molecular structure of 3d-4d hetero-dinuclear compound **1** with the atom-numbering scheme. The selected bond distances Cd1–O2 2.260 (2), Cd1–O3 2.261(2), Cd1–O5 2.428(3), Cd1–O6 2.386(3), Cd1–O8 2.362 (2), Cd1–O9 2.353(2), Zn1–O2 1.995(2), Zn1–O3 1.967(2), Zn1–O11 2.007(2), Zn1–N1 2.016(2), Zn1–N2 2.052(2) Å.

a bi-capped trigonal prism coordination geometries. The Zn–Cd distance is within 3.267 Å, showing weak interaction between Zn^u and Cd^u. The average lengths of the Zn–N and Zn–O bonds are in the ranges 2.016–2.052 and 1.9672–1.9954(19) Å, respectively. The Cd–O average length is in the range 2.353(2)–2.428(3) Å, which is comparable to those of hetero-bimetallic Zn–Cd Schiff base complexes.^{5d}

From Fig. 1, because the rigid benzene-1,2-diamine spacer between the nitrogen atoms in Schiff base ligand $(L^a)^{2-}$ was introduced a delocalization effect of the π electrons of the two five-numbered and two six-numbered conjugated rings in 1 exists, smaller bond length and bond angle variations in the chelate rings are observed (see Table S2†) and the whole Schiff base $(L^a)^{2-}$ molecule is almost in a plane with 0.1685 Å from the least square plane (N1, N2, O1, O2). Based on molecular conformation of compound 1, each neutral dinuclear molecular unit forms a series of acceptor/donor hydrogen bonds with the neighboring ones *via* intermolecular C–H···O hydrogen bonding interactions (Table S3†), leading to the formation of three-dimensional ordered supramolecular network as depicted in Fig. 2.

As presented in Fig. 3, compound 4 crystallizes in the monoclinic space group $P2_1/n$ with four $Cd_2L^b_2$ units per unit cell. A view of the X-ray structure of the complex 4 is shown in Fig. 3. Crystallographic details are provided in Table S1[†], and selected bond lengths and angles are given in Table S2[†]. Structure 4 contains two tridentate Schiff base ligand $(L^b)^-$ bonded to two Cd^u ions through the imine nitrogen, methoxy oxygen and phenolate oxygen (NOO) ions, two



Fig. 2 3D crystal packing of 1, viewed down the *a* axis, constructed by the hydrogen bonding $C-H\cdots O$ interaction.



Fig. 3 Molecular structure of homo-dinuclear compound **4** with atomnumbering scheme. The selected bond distances Cd1–O2 2.258(3), Cd1– O4 2.272(3), Cd1–O5 2.379(4), Cd1–O6 2.403(4), Cd1–N2 2.210(4), Cd1– N3 2.204(4), Cd2–O2 2.276(3), Cd2–O4 2.247(3), Cd2–O1 2.561(4), Cd2– O3 2.549(4), Cd2–Cl1 2.469, Cd2–Cl2 2.506 Å.

lattice water molecules, as well as two crystallographically indepentent cadmium(II) centres, in which one Cd (Cd2) has two terminal chloride atoms and the other Cd (Cd1) has two monodentate coordinated DMF molecules. The geometries of two six-coordinated cadmium centres are approximately distorted octahedral with two DMF molecules (Cd1)/chlorine ions (Cd2) occupying the apical sites and two benzimidazole nitrogen (N2, N3)/methoxy oxygen (O1, O3) atoms and two phenolate oxygen atoms (O2, O4) for Cd1/Cd2 in the basal planes. The bridging oxygens form asymmetric linkages to the cadmium ions with a range of Cd–O distances [2.247(3)–2.276(3) A] and with Cd1-O-Cd2 bridging angles of 103.1(1) and 103.6(1)°. The two deprotonated phenolate O-ions in face-to-face fashion bridge the two cadmium centres (Cd…Cd 3.550 Å) with 51° of the dihedral angle between two coordinated benzimidazole groups, in which the distance between the two cadmium centres suggests that there is no interaction between them.

Similar to complex 1, the existence of many intermolecular hydrogen bonding such as O–H···Cl and N–H···Cl *etc* interactions result in the formation of a three-dimensional supramolecular network in complex 4 (Fig. 4 and Table S3[†]).

From the descriptions and discussions above, the choice of anions and organic ligands is clearly critical in determining the molecular structures of the resultant complexes 1-4. As shown in Scheme 1, in complexes 1-4, the chloride and nitrate anions have strong coordination ability and usually present terminal coordination, although compound 3 has not been characterized by single crystal structure; accordingly, the present compounds 1, 3 and 4 are all di-nuclear, in which two terminal coordinating nitrate or chloride anions occupy the coordination sites of the metal ions and prevent more ligands from the further coordination to the dinuclear unit. However, in complex 2, through eight O-Cd coordination interactions, two precursors ZnL^a chelate perpendicularly to each other to one Cd²⁺ ion, leading to the formation of a trinuclear molecule Zn₂Cd. By comparison, CH₃COO⁻ anion has weak coordination ability with metal ions, and thus it does not coordinate with Zn^{II}/Cd^{II} ion in this case, resulting in the formation of mononuclear compounds ZnL^a and $Zn(L^{b})_{2}$. On the other hand, the Schiff base ligand $H_{2}L^{a}$ has an inner N2O2 cavity which is suited to the small radius Zn2+ ion, and the outer O₄ cavity is suited to the larger radius Cd²⁺ ion. Accordingly, it is very reasonable that the two-step reaction in H_2L^a system gives the heteronuclear complexes 1 and 2, accompanied by the formation of more five-/six-numbered chelating rings after coordination to metal ions. In contrast the NO₂ donor set in HL^b is linear, hence the two ligands HL^b simultaneously coordinate to one/two metal ions to satisfy the demand of their coordination geometry to give final stable complexes. Taking into account the steric factor in present case it is not difficult to understand that two-step reactions can only provide homo-binuclear Cd¹¹ complexes 3 and 4, derived from Cd²⁺ having a larger radius (0.84 Å) and Zn^{2+} smaller one (0.60 Å) (Scheme 1–2). At the same time, to reduce this steric hindrance, the benzene and benzimidazole rings in the same ligand HL^b have a dihedral angle of 25° achieved via the rotation of C-C single bond, and two benzene rings or benzimidazole rings in two different ligands HL^b also have the dihedral angle of 32° or 60° .

Metal–organic complexes have been reported to have abilities to affect the emission wavelength and intensity of the organic material through metal coordination.¹² Therefore, it is important to investigate the luminescent properties of metal–organic complexes in view of potential applications. The photoluminescent behaviors of compounds **1–4** and free ligands H_2L^a and HL^b are studied in the solid state at room temperature (Fig. S2 and Table S4†). Apparently, the emission spectra of the complexes resemble that of their corresponding ligands except for the emission intensity and peak positions, indicating that the fluorescence of the complexes are ligands is observed, where the maximum emission wavelength is 470 and



Fig. 4 The 3D crystal packing of 4 viewed down the *b*-axis, constructed by hydrogen bonding $N-H\cdots$ Cl (blue dotted lines) and $O-H\cdots$ Cl (pink dotted lines) interactions.



Scheme 2 Distribution of ligands around metal ions after coordination to metal ions in compounds 1–4.

485 nm (under 347 and 358 nm excitation) for the ligands H_2L^a and HL^b , 449, 469, 495, and 461 nm for the complexes 1, 2, 3 and 4 (corresponding excitation under 315, 347, 315, and 358 nm), respectively. Compared with the emission spectra of the corresponding ligands, a varying degree of blue shifts of 21 nm in 1, 10 nm in 2, red shifts of 11 nm in 3, 24 nm in 4 were observed, which are considered to be mainly arise from coordination of the metal centers to the ligands. Incorporation of metal ions effectively increases the conformational rigidity of ligand and reduces the loss of energy *via* vibrational motion. Thus, the enhanced fluorescence intensities of the four complexes are detected, which indicate that it is good candidate material for photochemical applications of these complexes.¹³

The thermal stability of the compounds 1, 2, 3 and 4 was examined and the TGA curves are shown in Fig. S3[†]. The experiments were performed on samples consisting of numerous single crystals of the compounds under N₂ atmosphere with a heating rate of $10 \degree C \min^{-1}$. The preliminary thermogravimetric analysis of Zn(DMF) $CdL^{a}(NO_{3})_{2}$ (1) shows no weight loss below 141 °C. It can be seen from TG curve of compound 1 that one DMF molecule was lost in the approximate temperature from 141 to 189 °C (calcd. 9.74%, found 9.21%). When heating to ca. 272 °C, the framework almost collapsed. Preliminary thermogravimetric analysis of Cd[Zn(La) $Cl_2 \cdot H_2O(2)$ shows that the first weight loss started at 83 °C, and is mainly attributed to water molecules in the lattice (calcd. 1.67%, found 2.03%). No weight loss occurred below 315 °C and coordination framework decomposition up to a temperature of 407 °C. Although the single crystal structure of 3 has not been obtained, the results of its EA and FAB-MS show that compounds 3 and 4 have analogous molecular compositions, and thus 3 was selected for the thermogravimetric analysis (TGA) to examine their thermal stability. From Fig. S3[†], two water molecules and two coordinated DMF molecules were lost in the approximate temperature range from 85 °C to 213 °C (calcd 18.03%, found 18.29%). A complicated decomposition reaction then took place when heating continued to 287 °C.

DPPH assay was used to evaluate the ability of antioxidants to quench the stable DPPH radical. Antioxidants convert DPPH to 2,2-diphenyl-1-picryl hydrazine. The assay provides stoichiometric information with respect to the number of electrons taken up by the test compounds in the presence of a stable radical. It is a very simple, sensitive and rapid method, which is very convenient for screening samples with different polarities. Hence, in present case, the potential antioxidant ability of methanol extracts containing compounds with different concentrations were evaluated by DPPH, results are shown in Fig. S4[†]. From Fig. S4[†], it can be clearly seen that the average radical scavenging activity of complex 1 (IC₅₀ = 1.25 mg mL^{-1}) for DPPH is the best achieved of all compounds. It increases with increasing concentration (see Fig. S4^{\dagger}). Compound 2 (IC₅₀ = 1.43 mg mL⁻¹) is the poorest effective inhibitor. However, with increasing concentration particularly in the range of 0.05-0.23 mg mL⁻¹, scavenging activity is rapidly enhanced. When compared with standard samples of VC and BHT, IC₅₀ values are 0.114 mg mL⁻¹ and 0.436 mg mL⁻¹, respectively, compound **1** is obviously a very good candidate antioxidant. At present, systematic research for biological activities is still in progress.

In summary, under the different temperatures, the two same reactants 3-methoxysalicylaldehyde and benzene-1,2-diamine, respectively, produce two different organic ligands, H_2L^a (at low temperature) and HL^b (at high temperature). Through a two-step synthetic strategy, four d¹⁰ Schiff base compounds **1–4** were obtained

and characterized *via* EA, IR, FAB-MS and TG. Compounds 1, 2 and 4 were confirmed by single crystal structure and 2 is in agreement with a previously reported structure. These results indicate that compounds 1 and 2 are hetero-multinuclear and 3 and 4 are homobinuclear. To the best of our knowledge, compound 1 is the first hetero-dinuclear 3d-4d compound containing the H_2L^a ligand, while 3 and 4 represent the first examples of multinuclear compounds based on the HL^b ligand. The strong fluorescence emission of these complexes makes them potentially useful as photoactive materials. In addition, the scavenging activities of compounds 1 to 4 on DPPH are more effective than those of the ligands H_2L^a and HL^b , of which compounds 1 and 4 were the most effective. It is clear that the scavenging activity of DPPH is enhanced by the formation of metal– ligand coordination complexes.

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Notes and references

[†] Preparation of 1 and 2: A mixture of Schiff-base ligand H₂L^a (0.4 mmol, 0.141 g) and Zn(OAc)₂·2H₂O (0.4 mmol,0.0878 g) in methanol (20 mL) was stirred for 30 min at room temperature. Then, a solution of Cd (NO₃)₂/CdCl₂ (0.2mmol, 0.0597/0.0457 g) in methanol/DMF was added dropwise, and the mixture was stirred for another 2 h at 70 °C. After being filtered, the reaction solution was put into the fridge to allow for solvent evaporation at 5 °C for one week, providing yellow single crystals at a yield of 0.078 g, 52% for 1 (based on Cd). Found: C 39.75, H 3.43, N 9.51%. Anal. calcd for C25H25N5O11ZnCd2: C 40.04, H 3.34, N 9.34%. IR (KBr, cm⁻¹): v 3565 (br, s), 2995 (m), 2963 (s), 2892 (s), 2797 (s), 1632 (vs), 1595 (s), 1541 (s), 1470 (vs), 1445 (vs), 1290 (vs), 1189 (vs), 1150 (s), 1021 (vs), 900 (vs), 792 (m), 765 (s), 676 (m), 637 (m), 601 (m), 572 (m), 531 (m), 468 (w). FAB-MS: m/z 676 ([M]+-DMF, 79%). For 2, 0.0512g, yield: 47% (based on Cd). Found: C 48.77, H 3.57, N 5.28%. Anal. calcd for C44H38Cl2N4O9Zn2Cd: C 48.89, H 3.54, N 5.18%. IR (KBr, cm⁻¹): v 3242-3208 (br, m), 2943 (m), 1639 (vs), 1462 (s), 1384 (w), 1241 (s), 1152 (m), 1043 (m), 896 (w), 750 (s), 644 (m), 570 (w), 473 (w). FAB-MS: m/z 1063 ([M]+-H₂O, 83%).

Preparation of 3 and 4: Compounds **3** and **4** were obtained using the same reaction procedure as described for compounds **1** and **2**, respectively, but using HL^b instead of H₂L^a. The yellow powder of **3** was isolated in about 52% yield (based on Cd). Found: C 40.51; H 4.01; N 10.95%. Anal. calcd for $C_{34}H_{40}Cl_2N_8O_{14}Cd_2$: C 40.42, H 3.96, N 11.10%. IR (KBr, cm⁻¹): ν 3493–3694 (br, w), 2957 (m), 2981 (m), 2842 (m), 1648 (vs), 1597 (s), 1468 (s), 1449 (s), 1396 (w), 1375 (w), 1338 (w), 1295 (s), 1239 (s), 1217 (vs), 1080 (s), 967 (m), 931 (m), 885 (m), 848 (m), 782 (m), 745 (s), 731 (s), 630 (w), 562 (w), 475 (w). FAB-MS: *mlz* 775 ([M]⁺–2DMF·2H₂O, 85%). For **4**, 65% yield (based on Cd). Found: C 42.55, H 4.25, N 8.73%. Anal. calcd for C₃₄H₄₀Cl₂N₆O₈Cd₂: C 42.66, H 4.18, N 8.78%. IR (KBr, cm⁻¹): ν 3531–3678 (br, w), 2926 (m), 2874 (w), 1636 (m), 1568 (s), 1471 (w), 1439 (m), 1410 (w), 1384 (w), 1342 (w), 1115 (w), 1021 (w), 928 (w), 654 (m), 527 (w), 479 (w). FAB-MS: *mlz* 828 ([M]⁺–2DMF·2H₂O, 85%).

§ *Crystallographic studies*: X-ray diffraction data were collected on a Bruker Apex II diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 298 K. Absorption corrections were applied using the multi-scan program SADABS. All of the structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen ions were refined with anisotropic displacement parameters. Hydrogen ions on organic ligands were generated by the riding mode (C–H 0.96 Å).

Crystal data for 1: $C_{25}H_{25}N_5O_{11}ZnCd$, MW = 749.27, monoclinic, P_{21}/c , a = 9.9306(7) Å, b = 18.8619(13) Å, c = 15.0246(10) Å, $\beta = 97.401(1)$,

V = 2790.8(3) Å³, Z = 4, F(000) = 1504, GOF = 1.028, $R_1 = 0.0281$, $wR_2 = 0.0622$ [$I > 2\sigma(I)$]. For 4: C₃₄H₄₀N₆O₈Cd₂, MW = 956.42, monoclinic, $P2_1/n$, a = 16.6799(12) Å, b = 10.6208(8) Å, c = 21.4547(16) Å, $\beta = 92.312$ (1), V = 3797.7(5)) Å³, Z = 4, F(000) = 1920, GOF = 1.031, $R_1 = 0.0408$, $wR_2 = 0.0858$ [$I > 2\sigma(I)$]. CCDC 823146 (1) and 823147 (4) contain the crystallographic data[†].

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