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Syntheses, characterizations and crystal structures of four zinc(II) and cadmium(II) complexes constructed by ligand bearing poly-coordination atoms

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ABSTRACT

Treatment of 3-(4-carboxyphenylhydrazono)pentane-2,4-dione (HL) with transition metal ions afforded four novel complexes, $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ (**1**), $[Zn(L)_2(MeOH)_4]$ (**2**), $\{[Cd_4(\eta^2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]\cdot MeOH\}$ (**3**) and $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ (**4**). Their crystal structures have been characterized by single-crystal X-ray crystallography. In polymer **1**, the acetate anions bridge the Zn(II) ions forming an infinite one-dimensional (1-D) chain with L^- units acting as monodentate ligands in the side chain. In mononuclear complex **2**, two L^- ligands act as monodentate fashion to coordinate to the Zn(II) ion. In its solid-state structure, $[Zn(L)_2(MeOH)_4]$ groups are joined together by hydrogen bonds forming a three-dimensional (3-D) supramolecular network. In tetranuclear complex **3**, four Cd(II) ions are linked by four $\mu_2\text{-}\eta^2\text{-}L^-$ ligands, and chelated by another four L^- ligands, respectively. In polymer **4**, the acetate anions bridge the Cd(II) ions leading to a 1-D chain containing chelating L^- units in the side chain.

1. Introduction

Recently, considerable efforts have been devoted to design various ligands to construct coordination frameworks with tunable properties [1–10]. People found that the geometry of ligating atoms within a polynucleating ligand, the flexibility of the ligand backbone, and the additional functional groups of the ligands all play important roles in directing the structural outcome of the resulting complex [11–20].

In the view of ligand design, compound 3-(4-carboxyphenylhydrazono)pentane-2,4-diketone (HL) is a very useful ligand. This compound contains three coordination units: carboxylate, hydrazono and β-diketone groups. Thus the compound should have potential strong coordination ability. The reasons are as follows: (1) for carboxylate group, they usually adopt various coordination modes as terminal monodentate, chelating to one metal center, bridging bidentate in a *syn–syn*, *syn–anti*, *anti–anti* configuration to two metal centers and bridging tridentate to two metal centers, etc. Moreover, hydrogen bonds are likely to be formed among the carboxylate compounds providing additional supporting force for supramolecular system [21–27]. (2) For chelating group β-diketone, as a constituent of polydentate ligands, it has been increasingly encountered in the context of metallo-supramolecular chemistry and widely used in coordination chemistry. Recently, several groups have reviewed the diketone ligands and related complexes [28–30]. (3) As for hydrazone unit, it obviously has strong coordination ability due to the existence of two N donors. However, up to now, reported complexes bearing HL ligand are still very limited [31–33]. It is to be pointed out that the reported complexes with HL ligand have only been characterized by elemental analysis and IR spectra, etc. There are no crystal data for these complexes yet.

These considerations have prompted us to further study the reaction of HL with other metal ions. We hope to obtain a series of new complexes with novel structures and desired properties. In this paper, the syntheses and crystal structures of four Zn(II) and Cd(II) complexes (Scheme 1), namely $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ (**1**), $[Zn(L)_2(MeOH)_4]$ (**2**), $\{[Cd_4(\eta^2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]\cdot MeOH\}$ (**3**) and $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ (**4**) are presented.

2. Results and discussion

2.1. Synthesis

From synthesis process of complexes **1**–**4**, it is to be found that utilization of different metal salts directs the structural outcome of the resulting complex. When we use the metal nitrate salts, $Zn(NO_3)_2$ or $Cd(NO_3)_2$, to react with NaL in solution, the mononuclear complex **2** or tetranuclear complex **3** have been produced. When metal acetate salts, $Zn(OAc)_2$ or $Cd(OAc)_2$, react with NaL in solution, two coordination polymers **1** and **4** can be obtained.

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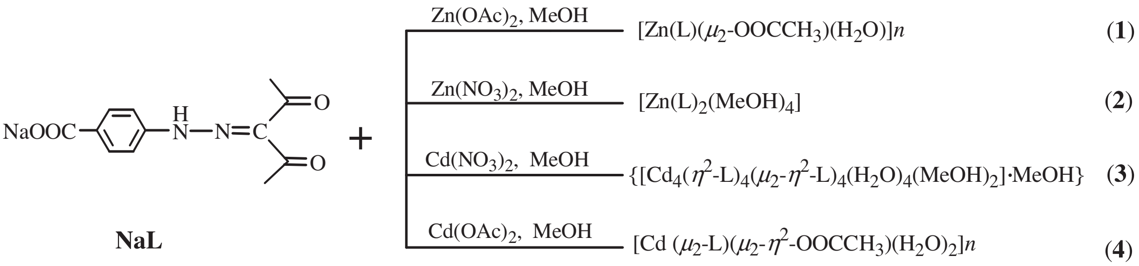


Scheme 1.

Obviously, the anion effect of metal salts is significant for the preparation of different structural complexes.

Another interesting feature of the complexes is the carboxylato coordination mode of the ligand L^-. In complexes **1–4**, L^- coordinates as a terminal monodentate ligand (in complexes **1** and **2**), or as chelating ligand (in complexes **3** and **4**), or as bridging tridentate ligand (in complex **3**). It is worth noticing that only the carboxylato group of the ligand L^- takes part in the coordination to central metal ion. This is largely different from that in the reported complexes bearing L^- units [31,32]. As shown in Scheme 2, the chelating β-diketone group (**A**) [32] or oxygen of carbonyl group and nitrogen of hydrazono unit of the ligand L^- (**B**) [33] join in the coordination to metal ion. This is may be due to the utilization of NaL to react with metal ions in our reaction. The sodium salt of ligand is in favor of the coordination ability of carboxylate group.

The ^{1}H NMR spectra exhibit signals at δ = 14.42, 7.43–7.91, 2.51 and 2.45 ppm (for **1**), 14.44, 7.45–7.90, 2.50 and 2.41 ppm (for **2**), 14.49, 7.40–7.88, 2.52 and 2.45 ppm (for **3**) and 14.51, 7.46–7.93, 2.57 and 2.48 ppm (for **4**), which are similar to those of the free ligand HL of δ = 14.58, 7.48–8.06, 2.59 and 2.51 ppm [31].

2.2. The molecular structure of crystalline $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ (*1*)

Single-crystal structural determination reveals that polymer **1** crystallizes in the monoclinic space group *P2(1)/c* with the composition of neutral asymmetric unit $[Zn(L)(\mu_2\text{-}OAc)(H_2O)]$ and assumes an infinite1-D chain.

As illustrated in Fig. 1, each Zn(II) atom is four-coordinated by two oxygen atoms from two acetate ions, one oxygen atom from one water molecule, and one oxygen atom from carboxylate group of ligand L^- to form a slightly distorted tetrahedron. The distances of Zn–O are in the range of 1.961(4)–2.005(4) Å, are close to those in previous carboxylate polymer $\{[Zn(FcCOO)_2(bpt)]\cdot 2.5H_2O\}_n$ (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$; bpt = *N,N′*-bis(3-pyridylmethyl)thiourea) [34] (Zn–O 1.946–1.977 Å). The bond angles around the central Zn(II) ion vary from 92.85° to 123.13°. Each acetate anion acts as bidentate ligand bridging the Zn(II) ions to form a 1-D chain, in which the intrachain distances between metallic cations are 4.397 Å for Zn1···Zn1A.

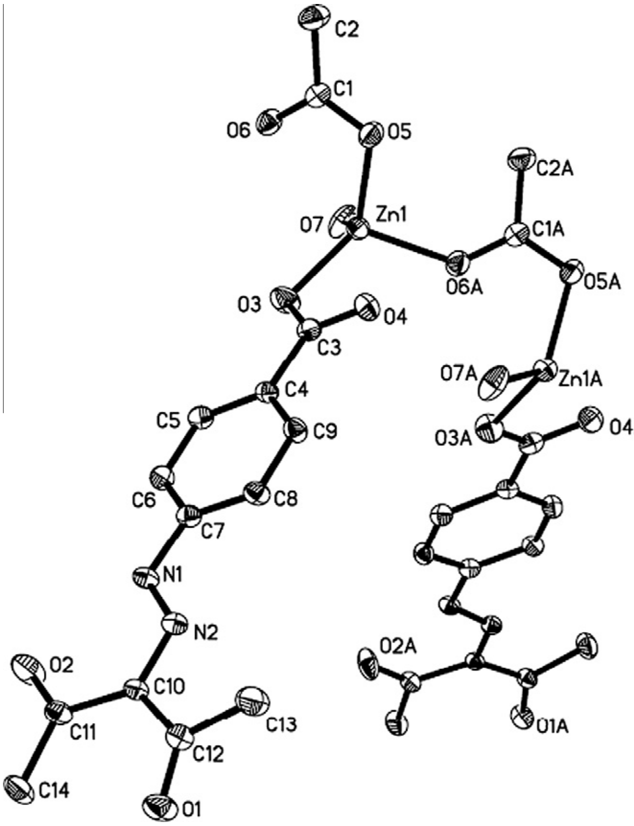
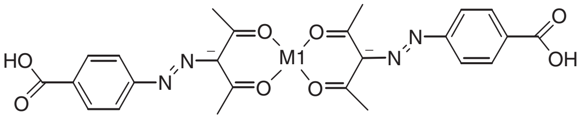
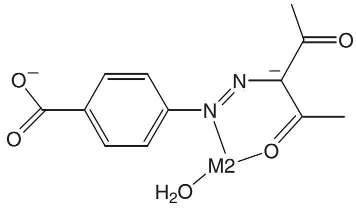


Fig. 1. Molecular structure of $[Zn(L)(\mu_2\text{-}CH_3COO)(H_2O)]_n$ (**1**) (H atoms omitted for clarity).



A (M1 = Cu^{2+}, Co^{2+}, Ni^{2+}) 32



B (M2 = Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}) 33

Scheme 2.

Within the same ligand L^-, the dihedral angle between the phenyl ring and carboxylate plane is 4.2°, which is significantly narrower than the 14.7° in the corresponding free ligand HL [31]. The nitrogen–nitrogen bond of the complex is very similar to (1.303(5) Å) that found in the crystal structure of the free HL (1.307(3) Å). The C–O bond lengths of the carboxylate group of **1** are longer [C3–O3 1.267(6), C3–O4 1.237(6) Å] than those in the free ligand [C–O 1.209 to 1.214 Å]. The C–O bond lengths of the pentane-2,4-dione fragment of **1** [C11–O2 1.227(6), C12–O1 1.201(6) Å] are near to those in the free ligand [C–O 1.220(3) to 1.213(3) Å].

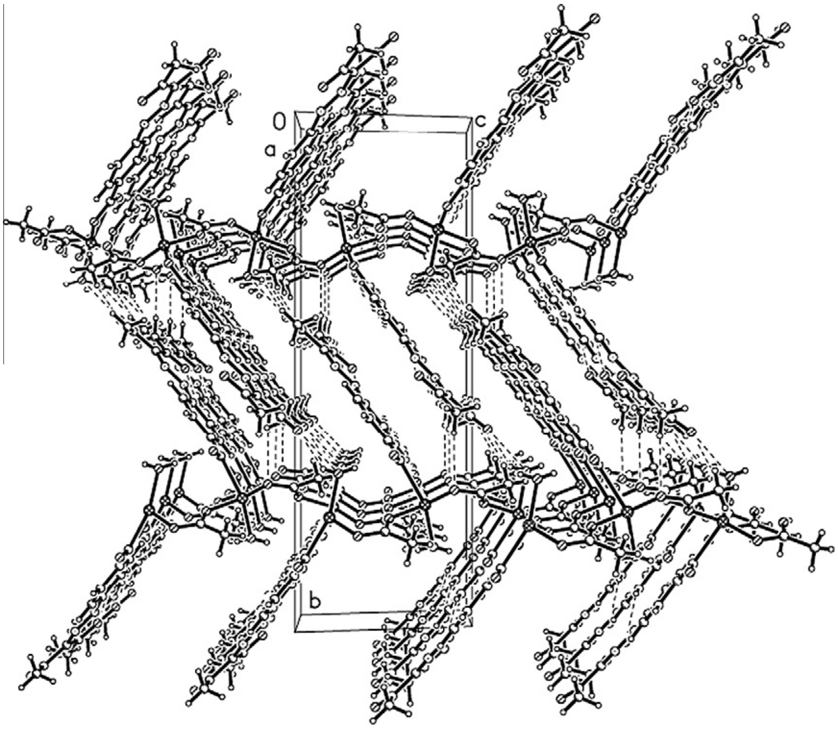


Fig. 2. Crystal packing view from the *a*-axis of $[Zn(L)(\mu_2\text{-}CH_3COO)(H_2O)]_n$ (**1**).

In the solid state structure of **1**, linear $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ chains are linked by intermolecular hydrogen bonds forming a 2-D sheet. It can be seen from Fig. 2, there are two kinds of intermolecular hydrogen bonds. One is between O unit of the diketone group from one $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ chain and OH of one coordination water molecule from neighboring $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$. The other originates from CH of the methyl group from one $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ chain with O from the OAc^- group of neighboring $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ unit. Thus, above H-bond interactions together with van der Waals forces represents the main contribution for the stabilization of the crystal packing (Fig. 2).

2.3. The molecular structure of crystalline $[Zn(L)_2(MeOH)_4]$ (2)

X-ray diffraction analysis of compound **2** shows that it crystallizes in the space group $P\bar{1}$. An ORTEP drawing of the structure with selected atoms labeling scheme is shown in Fig. 3.

Each Zn(II) is coordinated by six oxygen atoms forming a octahedron geometry, in which four oxygen atoms from four coordinated methanol molecules occupy the equatorial plane, and two oxygen atom from two L^- ligands locate at the axial position. The distances of Zn–O are in the range of 2.016–2.162 Å (the average Zn–O distance being 2.109 Å). These distances are slightly longer than those in some ferrocene-based carboxylate complexes, for example $[Zn_4(\mu_2\text{-}FcCOO)_6(\mu_4\text{-}O)]$ (Zn–O: 1.837–2.001 Å) and $\{[Zn(FcCOO)_2(bpt)]\cdot 2.5H_2O\}_n$ (Zn–O: 1.946–1.977) [34]. The angles around the central Zn(II) ion are in the range of 89.00°–180°. In the pentane-2,4-diketone fragment, the distances of O3–C9 and O4–C11 are 1.226(3) and 1.226(2) Å, respectively, which are close to those of complex **1**. The distance of N–N being 1.308 Å is also close to that found in the free HL ligand [31].

There are two kinds of hydrogen bonds in the compound **2**. One is intramolecular hydrogen bond [N1–H1···O3 1.90 Å, 132.9°]. The other is arising from the interaction of OH of the coordination methanol molecule with O of one dione unit of the ligand L^-. Thus, these $[Zn(L)_2(MeOH)_4]$ units are linked by intermolecular hydrogen bonds forming a one-dimensional ladder-like structure, then the ladder-like chains pack each other through the van der Waals interactions forming the 3-D supramolecular structure.

2.4. The molecular structure of crystalline $\{[Cd_4(\eta^2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]\cdot MeOH\}$ (3)

X-ray diffraction analysis reveals that compound **3** crystallizes in the space group $P\bar{1}$. The structure of **3** is made up of a tetranuclear array of $[Cd_4(\eta^2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]$ unit and a crystallization methanol molecule. The ORTEP plot showing the structural unit of **3** is illustrated in Fig. 4.

In the compound **3**, the four L^- ligands indicate two kinds of coordination conformation: chelating and bridging tridentate fashions. The four Cd(II) ions are bridged by four bridging tridentate L^- ligands leading to a tetranuclear core $[Cd_4(\mu_2\text{-}\eta^2\text{-}L)_4]$. The geometries around Cd1 and Cd2 are slightly different. Both Cd1 and Cd2 are seven-coordinated. For Cd1, five oxygen atoms from three L^- ligands occupy the equatorial plane, and two oxygen atoms from water and methanol molecules respectively occupy the axial positions, forming pentagonal bipyramid geometry. For Cd2, five oxygen atoms from three L^- ligands locate the equatorial plane; two oxygen atoms from respective water and another L^- ligand occupy the axial positions to form pentagonal bipyramid geometry as well. The bond lengths and bond angles around Cd1 and Cd2 are very similar. The dihedral angle between the planes Cd1–Cd2–O16–O11 (the mean deviation from the plane is 0.0567 Å) and Cd1A–O12A–Cd1–O12 (the mean deviation from the plane is 0.0000 Å) is 95.7°. The Cd1···Cd2 and Cd1···Cd1A distances are 3.794 and 3.915 Å, respectively. These distances are far shorter than that of the reported complex built up by bipyridine-based bridges $\{[Cd(o\text{-}O_2CC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$ (bpe = 1,2-bis(4-pyridyl)ethene) (Cd···Cd 14.047 Å) built up by bipyridine-based bridges [35].

Interestingly, there exist aromatic π–π stacking interactions of the neighboring benzene rings of the different L^- ligands. The dihedral between phenyl rings C2–C6 (the mean deviation from the

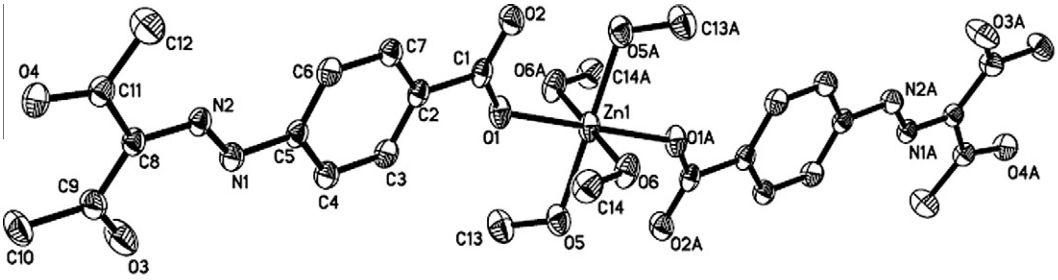


Fig. 3. Molecular structure of $[Zn(L)_2(MeOH)_4]$ (**2**) (H atoms omitted for clarity).

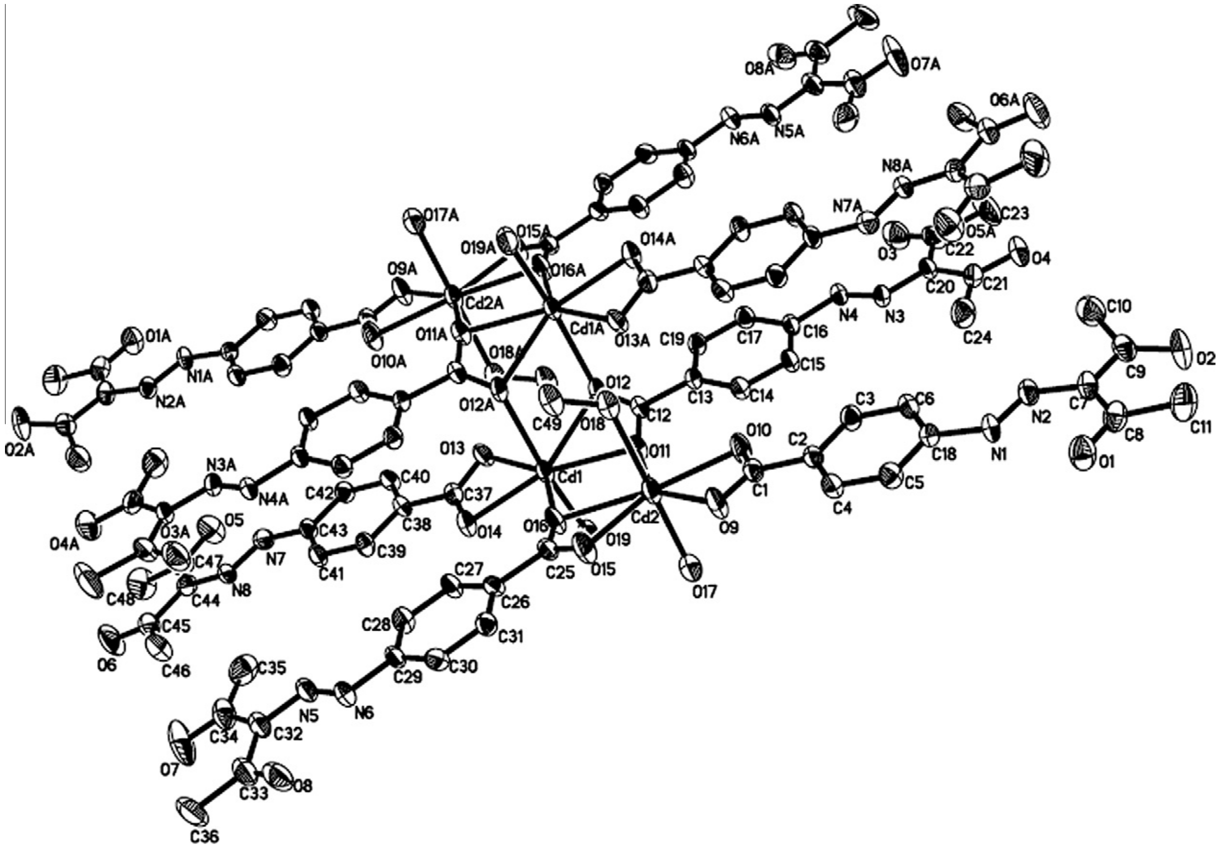


Fig. 4. Molecular structure of $\{[Cd_4(\eta^2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]\cdot MeOH\}$ (**3**) (H atoms and solvent molecule omitted for clarity).

plane is 0.0048 Å) and C38A–C43A (the mean deviation from the plane is 0.0049 Å) is 2.5° with the distance between the two rings being 3.562 Å. The dihedral between other two phenyl rings C26–C31 (the mean deviation from the plane is 0.0025 Å) and C13A–C19A (the mean deviation from the plane is 0.0082 Å) is 8.8° with the distance between the two rings being 3.612 Å.

The bond distances and bond angles within the L^- ligand of complex **3** are unexceptional and close to those in complexes **1** and **2**.

*2.5. The molecular structure of crystalline $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ (**4**)*

The structure determination of **4** reveals that each OAc^- anion acts as a tridentate fashion bridging the central Cd(II) ions forming a 1-D chain. This molecule crystallizes in the space group *P2(1)/n*. An ORTEP drawing of the chain structure with atom labeling scheme is shown in Fig. 5.

Each Cd(II) atom is seven-coordinated, and is in a single-cap triangular prism environment with three oxygen atoms O3, O4 and O3A from two $\mu_2\text{-}\eta^2\text{-}OOCCH_3$ units, two oxygen atoms O1 and O4 from one chelating L and two oxygen atoms O5 and O6 from two water molecules (Fig. 6). Selected geometrical parameters are listed in Table 1.

The Cd–O distances range from 2.232(6) to 2.554(6) Å, which compares with 2.269(4) Å in the polymer $[Cd(O_2CC_6H_4\{C(O)Fc\text{-}o\})_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$ [35]. The angles around the Cd1 are in the range of 53.1°–174.8°. The Cd1···Cd1A separation of 4.433 Å is slightly longer than that in complex **3**.

The bond distances and bond angles within the L^- ligand of complex **4** are unexceptional and close to those in complexes **1**, **2** and **3**.

Like complex **2**, both the intramolecular and intermolecular hydrogen bonds contribute to the stabilization of the complex **4**. The H-bond within the same ligand L^- is between NH unit and O8 [N1–H1···O8 1.95 Å, 131.5°]. The intermolecular hydrogen

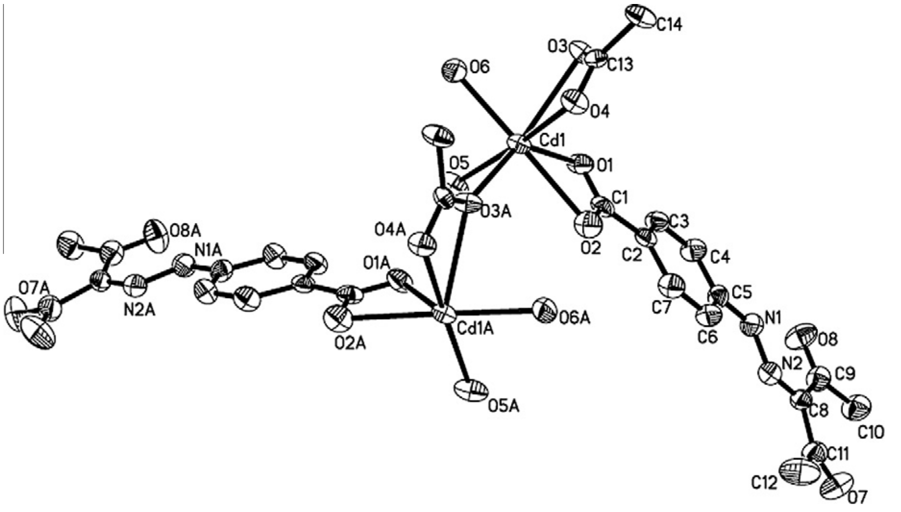


Fig. 5. 1-D chain structure of $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}CH_3COO)(H_2O)_2]_n$ (**4**) (H atoms omitted for clarity).

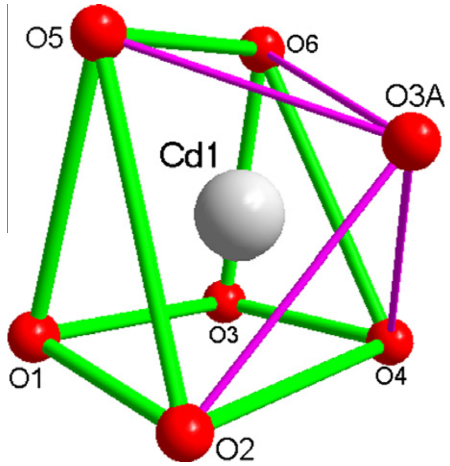


Fig. 6. The coordination conformation of Cd1 in complex **4**.

bonds originate OH units of the coordination water molecules with O of OAc^- anion and carboxylate unit of L^- of adjacent $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ chain [O5–H5A···O1A 1.92 Å, 175.6°; O5–H1 W···O4D 2.09 Å, 149°]. Thus, in the solid state structure of **4**, linear $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ chains are linked by intermolecular hydrogen bonds forming a 2-D sheet. These 2-D sheets pack each other through the van der Waals interactions forming the 3-D supramolecular structure (Fig. 7).

2.6. IR spectroscopy

According to Refs. [31–33,36], the characteristic IR bands of HL are the existence of an NH vibration around 3260 cm^{-1} and a ν(C=N) frequency between 1587 and 1606 cm^{-1}, which can be found in the four complexes (3249 and 1547–1629 $cm^{-1}$for **1**; 3247 and 1547–1630 cm^{-1} for **2**; 3250 and 1595–1630 cm^{-1} for **3**; 3396 and 1522–1627 cm^{-1} for **4**). The strong bands at 1623 and 1553 cm^{-1} for **1**, 1456 and 1549 cm^{-1} for **2**, 1661 and 1382 cm^{-1} for **3** and 1669 and 1411 cm^{-1} for **4** are assigned to $\nu as(COO^-)$ and $\nu s(COO^-)$ vibrations, while those at 1324 and 788 cm^{-1} (**1**), 1324 and 788 cm^{-1} (**2**), 1318 and 799 cm^{-1} (**3**), 1320 and 782 cm^{-1} (**4**) are due to $\nu(CO\text{–}CH_3)$ and ν(Ar–H) vibrations, respectively. In conclusion, these IR data are consistent with the crystal data of the four complexes.

3. Conclusions

By reacting of the organic ligand NaL with metal ions under mild conditions, four crystalline products have been successfully prepared. The X-ray diffraction results indicate that the L^- ligands in our complexes indicate interesting carboxylato coordination mode. In particular, complex **3** shows novel tetranuclear structure. The IR data are consistent with the X-ray analysis results.

4. Experimental

4.1. General materials and instruments

All reagents were got from commercial sources and used without further purification.

3-(4-Carboxyphenylhydrazono)pentane-2,4-dione is prepared according to reference procedure [36]. Its sodium salt was prepared with sodium methoxide.

Infrared spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Elemental analyses (EAs) were carried out on a FLASH EA1112 Elemental Analyzer. ^1H NMR spectra were recorded at room temperature with a Bruker DPX 400 spectrometer.

*4.2. Syntheses of the complex $[Zn(L)(\mu_2\text{-}CH_3COO)(H_2O)]_n$ (**1**)*

$Zn(OAc)_2 \cdot 2H_2O$ (0.011 g, 0.05 mmol) and NaL (0.025 g, 0.1 mmol) in methanol solution (5 ml) was stirred for 30 min. The resulting mixture was filtered and the filtrate was allowed to stand at room temperature. After 1 month, good quality yellow single crystals of **1** were obtained. Crystals of **1** are stable in the air. Yield: 68% based on Zn. *Anal.* Calc. (%) for $C_{14}H_{15}O_7N_2Zn$: C, 43.19; H, 4.11; N, 7.20. Found: C, 43.22; H, 4.15; N, 7.15%. IR (cm^{-1}, KBr): 3400(s), 3249(s), 2924(m), 1655(s), 1630(s), 1598(s), 1547(s), 1505(w), 1464(w), 1406(w), 1372(m), 1279(m), 1196(s), 1162(s), 1099(m), 1055(w), 1025(m), 990(m), 939(s), 870(s), 839(s), 788(s), 699(s), 613(s). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (s, 3 H, CH_3CO), 2.51 (s, 3 H, CH_3CO), 7.43 (s, 2 H, Ar–H), 7.91 (s, 2 H, Ar–H), 14.42 (s, 1 H, NH).

*4.3. Syntheses of the complex $[Zn(L)_2(MeOH)_4]$ (**2**)*

The synthesis of **2** was similar to that of **1** except that $Zn(NO_3)_2 \cdot 6H_2O$ (0.0149 g, 0.05 mmol) was used instead of

Table 1
Selected bond distances (Å) and angles (°) for **1**, **2**, **3** and **4**.[a]

1			
Zn(1)–O(3)	1.961(4)	Zn(1)–O(5)	1.974(4)
Zn(1)–O(6)#1	1.993(4)	Zn(1)–O(7)	2.005(4)
N(1)–N(2)	1.303(5)	O(6)–Zn(1)#2	1.993(4)
C(3)–O(3)	1.267(6)	C(3)–O(4)	1.237(6)
C(11)–O(2)	1.227(6)	C(12)–O(1)	1.201(6)
O(3)–Zn(1)–O(5)	123.13(17)	O(3)–Zn(1)–O(6)#1	116.75(16)
O(5)–Zn(1)–O(6)#1	103.06(15)	O(3)–Zn(1)–O(7)	102.84(17)
O(5)–Zn(1)–O(7)	114.44(17)	O(6)#1–Zn(1)–O(7)	92.85(15)
2			
Zn(1)–O(1)#1	2.0158(12)	Zn(1)–O(1)	2.0158(12)
Zn(1)–O(5)	2.1480(16)	Zn(1)–O(5)#1	2.1481(16)
Zn(1)–O(6)	2.1622(15)	Zn(1)–O(6)#1	2.1622(15)
N(1)–N(2)	1.308(2)		
O(1)#1–Zn(1)–O(1)	180.00(10)	O(1)#1–Zn(1)–O(5)	90.39(6)
O(1)–Zn(1)–O(5)	89.61(6)	O(1)#1–Zn(1)–O(5)#1	89.61(6)
O(1)–Zn(1)–O(5)#1	90.39(6)	O(5)–Zn(1)–O(5)#1	180.0
O(1)#1–Zn(1)–O(6)	89.00(6)	O(1)–Zn(1)–O(6)	91.00(6)
O(5)–Zn(1)–O(6)	89.94(6)	O(5)#1–Zn(1)–O(6)	90.06(6)
O(1)#1–Zn(1)–O(6)#1	91.00(6)	O(1)–Zn(1)–O(6)#1	89.00(6)
O(5)–Zn(1)–O(6)#1	90.06(6)	O(5)#1–Zn(1)–O(6)#1	89.94(6)
O(6)–Zn(1)–O(6)#1	179.999(1)		
3			
Cd(1)–O(14)	2.309(2)	Cd(1)–O(16)	2.315(3)
Cd(1)–O(19)	2.310(2)	Cd(1)–O(11)	2.348(2)
Cd(1)–O(12)#1	2.406(3)	Cd(1)–O(13)	2.418(2)
Cd(1)–O(12)	2.473(2)	Cd(2)–O(10)	2.279(2)
Cd(2)–O(17)	2.286(3)	Cd(2)–O(18)	2.294(3)
Cd(2)–O(15)	2.309(3)	Cd(2)–O(9)	2.427(3)
Cd(2)–O(16)	2.468(2)	Cd(2)–O(11)	2.498(2)
N(1)–N(2)	1.296(4)	N(3)–N(4)	1.298(4)
N(5)–N(6)	1.305(4)	N(7)–N(8)	1.321(4)
O(14)–Cd(1)–O(16)	89.76(8)	O(14)–Cd(1)–O(19)	84.66(8)
O(16)–Cd(1)–O(19)	98.47(8)	O(14)–Cd(1)–O(11)	161.33(9)
O(16)–Cd(1)–O(11)	78.60(8)	O(19)–Cd(1)–O(11)	82.70(8)
O(14)–Cd(1)–O(12)#1	98.14(8)	O(16)–Cd(1)–O(12)#1	96.66(9)
O(19)–Cd(1)–O(12)#1	164.63(8)	O(11)–Cd(1)–O(12)#1	97.68(8)
O(10)–Cd(2)–O(17)	91.43(9)	O(10)–Cd(2)–O(18)	90.10(9)
O(17)–Cd(2)–O(18)	170.54(9)	O(10)–Cd(2)–O(15)	140.26(9)
O(17)–Cd(2)–O(15)	93.56(10)	O(18)–Cd(2)–O(15)	91.23(10)
O(10)–Cd(2)–O(9)	54.56(9)	O(17)–Cd(2)–O(9)	92.50(10)
O(18)–Cd(2)–O(9)	95.99(9)	O(15)–Cd(2)–O(9)	85.83(9)
O(10)–Cd(2)–O(16)	165.50(9)	O(17)–Cd(2)–O(16)	89.59(9)
O(18)–Cd(2)–O(16)	86.63(9)	O(15)–Cd(2)–O(16)	54.02(9)
O(9)–Cd(2)–O(16)	139.84(8)	O(10)–Cd(2)–O(11)	92.61(8)
O(17)–Cd(2)–O(11)	87.10(9)	O(18)–Cd(2)–O(11)	83.50(9)
O(15)–Cd(2)–O(11)	126.99(8)	O(9)–Cd(2)–O(11)	147.16(7)
O(16)–Cd(2)–O(11)	73.00(8)		
4			
Cd(1)–O(3)#1	2.232(6)	Cd(1)–O(6)	2.262(7)
Cd(1)–O(1)	2.327(6)	Cd(1)–O(4)	2.359(6)
Cd(1)–O(5)	2.367(7)	Cd(1)–O(2)	2.460(6)
Cd(1)–O(3)	2.554(6)	O(3)–Cd(1)#2	2.232(6)
N(1)–N(2)	1.307(11)		
O(3)#1–Cd(1)–O(6)	97.3(2)	O(3)#1–Cd(1)–O(1)	132.4(2)
O(6)–Cd(1)–O(1)	121.6(3)	O(3)#1–Cd(1)–O(4)	91.9(2)
O(6)–Cd(1)–O(4)	95.6(2)	O(1)–Cd(1)–O(4)	108.7(2)
O(3)#1–Cd(1)–O(5)	78.7(2)	O(6)–Cd(1)–O(5)	79.9(3)
O(1)–Cd(1)–O(5)	82.1(2)	O(4)–Cd(1)–O(5)	168.9(2)
O(3)#1–Cd(1)–O(2)	84.8(2)	O(6)–Cd(1)–O(2)	174.8(3)
O(1)–Cd(1)–O(2)	54.3(2)	O(4)–Cd(1)–O(2)	89.0 (2)
O(5)–Cd(1)–O(2)	95.8(2)	O(3)#1–Cd(1)–O(3)	142.6(3)
O(6)–Cd(1)–O(3)	76.3(2)	O(1)–Cd(1)–O(3)	77.9(2)
O(4)–Cd(1)–O(3)	53.1(2)	O(5)–Cd(1)–O(3)	134.1(2)
O(2)–Cd(1)–O(3)	104.9(2)		

[a] Symmetry transformations used to generate equivalent atoms. For complex **1**: #1 = *x*, −*y* + 3/2, *z* − 1/2; #2 = *x*, −*y* + 3/2, *z* + 1/2. For complex **2**: #1 = −*x*, −*y* + 3, −*z*. For complex **3**: #1 = −*x* + 3, −*y*, −*z*. For complex **4**: #1 = *x* − 1/2, −*y* + 1/2, *z* − 1/2; #2 = *x* + 1/2, −*y* + 1/2, *z* + 1/2.

$Zn(OAc)_2 \cdot 2H_2O$. Good quality white crystals for **2** were obtained after 2 weeks. Crystals of **2** are stable in the air. Yield: 73.0% based on Zn. *Anal.* Calc. (%) for $C_{28}H_{38}N_4O_{12}Zn$: C, 48.88; H, 5.57; N, 8.14. Found: C, 48.46; H, 5.23; N, 8.13%. IR (cm^{-1}, KBr): 3247(m), 2929(w), 1655(s), 1629(w), 1598(s), 1547(m), 1505(s), 1465(w), 1406(s), 1372(s), 1324(s), 1280(w), 1197(s), 1163(s), 939(s), 870(m), 840(m), 788(s), 699(m), 665(w), 614(w), 544(m), 436(m). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.41$ (s, 3 H, CH_3CO), 2.50 (s, 3 H, CH_3CO), 7.45 (s, 2 H, Ar–H), 7.90 (s, 2 H, Ar–H), 14.44 (s, 1 H, NH).

4.4. *Syntheses of the complex {$[Cd_4(\mu_2\text{-}L)_4(\mu_2\text{-}\eta^2\text{-}L)_4(H_2O)_4(MeOH)_2]\cdot MeOH$} (**3**)*

NaL (0.025 g, 0.1 mmol) was dissolved in methanol 3 ml. The solution was added slowly dropwise to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0155 g, 0.05 mmol) in 3 ml methanol. The resulting mixture was filtered, and the filtrate was allowed to stand at room temperature. Good quality yellow crystals for **3** were obtained after 1 month. Crystals of **3** are stable in the air. Yield: 62% based on Cd. *Anal.* Calc. (%) for $C_{100}H_{112}N_{16}O_{40}Cd_4$: C, 45.67; H, 4.26; N, 8.52. Found: C, 45.25; H, 3.85; N, 8.13%. IR (cm^{-1}, KBr): 3422(m), 1661(s), 1630(w), 1595(m), 1519(s), 1382(s), 1318(m), 1182(s), 1162(m), 935(w), 838(m), 780(m), 6679(w), 441(m). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (s, 3 H, CH_3CO), 2.52 (s, 3 H, CH_3CO), 7.40 (s, 2 H, Ar–H), 7.88 (s, 2 H, Ar–H), 14.49 (s, 1 H, NH).

4.5. *Syntheses of the complex $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}OOCCH_3)(H_2O)_2]_n$ (**4**)*

The synthesis of **4** was similar to that of **3** except that $Cd(OAc)_2 \cdot 2H_2O$ (0.0134 g, 0.05 mmol) was used instead of $Cd(NO_3)_2 \cdot 4H_2O$. Good quality yellow single crystals for **4** were obtained after 1 month. Crystals of **4** are stable in the air. Yield: 57% based on Cd. *Anal.* Calc. (%) for $C_{14}H_{18}O_8N_2Cd$: C, 37.00; H, 3.96; N, 6.17. Found: C, 37.13; H, 3.99; N, 6.12%. Yield: 57%. IR (cm^{-1}, KBr): 3396(s), 2929(m), 1926(m), 1669(s), 1627(m), 1597(s), 1522(s), 1411(s), 1356(w), 1320(s), 1294(w), 1273(s), 1201(m), 1185(w), 1166(s), 1026(m), 937(m), 871(m), 859(s), 840(s), 782(s), 685(s), 660(m), 617(s), 453(s). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.48$ (s, 3 H, CH_3CO), 2.57 (s, 3 H, CH_3CO), 7.46 (s, 2 H, Ar–H), 7.93 (s, 2 H, Ar–H), 14.51 (s, 1 H, NH).

4.6. *X-ray crystallography*

The crystallographic data for complexes **1**–**4** are listed in Table 2. All measurements were made on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Single crystals of **1** (0.45 × 0.24 × 0.23 mm), of **2** (0.44 × 0.36 × 0.22 mm) and of **3** (0.38 × 0.24 × 0.21 mm), of **4** (0.43 × 0.15 × 0.21 mm) were selected and mounted on a glass fiber. All data were collected at a temperature of 293(2) K using the $\omega - 2\theta$ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The four structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 6819 observed reflections and 2678 variable parameters for **1** [$R_{int} = 0.0313$], 5930 observed reflections and 2942 variable parameters for **2** [$R_{int} = 0.0171$], 14 662 observed reflections and 10 195 variable parameters for **3** [$R_{int} = 0.0411$], and 9248 observed reflections and 2964 variable parameters for **4** [$R_{int} = 0.0817$]. All calculations were performed using the SHELX-97 [37] crystallographic software package. The selected bond lengths and bond angles are listed in Table 1.

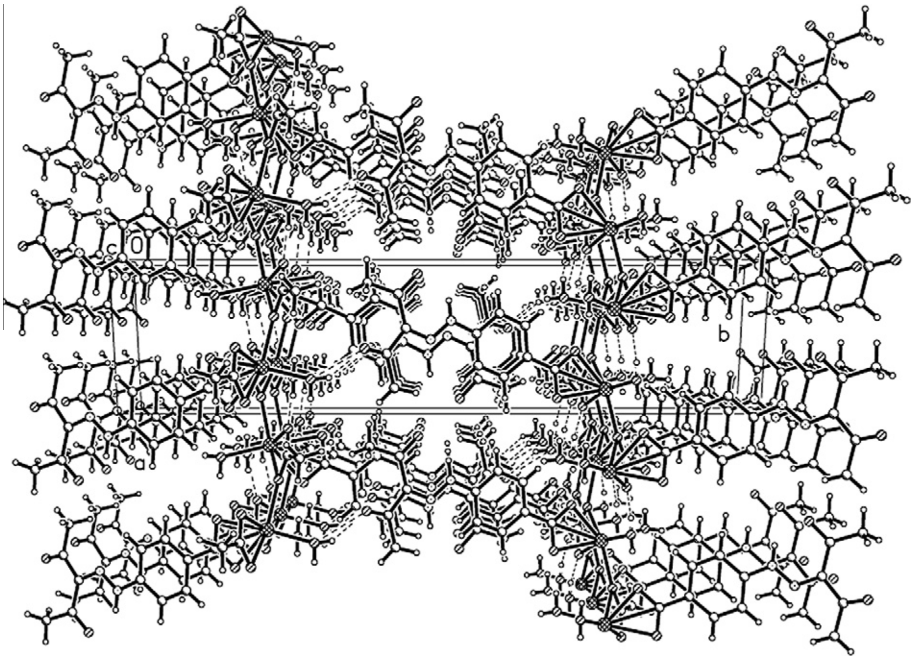


Fig. 7. Crystal packing view from the *c*-axis of $[Cd(\eta^2\text{-}L)(\mu_2\text{-}\eta^2\text{-}CH_3COO)(H_2O)_2]_n$ (**4**).

Table 2
The crystallographic data for complexes **1**, **2**, **3** and **4**.

Complex	**1**	**2**	**3**	**4**
Formula	$C_{14}H_{15}N_2O_7Zn$	$C_{28}H_{38}N_4O_{12}Zn$	$C_{100}H_{112}N_{16}O_{40}Cd_4$	$C_{14}H_{18}O_8N_2Cd$
Formula weight	388.65	687.99	2627.66	454.70
T (K)	291(2)	293(2)	291(2)	291(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
Crystal size (mm^3)	0.45 × 0.24 × 0.23	0.44 × 0.36 × 0.22	0.38 × 0.24 × 0.21	0.43 × 0.15 × 0.21
a (Å)	7.9200(16)	7.9778(11)	11.880(2)	7.4915(5)
b (Å)	24.480(5)	8.1168(11)	15.820(3)	29.088(2)
c (Å)	8.7400(17)	14.183(2)	16.410(3)	8.5568(5)
α (°)	90.00	75.734(2)	114.54(3)	90.00
β (°)	107.25(3)	83.992(2)	90.33(3)	113.315(4)
γ (°)	90.00	63.110(2)	96.19(3)	90.00
V (Å^3)	1618.3(6)	793.81(19)	2784.8(10)	1712.4(2)
D_c (Mg m^{-3})	1.595	1.439	1.567	1.764
Z	4	1	1	4
μ (mm^{-1})	1.556	0.841	0.846	1.320
$F(0\,0\,0)$	796	360	1336	912
Reflections collected/unique	6819/2678, R_{int} = 0.0313	5930/2942, R_{int} = 0.0171	14662/10195, R_{int} = 0.0411	9248/2964, R_{int} = 0.0817
Data/restraints/parameters	2678/0/220	2942/0/209	10195/5/723	2964/0/234
Final R indices $[I > 2\sigma(I)]$	R_1 = 0.0672, wR_2 = 0.1911	R_1 = 0.0316, wR_2 = 0.0861	R_1 = 0.0494, wR_2 = 0.0972	R_1 = 0.0722, wR_2 = 0.1747
R indices (all data)	R_1 = 0.0798, wR_2 = 0.2175	R_1 = 0.0357, wR_2 = 0.0894	R_1 = 0.0937, wR_2 = 0.1110	R_1 = 0.1093, wR_2 = 0.1895
Goodness-of-fit (GOF) on F^2	1.093	1.048	1.005	1.042

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Appendix A. Supplementary material

CCDC 687360, 687362, 687359, and 687361 contain the supplementary crystallographic data for **1**–**4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.04.037.

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