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Three 3D complexes constructed from azelaic aci and rigid bis(imidazole) ligand: Syntheses, structures, thermal and photoluminescent properties

Fang-Hua Zhao, Yun-Xia Che, Ji-Min Zheng *

Department of chemistry, Nankai University, Tianjin300071, PR China

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ABSTRACT

Three new 3D transition metal coordination complexes, namely, [Co(Aze)(L)] (**1**), $[Cu(Aze)(L)]_2$ (**2**) and $[Cd(Aze)(L)]\cdot 3H_2O$ (**3**) (Aze = azelaic acid, L = 1,4-bis (1-imidazolyl)-benzene) have been synthesized hydrothermally from the self-assembly of the transition metal ions (M^{2+}) with flexible aliphatic dicarboxylate ligand (Aze) and the rigid bis(imidazole) ligand (L). All complexes display three-dimensional (3D) structures. Complex **1** shows a three-fold interpenetrating 4-connected **dmp** net. Complex **2** shows a noninterpenetrating 4-connected **cds** net. Complex **3** shows the **pcu** net built on 6-connected Cd_2 units and particularly there exists weave-like water chains penetrating the channels of the **pcu** net along *b* direction. Furthermore, thermogravimetric studies of **1**, **2** and **3**, and photoluminescent property of **3** have also been investigated.

The design and synthesis of coordination complexes is now of great interest owing to their intriguing topologies and potential applications in many fields such as gas storage, ion exchange, catalysis and magnetism [1]. In construction of the coordination complexes, the selection of appropriate organic linkers is central to determining the structures of the resulting coordination complexes. It is well known that the carboxylate-containing ligands play an important role in coordination chemistry. And so far, extensive work has been carried out using rigid carboxylate ligands; for example, benzoic acid and its derivative ligands such as 1,4-benzenedicarboxylate and 1,3,5-benzenetricarboxylate, have been extensively employed to construct high-dimensional structures [2,3]. As good carboxylate ligands, the flexible carboxylate ligands have also received considerable attention in the construction of coordination complexes, the flexibility and conformational freedoms of such ligands may produce diverse frameworks with unique structures and useful properties [4].

On the other hand, the ligands containing N-donor such as imidazole, pyridine and their derivatives have also attracted great attention to construct metal–organic complexes [5]. The rigid 1,4-bis(1-imidazolyl)-benzene (L) ligand, as good N-donor ligand, has already proven a certain ability to give interpenetrating networks in our previous works [6]. And several other complexes based on L and polycarboxylate ligands have also been reported [7]. Upon careful inspection of such reported complexes, most of them are focused on the metal–L–aromatic polycarboxylate system; by contrast, the exploration of metal–L–flexible polycarboxylate system is less documented [7e,8]. In our recent work, we have reported three 2D metal–L–Pim complexes with helical chains using flexible pimelic acid with L ligand [8]. In this work, we use the longer azelaic acid instead of pimelic acid (Pim) with rigid L ligand to construct complexes. Three metal–L–Aze complexes are sucessfully prepared under the hydrothermal conditions, [Co(Aze)(L)] (**1**), $[Cu(Aze)(L)]_2$ (**2**) and $[Cd(Aze)(L)]\cdot 3H_2O$ (**3**). Interestingly, compared to the three 2D structures of metal–L–Pim complexes, the three metal–L–Aze complexes all display 3D structures which can be attributed to the longer length of the Aze acid than Pim acid. The syntheses, structures, thermal and photoluminescent studies in detail are listed below.

The purple block-shaped crystals of complex **1** were prepared by the reaction of $Co(NO_3)_2\cdot 6H_2O$ with Aze and L in a 1:1:1 molar ratio under hydrothermal conditions [9]. Single crystal X-ray analysis [10] reveals that complex **1** crystallizes in the orthorhombic space group *P*nna. In the asymmetric unit, there are half a Co^{2+} ion, half an Aze^{2-} anion and half an L ligand. As shown in Fig. 1a, the Co(II) ion is coordinated by four oxygen atoms of two Aze^{2-} anions and two nitrogen atoms of two L molecules to give the distorted CoO_4N_2 octahedral geometry. The Co–O/N bond lengths in the range of 2.089(3)–2.253(3) Å (Table S1) are comparable with the normal Co–O/N bond lengths. Each completely deprotonated Aze^{2-} anion connects two Co(II) centers with the μ_2–η^2:η^2 coordinated mode (Scheme 1, I), and each L connects two Co(II) centers in the *trans* fashion with the two imidazole rings being almost coplanar (dihedral angle = 0.36°). The Co(II) ions are connected by the two types of ligands into a 3D framework with Co···Co separation of 11.929(3) Å and 13.413(2) Å, respectively. (Fig. 1b). From the topological view, the Aze^{2-} and L ligands can be regarded as the linear two-connected linker, each Co atom is linked by two Aze^{2-} anions and two L ligands with the same ligands arranging on the same side, so it can be considered as the four-connected node, the 3D framework can be simplified into a

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* Corresponding author. Tel./fax: +86 22 23508056.
E-mail address: jmzheng@nankai.edu.cn (J.-M. Zheng).

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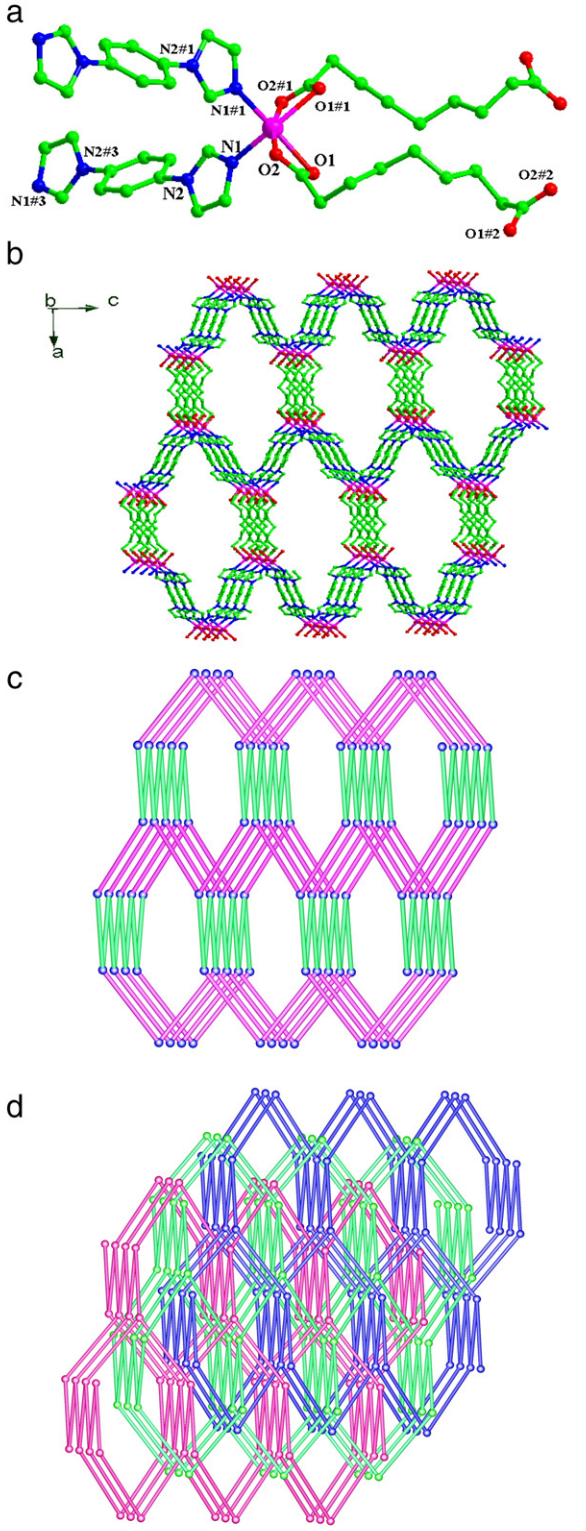
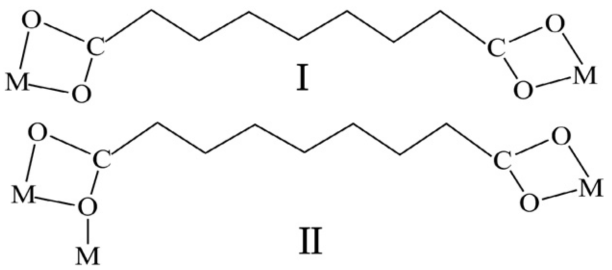


Fig. 1. (a) The immediate coordination environment around the Co(II) center in **1**, symmetry code: #1 = x, 0.5 − y, 1.5 − z; #2 = 1.5 − x, −y, z; 3# = −x, 1 − y, 1 − z; (b) the 3D framework of **1** viewed along *b* direction; (c) schematic description of the 4-connected $(6^5{\cdot}8)$ **dmp** net of **1**. Aze, green; L, pink. (d) The schematic view of 3-fold interpenetrating **dmp** net of **1**.



Scheme 1. Coordination modes of Aze^{2-}.

uninodal four-connected **dmp** net with Point Schläfli symbol of $(6^5{\cdot}8)$ and extended Schläfli symbol of $6{\cdot}6{\cdot}6{\cdot}6{\cdot}6_2{\cdot}8_3$ (Fig. 1c). The 4-connected nets such as **dia**, **cds**, **qtz** nets are very common, while **dmp** net is rare in coordination complexes [11]. Moreover, the 3D framework constructed from long Aze^{2-} and L ligands has a large enough vacancy to allow the inclusion of another two identical 3D frameworks. Therefore, the overall structure of **1** is a three-fold interpenetrating **dmp** net (Fig. 1d).

Complex **2** crystallizes in the triclinic space group *P*-1. In the asymmetric unit, there are two types of Cu^{2+} ions with the occupancy of 0.5, one independent Aze^{2-} anion and one independent L ligand. From Fig. 2a, both the Cu1 and Cu2 atoms are coordinated by four Aze^{2-} oxygen atoms and two L nitrogen atoms to give the distorted CuO_4N_2 octahedral geometry. The Cu–O/N bond lengths are in the range of 1.9541(14)–2.6560(18) Å. The completely deprotonated Aze^{2-} ligands and L ligands display the same coordinated modes as those in **1**. The L ligands also exhibit *trans* fashion with the two imidazole rings being almost coplanar (dihedral angle = 0.00° and 0.26°). However, the arrangement of the two types of ligands around the metal center are different from that in **1**, the same ligands arrange in the two sides of the Cu center in complex **2**. Thus a different 3D framework is constructed (Fig. 2b). From the topological view, the 3D framework of **2** also represents a uninodal four-connected net with the same Point Schläfli symbol of $(6^5{\cdot}8)$ but different extended Schläfli symbol of $6{\cdot}6{\cdot}6{\cdot}6{\cdot}6_2{\cdot}8_\infty$ (Fig. 2c). Such topology is assigned to **cds** net which is obviously different from that of **1**. The reason why such difference can be related to the different arrangement of the two types of ligands around the metal center.

Complex **3** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of one independent Cd(II) ion, one Aze^{2-} anion, one L ligand and three free water molecules. As shown in Fig. 3a, the Cd(II) ions are coordinated by five Aze^{2-} oxygen atoms and two L nitrogen atoms to give the distorted CdO_5N_2 pentagonal bipyramid geometry. The Cd–O/N bond lengths are in the range of 2.271(5)–2.502(5) Å. The completely deprotonated Aze^{2-} ligands adopt the μ_3–η^3:η^2 coordinated mode (Scheme 1, II). The L ligands exhibit *trans* fashion with the two imidazole rings being nearly coplanar (dihedral angle = 6.74°). Two adjacent Cd(II) ions are bridged by carboxyl group into the Cd_2 units with Cd···Cd distance of 3.794(4) Å. Each Cd_2 unit is connected with six identical Cd_2 units via four single Aze^{2-} bridges along *b* and *c* direction and two double L bridges along *a* direction, finally forming a 3D framework (Fig. 3b) which displays a 6-connected **pcu** net with $(4^{12}{\cdot}6^3)$ topology symbol (Fig. 3c). Although lots of complexes with **pcu** net have been reported, they all contain one kind of edge (all single or all double) [12], while this unusual **pcu** net contains both single and double edges. More interestingly, the three free water molecules are connected by O–H···O hydrogen bonds (Table S2) and short O···O contacts into 1D weave-like water chain penetrating the channels of the 3D framework along *b* direction (Fig. 3d) (O5···O6 2.768(5) Å, O6···O7 2.802(1) Å, O7···O5A 2.745(3) Å). The free water molecules occupy the space with a total volume of 375.0 $Å^3$ estimated by Platon [13], which represents 15.6% of the cell volume. The water chains are connected with the host framework by the O–H···O hydrogen bonds between the water molecules and the carboxyl groups of Aze^{2-} (Table S2), which further stablize the 3D structure of **3**.

Comparing the structures of the three metal–L–Aze complexes with those of our recent reported metal–L–Pim complexes [8], only the

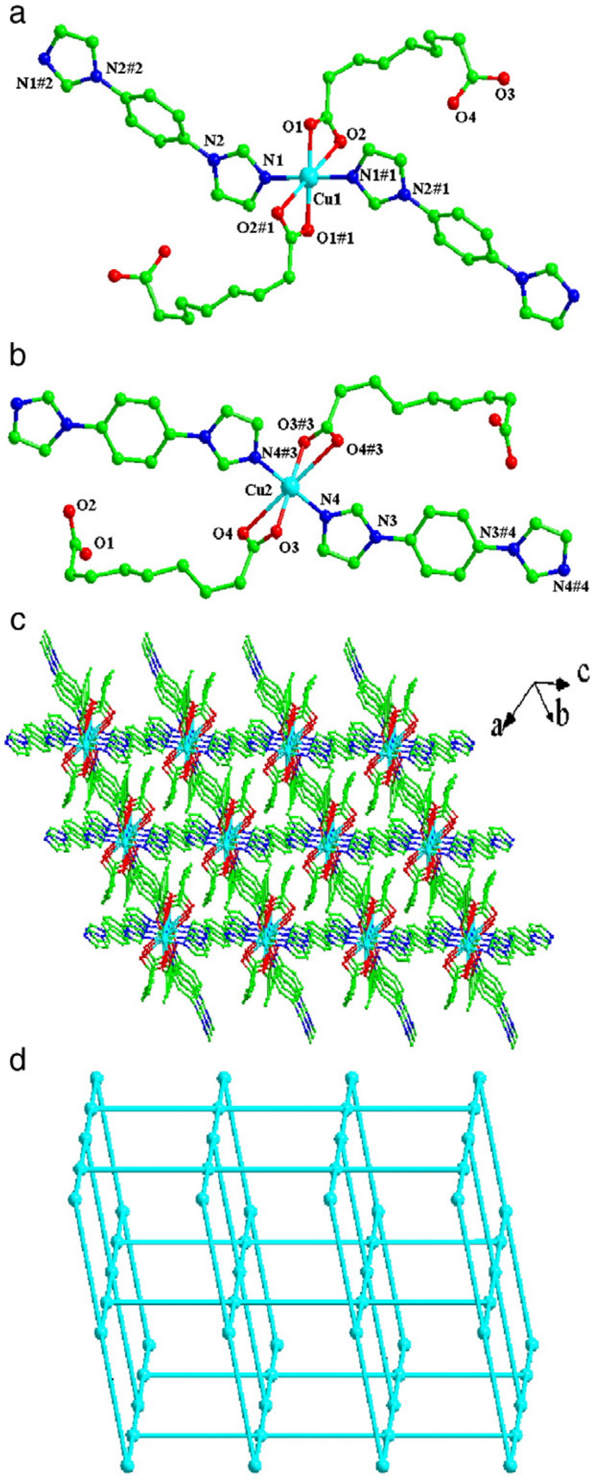


Fig. 2. (a) and (b) The immediate coordination environment around the Cu(II) center in **2**, symmetry code: #1 = 1 − x, 1 − y, −z; #2 = −x, 1 − y, −1 − z; 3# = 2 − x, −y, 1 − z; 4# = 3 − x, −1 − y, 1 − z; (c) the 3D framework of **2**; (d) schematic description of the 4-connected $(6^5{\cdot}8)$ **cds** net of **2**.

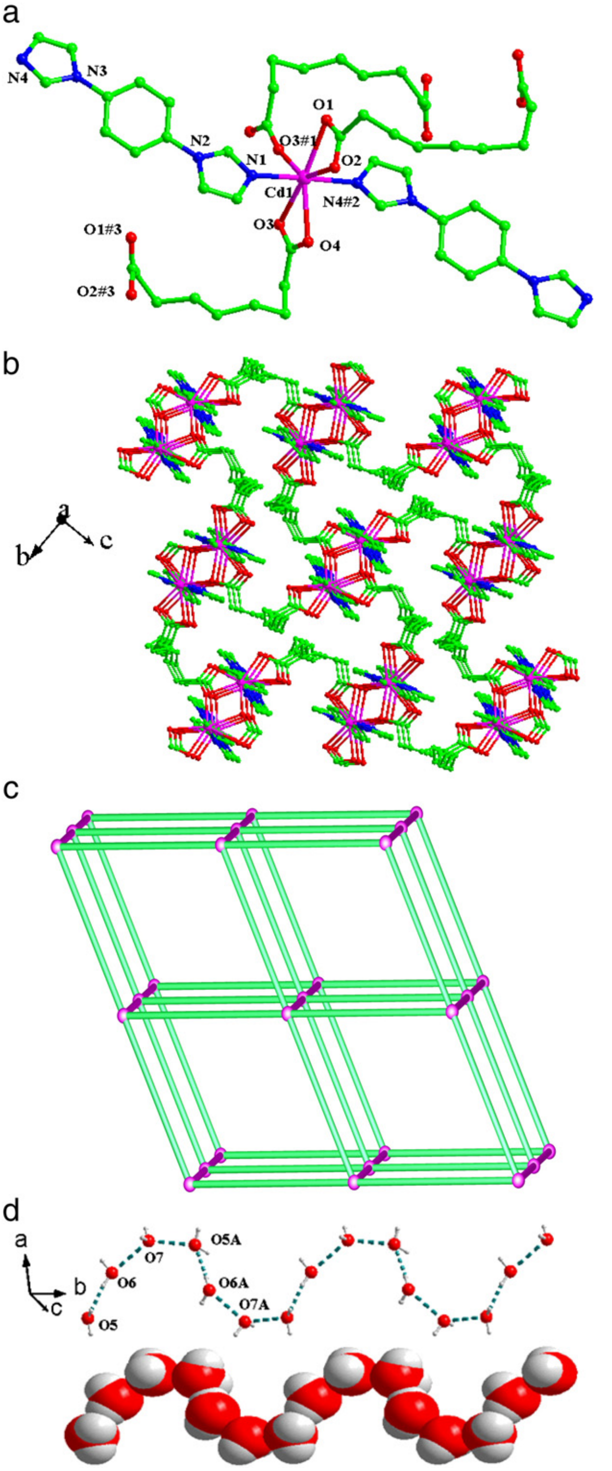


Fig. 3. (a) The immediate coordination environment around the Cd(II) center in **3**, symmetry code: #1 = 2 − x, −y, 1 − z; #2 = 1 + x, y, z; 3# = x, 0.5 − y, 0.5 + z; (b) the 3D structure of complex **3**. (c) The 3D 6-connected **pcu** net with $(4^{12}{\cdot}6^3)$ topology of **3**. Aze, green; L, pink. (d) The 1D weave-like water chain in **3**.

flexible dicarboxylate acid is changed from pimelic to azelaic acid, the final dimension of the complexes becomes 3D from 2D. In our reported metal–L–Pim complexes, all consist of left- and right-handed helical chains, while no helical chains can be observed in the metal–L–Aze complexes of this work. Therefore, it is evident that the different lengths of the flexible dicarboxylate ligands (Pim and Aze) play a significant role in determining the structures of the two groups of complexes.

To study the stability of the three complexes, thermogravimetric analysis (TGA) was performed on the single crystal samples of the three complexes under N_2 atmosphere with a heating rate of 5 °C/min. As shown in Fig. S1, complex **1** shows no weight loss until the temperature reaches 303 °C, and after that, it begins to chemically decompose, it does not decompose completely until 800 °C. For complex **2**, it can be stable up to 245 °C, and above that a rapid weight loss occurred,

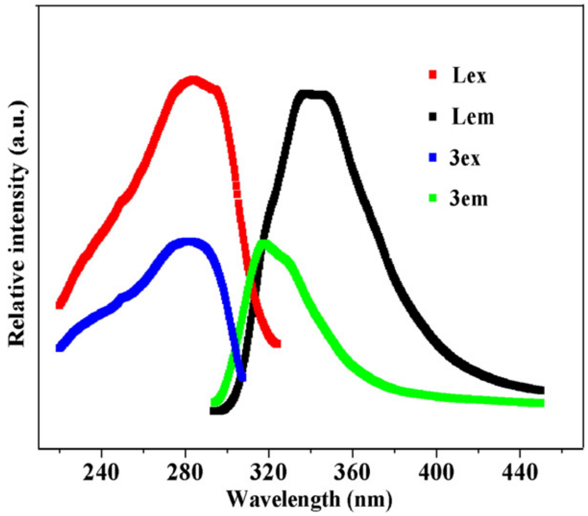


Fig. 4. Excitation (left) and emission (right) spectra of **3** and L ligand.

corresponding to the decomposition of the organic ligands, after 354 °C, it shows slow weight loss without completely decomposing until 800 °C. For complex **3**, it shows a weight loss of 9.43% from 30 °C to 125 °C, corresponding to the loss of three free water molecules (calcd. 9.59%), and there is almost no weight loss from 125 °C to 285 °C; and after that, a rapid weight loss is observed which is attributed to the decomposition of the organic ligands. And finally, the remnants are 22.87%, which should be CdO (calcd. 22.81%).

In recent years, the photoluminescent properties of many d^{10} metal coordination complexes have been studied, and the studies reveal that their luminescence behaviors are closely associated with the central metal ions and the ligands coordinated with them [14]. Herein, photoluminescent properties of Cd-containing complex **3** and the free ligands were performed at room temperature in the solid state. The emission band for the free rigid L ligand is demonstrated at 337 nm ($\lambda_{ex}=281$ nm) which can be assigned to the ligand-centered $\pi\rightarrow\pi^*$ transition of the benzene-imidazole rings [15], whereas the flexible dicarboxylate ligand (Aze) is non-luminescent. As shown in Fig. 4, complex **3** exhibits the emission peak at 318 nm when it was excited at 281 nm, which is similar with that observed in complex [Cd(Pim)(L)] [8]. The integral spectra of complex **3** have similar characteristics to the free L ligand, therefore, the emission of **3** should be assigned as the ligand-centered $\pi\rightarrow\pi^*$ transition of the benzene-imidazole rings. The slight shift of the emission peaks should be ascribed to the coordination action of the L ligands and carboxylate anions to Cd(II) ions. The weaker luminescence intensity for **3** relative to the L ligand may be attributed to the formation of hydrogen bonds for the free water molecules. Fluorescent quenching by hydrogen bonds formation is normally found in supramolecular chemistry [16]. Another reason is the flexibility of Aze ligand coordinated to the Cd(II) center, which increases the flexibility of the overall framework and reduces the nonradiative decay [17].

In summary, three novel metal–organic complexes based on flexible Aze acid and rigid bis(imidazole) ligand (L) have been synthesized under hydrothermal conditions and structurally characterized. This work further enriches the coordination chemistry of flexible dicarboxylate with rigid L ligands. The three complexes all display 3D structures. Complexes **1** and **2** show similar 4-connected ($6^5\cdot8$) net as 3-fold interpenetrating **dmp** net and noninterpenetrating **cds** net, respectively, the reason for the difference can be attributed to the different arrangements of the two types of ligands around the metal centers. Complex **3** displays a **pcu** net with both single and double edges containing the weave-like water chains along the *b* direction. Furthermore, by comparison of the metal–L–Aze complexes with our recent reported metal–L–Pim complexes, it indicates that the different lengths of Pim and Aze ligands play a significant role in constructing the novel structures.

Acknowledgements

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Appendix A. Supplementary data

CCDC-883021-883023 contain the supplementary crystallographic data for **1**–**3**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Additional thermogravimetric curves of **1**–**3**, materials and measurements, selected bonds data are available as electronic supplementary information in the online version, at http://dx.doi.org/10.1016/j.inoche.2012.07.012.

Appendix B. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.07.012.

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[9] Synthesis of **1**: a mixture of $Co(NO_3)_2\cdot 6H_2O$ (145 mg, 0.5 mmol), Aze (94 mg, 0.5 mmol), L (105 mg, 0.5 mmol) was dissolved in 8 mL distilled water. The pH value was adjusted to 6.0 with 1 M NaOH solution. The resulting mixture was sealed in a 25 mL teflon-lined stainless steel vessel and heated at 160 °C for 3 days in an oven and then slowly cooled to room temperature. Purple block-shaped crystals of **1** were obtained in 62% yield (based on Co). Elemental analysis(%): Calcd. for (1): C 55.39, H 5.31, N 12.30. Found: C 55.32, H 5.37, N 12.35. IR (KBr): ν (cm^{-1}) = 3090.22(w) 2924.75(w) 2852.10(w) 1557.14(s) 1532.62(s) 1419.69(m) 1307.62(w) 1275.12(w) 1251.67(w) 1128.82(w) 1069.87(m) 960.52(m) 834.93(m) 737.03(w) 661.19(w) 538.24(w). Synthesis of **2**: Similar procedures to complex **1** were performed except that $Co(NO_3)_2\cdot 6H_2O$ was replaced by $Cu(NO_3)_2\cdot 4H_2O$ (122 mg, 0.5 mmol). Blue block-shaped crystals of **2** were obtained in 76% yield (based on Cu). Elemental analysis(%): Calcd. for (**2**): C 54.83, H 5.26, N 12.18. Found: C 54.87, H 5.20, N 12.12. IR (KBr): ν (cm^{-1}) = 3101.77(w) 2926.02(w) 2851.51(w) 1572.00(s) 1527.32(s) 1498.16(w) 1399.95(m) 1305.83(m) 1266.82(w) 1238.64(w) 1142.78(w) 1061.80(m) 959.98(m) 835.21(m) 654.04(w). Synthesis of **3**: Similar procedures to complex **1** were performed except that $Co(NO_3)_2\cdot 6H_2O$ was replaced by $Cd(NO_3)_2\cdot 4H_2O$ (154 mg, 0.5 mmol). Colourless needle-like crystals of **3** were obtained in 54% yield (based on Cd). Elemental analysis(%): Calcd. for (**3**): C 44.81, H 5.37, N 9.95. Found: C 44.87, H 5.31, N 9.99. IR (KBr): ν (cm^{-1}) = 3406.91(w) 3120.02(w) 2930.00(w) 2855.30(w) 1533.50(s) 1411.82(s) 1307.13(m) 1247.47(w) 1134.13(w) 1068.50(m) 961.07(m) 840.98(w) 646.25(w).

[10] Suitable single crystals of **1** to **3** were selected and mounted in air onto thin glass fibers. Accurate unit cell parameters of the three complexes were determined by a least-squares fit of 2θ values, and intensity data were measured on a Rigaku r-axis rapid IP area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 113 K. The intensity was corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan technique. The structures were solved by direct method and refined by full-matrix least-squares fitting on F^2 with the program SHELXL-97. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms bound to carbon atoms were calculated theoretically and those to oxygen atoms were determined by difference Fourier maps. Crystal data for **1**: $C_{21}H_{24}CoN_4\ O_4$, $Mr = 455.37$, orthorhombic, space group *P*nna, $a = 13.648(3)$ Å, $b = 11.245(2)$ Å, $c = 14.040(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2154.7(8)$ Å^3, $Z = 4$, $D\mathrm{c} = 1.404$ g/cm^3, $F(0\ 0\ 0) = 948$, $S = 1.062$, final $R_1 = 0.0722$, $\omega R_2 = 0.2019$. Crystal data for **2**: $C_{42}H_{48}Cu_2N_8O_8$, $Mr = 919.98$, triclinic, space group *P*-1, $a = 8.3461(17)$ Å, $b = 10.412(2)$ Å, $c = 12.667(3)$ Å, $\alpha = 102.85(3)°$, $\beta = 104.83(2)°$, $\gamma = 90.14(3)°$, $V = 1035.4(4)$ Å^3, $Z = 1$, $D\mathrm{c} = 1.475$ g/cm^3, $F(0\ 0\ 0) = 478$, $S = 1.007$, final $R_1 = 0.0476$, $\omega R_2 = 0.1204$. Crystal data for **3**: $C_{21}H_{30}CdN_4O_7$, $Mr = 562.89$, monoclinic, space group $P2_1/c$, $a = 13.875(3)$ Å, $b = 12.242(2)$ Å, $c = 18.408(6)$ Å, $\alpha = \gamma = 90°$, $\beta = 129.934\ (18)°$, $V = 2397.5(10)$ Å^3, $Z = 4$, $D\mathrm{c} = 1.559$ g/cm^3, $F(0\ 0\ 0) = 1152$, $S = 1.009$, final $R_1 = 0.0674$, $\omega R_2 = 0$.

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