Available online at www.sciencedirect.com
SCIENCE DIRECT®

Inorganic Chemistry Communications 8 (2005) 708–712

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Syntheses, crystal structures and magnetic properties of two new 3-cyanobenzate coordination complexes

Yan Li [a,b], A-Qing Wu [a], Fa-Kun Zheng [a,*], Ming-Lai Fu [a,b],
Guo-Cong Guo [*,a], Jin-Shun Huang [a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Yangqiao West Road 155, Fuzhou, Fujian 350002, People's Republic of China
[b] Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received 24 March 2005; accepted 7 May 2005
Available online 16 June 2005

Abstract

Two new 3-cyanobenzate complexes, $[Cu(3\text{-cba})_2(Py)(H_2O)]_n$ **1** and $[Cd(3\text{-cba})_2(Py)_2(H_2O)]$ **2** (3-cba = 3-cyanobenzate, Py = pyridine), were synthesized and structurally characterized by single-crystal X-ray diffraction. Three different coordination modes of 3-cba group exist in the two obtained complexes, which results in different molecular architectures: **1** with a 1-D chained structure and **2** with an isolated configuration. Variable-temperature magnetic susceptibility data show the presence of antiferromagnetic interactions in **1**.

Keywords: 3-Cyanobenzate complex; Crystal structure; Magnetic properties; Hydrogen bonds; π–π Stacking

Carboxylate coordination complexes have been extensively investigated in past decades because of their excellent coordination capability and the possibility of offering new functional materials [1,2]. Especially, aromatic carboxylate coordination complexes, possessing special physical properties and intriguing structural features [2–4], have attracted increasing interest. Cyanobenzate compounds having two functional coordination groups can be used to bind metal atoms and should exhibit versatile coordination modes. However, only carboxylate group participates in coordination in most of the reported cyanobenzate complexes [5–15]. So far the unique example of cyanobenzate complex has been obtained with both carboxylate and cyano groups bound to the metal atoms [16]. Furthermore the magnetic properties of cyanobenzate complexes have not ever been investigated. Herein, we report syntheses and crystal structures of two new 3-cyanobenzate complexes, a coordination polymer $[Cu(3\text{-cba})_2(Py)(H_2O)]_n$ **1** showing antiferromagnetic behaviour, a second instance in which two functional coordination groups of 3-cba ligand are both involved in coordination, and an isolated mononuclear complex $[Cd(3\text{-cba})_2(Py)_2(H_2O)]$ **2**.

The blue prism crystals of **1** were obtained via solution synthetic methods [17]. However, the colorless prism crystals of **2** were yielded via solvent-thermal route [18]. The structures of **1** and **2** were determined by single-crystal X-ray diffraction analyses [19].

As shown in Fig. 1(a), the structure of **1** consists of a 1-D coordination polymer with a basic unit $[Cu(3\text{-cba})_2(Py)(H_2O)]$. The coordination environment around the Cu(II) atom can be described as a distorted square-pyramid, with the equatorial positions occupied by two carboxylate O atoms from two different 3-cba ligands

---

[*] Corresponding author. Tel.: +86 591 8370 4827/5054; fax: +86 591 8371 4946
E-mail address: zfk@ms.fjirsm.ac.cn (F.-K. Zheng).

1387-7003/$ - see front matter
doi:10.1016/j.inoche.2005.05.008

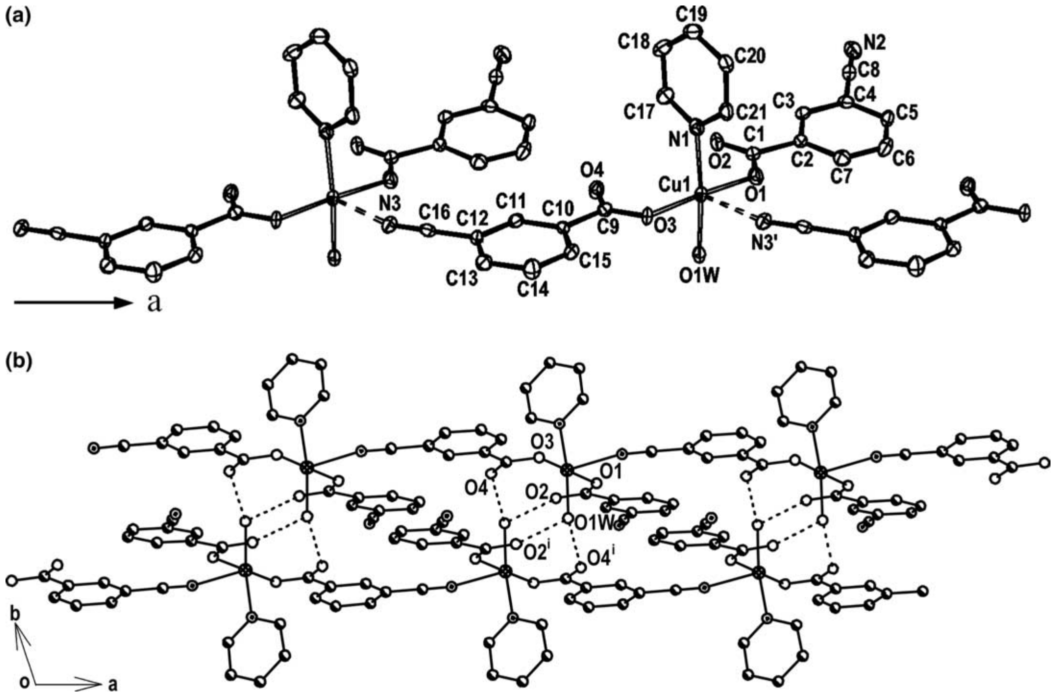

Fig. 1. (a) Structure of **1** with 50% probable thermal ellipsoid. The dashed lines show the weak coordination between Cu(1) and N(3′). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu(1)–O(1), 1.921(3); Cu(1)–O(3), 1.929(3); Cu(1)–O(1W), 1.973(3); Cu(1)–N(1), 2.018(3); Cu(1)–N(3′), 2.442(3); N(2)–C(8), 1.140(5); N(3)–C(16), 1.140(5); O(1)–Cu(1)–O(3), 176.75(11); O(1)–Cu(1)–O(1W), 88.54(11); O(3)–Cu(1)–O(1W), 89.73(11); O(1)–Cu(1)–N(1), 89.71(12); O(3)–Cu(1)–N(1), 92.49(12); O(1W)–Cu(1)–N(1), 169.27(12); O(1)–Cu(1)–N(3′), 82.37(12); O(3)–Cu(1)–N(3′), 95.04(11); O(1W)–Cu(1)–N(3′), 95.08(11); N(1)–Cu(1)–N(3′), 95.17(12). (Symmetry code′: $1 + x, y, z$). (b) A double-chained structure of **1** connected by hydrogen bonds. Hydrogen atoms are omitted for clarity. (Symmetry code^{i}: $1 - x, -y, 1 - z$).

(Cu(1)–O(1) = 1.921(3) Å and Cu(1)–O(3) = 1.929(3) Å), one pyridine N atom (Cu(1)–N(1) = 2.018(3) Å), and one water O atom (Cu(1)–O(1W) = 1.973(3) Å). The Cu–O and Cu–N$_{\text{(equatorial)}}$ distances are similar to those in the reported complexes [14,20]. The apical position is occupied by one cyano N atom of 3-cba bridging ligand with a long Cu(1)–N(3′) distance of 2.442(3) Å due to the *Jahn–Teller* effects of Cu(II) ions with a d^{9} electron configuration (Symmetry code′: $1 + x, y, z$). It is noteworthy that the C–N distances of cyano groups of the two 3-cba ligands are almost equal (mean value of the C–N distances: 1.140 Å), indicating that the C(16)–N(3) bond still bears the characteristic of triple bond. Meanwhile, the cyano stretching vibration v(C$\equiv$N) occurs at the almost same frequency as that recorded for the free 3-Hcba ligand (see Fig. S1). This can be concluded by the matter that the Cu atom bonds to the N atom of cyano group with its lone electronic pair (mainly contributed by 2s^{2}) and the triple bond C$\equiv$N is almost unperturbed. The most interesting structural feature of **1** is the coordination modes of 3-cba ligands. One acts as a terminal ligand with the carboxylate O atom accomplishing the coordination of the Cu(II) atom. The other serves as a bridging ligand linking the neighboring copper(II) atoms by the unidentated carboxylate O atoms and cyano N atoms to form an infinite chain along the *a*-axis, which is obviously different from the situation in the first reported complex also with both carboxylate and cyano groups coordinating the metal atoms [16]. In the latter, carboxylate groups of 3-cba ligand display a bridging bis-monodentate coordination mode, bringing on dinuclear metals, which is further linked by carboxylate O atoms and cyano N atoms of 3-cba ligands in pairs to form infinite intersect double-chains. Notably, the carboxylate group O(1)C(1)O(2) is not coplanar with the corresponding aromatic ring [dihedral angles 7.01(43)°], while the carboxylate group O(3)C(9)O(4) and the aromatic ring of the other 3-cba ligand constitute reasonably good plane (maximum deviation of atoms: 0.0250(23) Å).

In **1** the two adjacent chains are further connected by O–H· · ·O hydrogen bonds to give an infinite double-chain with the distances O(1W)· · ·O(2^{i}) = 2.680(4) Å and O(1W)· · ·O(4^{i}) = 2.722(4) Å, and the angles O(1W)–H(1WB)· · ·O(2^{i}) = 154(4)° and O(1W)–H(1WA)· · ·O(4^{i}) = 171(4)° (Symmetry code^{i}: $1 - x, -y, 1 - z$), as depicted in Fig. 1(b). The pyridine ligands are located on the two sides of the double-chain. The nearest separation of Cu(II)· · ·Cu(II) in interchains (4.6827(16) Å) is much shorter than that in intrachains (10.327(4) Å), which are obviously longer than that in the presented complex (2.664(2) Å) [16].

The complex **2** has a crystallographic two-fold axis passing through the Cd(II) and water O atoms, as illustrated in Fig. 2(a). The cyano group of 3-cba remains uncoordinated and the carboxylate group adopts a chelating bidentate fashion. The Cd atom is seven-coordinated with four carboxylate O atoms from two 3-cba ligands, one water O atom and two pyridine N atoms. The coordination geometry around the Cd atom may be described as a distorted pentagonal bipyramid. The O(1), O(2), O(1′), O(2′) and O(1W) atom all lie close to a plane with a maximum deviation of atoms 0.0589(13) Å, while the axial positions are occupied by N(1) and N(1′) atoms with axial angle N(1)–Cd(1)–N(1′) of 169.54(8)° as opposed to the ideal angle of 180° (Symmetry code′: 1 − *x*, *y*, 3/2 − *z*). The Cd–$O_{(3-\mathrm{cba})}$ distances of 2.3953(13) and 2.4680(14) Å, which are longer than those of Cd(1)–N(1) (2.3384(16) Å) and Cd(1)–O(1W) (2.281(2) Å). The carboxylate group is not coplanar with the aromatic ring in the 3-cba ligand [dihedral angles 11.23(19)°].

Besides covalent forces in **2**, supermolecular interactions also play an important role in crystal packing as

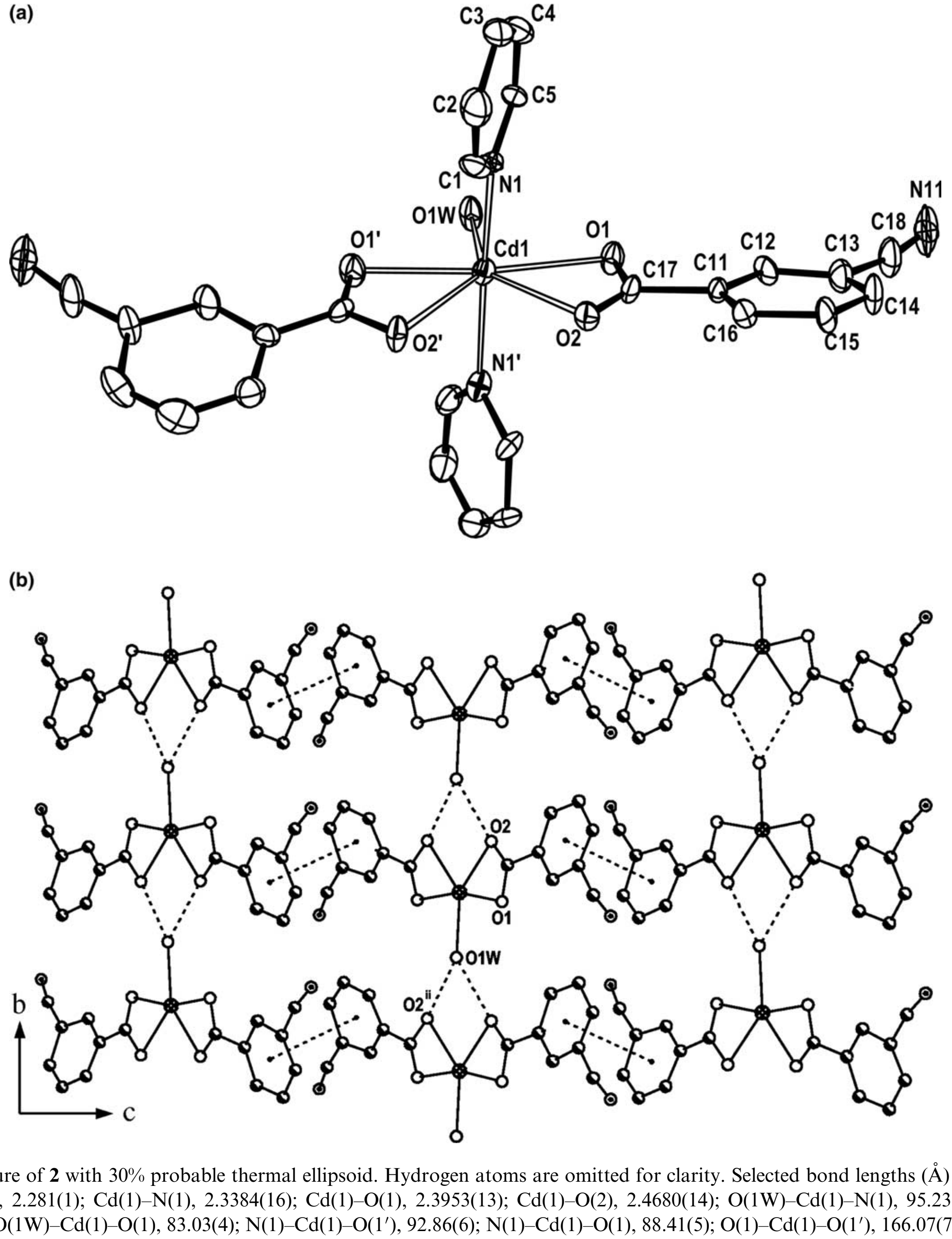

Fig. 2. (a) Structure of **2** with 30% probable thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cd(1)–O(1W), 2.281(1); Cd(1)–N(1), 2.3384(16); Cd(1)–O(1), 2.3953(13); Cd(1)–O(2), 2.4680(14); O(1W)–Cd(1)–N(1), 95.23(4); N(1)–Cd(1)–N(1′), 169.54(8); O(1W)–Cd(1)–O(1), 83.03(4); N(1)–Cd(1)–O(1′), 92.86(6); N(1)–Cd(1)–O(1), 88.41(5); O(1)–Cd(1)–O(1′), 166.07(7); O(1W)–Cd(1)–O(2), 136.79(3); N(1)–Cd(1)–O(2), 82.59(5); N(1)–Cd(1)–O(2′), 89.77(5); O(1)–Cd(1)–O(2′), 140.10(5); O(1)–Cd(1)–O(2), 53.82(5); O(1W)–Cd(1)–O(2′), 136.79(3); O(2)–Cd(1)–O(2), 86.43(6). (Symmetry code′: 1 − *x*, *y*, 3/2 − *z*). (b) View of the layer structure formed by isolated molecules of **2** linked through hydrogen bonds π–π stacking interactions to give a 2-D structure. The atoms of the Py rings and hydrogen atoms have been omitted for clarity.

in **1**. Intermolecular hydrogen bonds occur via the carboxylate groups and coordinated water molecules with the distances O(1W)···O(2^{ii}) of 2.755(2) Å and the angles O(1W)–H(1WA)···O(2^{ii}) of 154(2)° (Symmetry code^{ii}: $1 - x$, $-1 + y$, $3/2 - z$), resulting in a 1-D chain parallel to the *b*-axis. Furthermore, the adjacent chains are connected via π–π stacking interactions between the aromatic groups of 3-cba, with a centroid-to-centroid distance of 3.77 Å, giving a 2-D network parallel to the *bc* plane, as shown in Fig. 2(b) The nearest Cd(II)···Cd(II) distance is 6.2547(5) Å through hydrogen bonds, much shorter than the value of 12.1449(9) Å through π–π stacking interactions.

Variable-temperature magnetic behavior of **1** is plotted in Fig. 3. For **1**, a non-linear fit $\chi_M = C/(T - \theta) + \chi_0$ above 20 K reveals a Curie-Wesis behavior with the Curie constant $C = 0.361(2)\ \mathrm{cm^3\,mol^{-1}\,K}$, the Weiss constant $\theta = -5.2(1)$ K, and background susceptibility $\chi_0 = -7.7(1) \times 10^{-4}\ \mathrm{cm^3\,mol^{-1}}$. The χ_M value increases with decreasing the temperature, reaching a maximum of 0.02 $\mathrm{cm^3\,mol^{-1}}$ at around 8.5 K, and then decreases very quickly. The value of $\chi_M T$ is 0.367 $\mathrm{cm^3\,mol^{-1}\,K}$ at room temperature, which is somewhat smaller than the value (0.38 $\mathrm{cm^3\,mol^{-1}\,K}$) expected for a non-interacting Cu(II) ion. On lowering the temperature, the value of$\chi_M T$ decreases smoothly until approximately 50 K and then decreases at a faster rate, reaching a value of 0.043 $\mathrm{cm^3\,mol^{-1}\,K}$ at 2 K. This is characteristic of significant antiferromagnetic ordering ($T_N = 8.5$ K).

According to the structure of **1**, two possible magnetic exchange coupling pathways are taken into consideration: one is via hydrogen bonds and the other through 3-cba ligands. Since the shorter interchained Cu···Cu distance (4.6827(16) Å) connected by hydrogen bonds is less than half of the intrachained Cu···Cu distance (10.327(4) Å) bridged by 3-cba groups, sizable magnetic exchange interactions would occur in interchains. Actually, the magnetic behavior is well interpreted based on the modified analytical expression [21], which is derived from the Fisher classical Heisenberg model [22] for infinite linear chains. By using a least-squares method, a very satisfactory fit of the data at 20–300 K was obtained using the set of parameters of $J = 5.29\ \mathrm{cm^{-1}}$, $g = 1.95$, and $J = -15.61\ \mathrm{cm^{-1}}$ with $R = 1.2 \times 10^{-4}$. The positive J parameter may be assigned to the intrachained ferromagnetic exchange interactions and the negative J' value to the interchained antiferromagnetic exchange interactions. Certainly, the shorter interchained Cu···Cu distance generates a stronger magnetic interactions, which dominate the overall magnetic behavior in **1**. On the basis of this model, the antiferromagnetic interactions are present in **1**, in line with the minus sign of the Weiss constant values, similar to those of the 1-D copper (II) complexes bridged by terephthalato dianions [23].

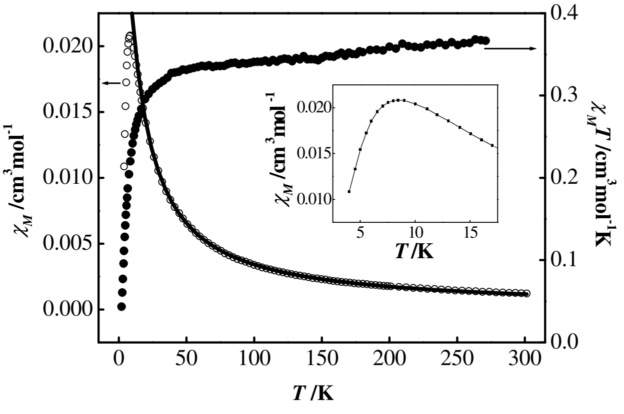

Fig. 3. Temperature dependence of χ_M and $\chi_M T$ for **1** with the solid line showing the best fit obtained through χ_M values. Inset: low temperature region of χ_M.

Thermogravimetric analyses (TGA) show that **1** and **2** undergo different thermal decomposition process, as demonstrated in Figs. S2 and S3. The TGA curve of **1** reveals that the dehydration of one coordinated water molecule occured in the range 108–128 °C with a weight loss of 4.05% (calcd. 3.98%); then the loss of pyridine ligands followed in the temperature range 128–187 °C with the weight loss of 17.19% (calcd. 17.47%). The decomposition process of the 3-cba ligand occured above 360 °C and heating to 600 °C gave black solid reside which is likely to be CuO with the weight loss of ca. 82.81%, close to the theoretical value of 82.45%. However, when **2** were heated, the weight loss of 29.41% was observed from 99 to 318 °C, which is attributed to the release of both Py and coordinated water molecules (calcd. 30.34%). The decomposition process of the 3-cba ligand began from 318 °C and the final inorganic reside was formed above 463 °C with a weight loss of ca. 41.29%.

In summary, two new 3-cba coordination complexes have been synthesized and structurally characterized. The coordination modes of 3-cba ligands in the two complexes are different from each other, resulting in different structures: **1** with a 1-D chained structure and **2** with an isolated configuration. Variable-temperature magnetic susceptibility data indicate that **1** exhibits antiferromagnetic interactions through hydrogen bonds owing to the shorter distance between the Cu(II) magnetic centers. The thermogravimetric analyses of the two complexes have also been performed.

Acknowledgements

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (20131020) and Natural Sciences Foundation of Fujian Province (2003I031, A0420002).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2005.05.008.

References

[1] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466.

[2] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Scince 295 (2002) 469.

[3] L. Pan, M.B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J.K. Johnson, J. Am. Chem. Soc. 126 (2004) 1308.

[4] M. Eddaudi, J. Kim, J.B. Wachter, H.K. Chae, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 4368.

[5] A. Keys, S.G. Bott, A.R. Barron, Polyhedron 17 (1998) 3121.

[6] B.Q. Ma, S. Gao, Z.M. Wang, T. Yi, C.H. Yan, G.X. Xu, Acta Cryst. C55 (1999) 1420.

[7] F.K. Zheng, X. Zhang, G.C. Guo, J.S. Huang, Chinese J. Struct. Chem. 20 (2001) 391.

[8] R.X. Yuan, R.G. Xiong, Z.F. Chen, X.Z. You, S.M. Peng, G.H. Lee, Inorg. Chem. Commun. 4 (2001) 430.

[9] S.L. Schiavo, F. NicolÒ, G. Tresoldi, P. Piraino, Inorg. Chim. Acta 343 (2003) 351.

[10] H.Y. He, A.Q. Ma, L.G. Zhu, Acta Cryst. E59 (2003) m333.

[11] Y.L. Zhou, H.Y. He, Y. Zhang, L.G. Zhu, Acta Cryst. E59 (2003) m605.

[12] H.Y. He, L.G. Zhu, Acta Cryst. E59 (2003) o174.

[13] H.Y. He, L.G. Zhu, Acta Cryst E59 (2003) m1192.

[14] M.S. Wang, L.Z. Cai, G.W. Zhou, G.C. Guo, J.S. Huang, Inorg. Chem. Commun. 6 (2003) 855.

[15] F.K. Zheng, A.Q. Wu, Y. Li, C.G. Guo, M.S. Wang, Q. Li, J.S. Huang, J. Mol. Struct. 740 (2005) 147.

[16] S. Cueto, P. Rys, H.P. Straumann, Acta Cryst. C18 (1992) 2122.

[17] Synthesis of **1**: a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.3 mmol, 72 mg) and 3-cba (1.2 mmol, 177 mg) in ethanol (15 mL) was stirred thoroughly and pyridine (0.8 mL, 2.5 mmol) was added. The resulting mixture was heated and refluxed for 3 h, then filtered, and the filtrate was left undisturbedly at room temperature. The blue prism crystals of **1** were obtained after a few days. Anal. Calc. for $[Cu(3\text{-cba})_2(Py)(H_2O)]_n$: C, 55.69%; H, 3.34%; N, 9.28%. Found: C, 55.93%; H, 3.53%; N, 9.09%. IR data (KBr): 3436w, 2924m, 2854w, 2232s (ν(CN)), 1630s ($\nu_{asym}(CO_2)$), 1575m, 1488w, 1447m, 1433m, 1386s ($\nu_{sym}(CO_2)$), 1376s ($\nu_{sym}(CO_2)$), 1071w, 1046w, 766s, 696m, 678m, 641w, 565w, 469w, 444w (cm^{-1}).

[18] Synthesis of **2**: a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.5 mmol, 154 mg), pyridine (0.8 mL, 2.5 mmol) and 3-cba (1.0 mmol, 147 mg) in ethanol (10 mL) was sealed in a polyfluoro-ethylene-lined stainless steel bomb, and kept at 100 °C under autogenous pressure for 3 days. After slowly cooling at 1 °C/h to room temperature, the colorless prism crystals of **2** were obtained by filtration and air-dried. Anal. Calc. for $[Cd(3\text{-cba})_2(Py)_2(H_2O)]$: C, 53.46%; H, 3.57%; N, 9.47%. Found: C, 53.71%; H, 3.47%; N, 9.64%. IR data (KBr): 3409br, 2232s (ν(CN)), 1601m, 1591m, 1551vs ($\nu_{asym}(CO_2)$), 1484w, 1443s, 1429s, 1393vs ($\nu_{sym}(CO_2)$), 1215w, 1068w, 1038w, 1013w, 787m, 769s, 701s, 683w, 629w (cm^{-1}). It's evident that the separation between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ frequencies for **1** (av. 249 cm^{-1}) with unidentate coordination mode of carboxylate group is much larger than that for **2** (158 cm^{-1}) with chelating.

[19] Crystal data for **1**: $[Cu(3\text{-cba})_2(Py)(H_2O)]_n$, monoclinic, space group, $P2\bar{1}/n$, $a = 10.328(4)$, $b = 8.082(3)$, $c = 22.896(9)$ Å, $\beta = 93.609(4)°$, $V = 1907.3(13)$ Å^3, $T = 130(1)$ K, $Z = 4$, $M_r = 452.90$, $D_c = 1.577$ g/cm^3, $F(0\,0\,0) = 924$, $\mu = 1.185$ mm^{-1}, $\lambda = 0.71073$ Å, total 14091 reflections ($3.09 \leqslant \theta \leqslant 27.48°$), 4359 unique ($R_{int} = 0.0415$). Structure solution and refinement based on 3599 observed reflections with $I > \sigma(I)$ and 277 parameters gave final $R = 0.0473$, $wR = 0.1596$ and $S = 1.003$. Crystal data for **2**: $[Cd(3\text{-cba})_2(Py)_2(H_2O)]$, monoclinic, space group, $C2/c$, $a = 16.8115(15)$, $b = 6.2547(5)$, $c = 23.8961(18)$ Å, $\beta = 91.103(5)°$, $V = 2512.2(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $M_r = 580.86$, $D_c = 1.536$ g/cm^3, $F(0\,0\,0) = 1168$, $\mu = 0.913$ mm^{-1}, $\lambda = 0.71073$ Å, total 7198 reflects ($3.57 \leqslant \theta \leqslant 24.99°$), 2159 unique ($R_{int} = 0.0208$). Structure solution and refinement based on 2068 observed reflections with $I > \sigma(I)$ and 167 parameters gave final $R = 0.0199$, $wR = 0.0521$ and $S = 1.007$. All of the calculations were performed by the SHELXTL™ 5 program. Crystallographic data in cif format have been deposited in the Cambridge Crystallographic Data Center, CCDC No. 267002 for **1** and 267003 for **2**.

[20] A.F. Cameron, D.W. Taylor, R.H. Nuttall, J. Chem. Soc., Dalton Trans. (1972) 1603.

[21] J.N. McElearney, S. Merchant, R.L. Carlin, Inorg. Chem. 12 (1973) 906.

[22] M.E. Fisher, Am. J. Phys. 32 (1964) 343.

[23] E.G. Bakalbassis, A.P. Bozopoulos, J. Mrozinski, P.J. Rentzeperis, C.A. Tsipis, Inorg. Chem. 27 (1988) 529.