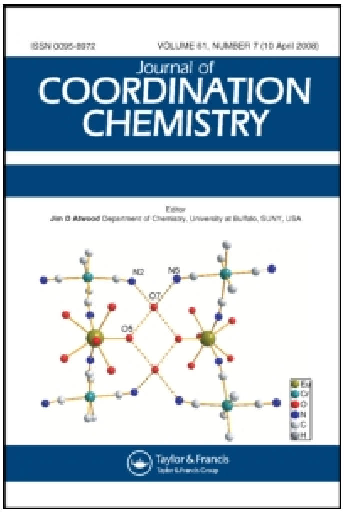

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# Synthesis and crystal structure of a bicadmium(II) cryptate derived from condensation of 2-aminoethyl-bi(3-aminopropyl)amine with sodium 2,6-diformyl-4-methylphenolate

Jian Gao[a]; Xing-You Xu[ab]; Jun Chen[b]; Shu-An Li[b]; Xu-Jie Yang[a]; Lu-De Lu[a]; Xin Wang[a]
[a] Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, P. R. China [b] Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P. R. China

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# SYNTHESIS AND CRYSTAL STRUCTURE OF A BICADMIUM(II) CRYPTATE DERIVED FROM CONDENSATION OF 2-AMINOETHYL-BI(3-AMINOPROPYL)AMINE WITH SODIUM 2,6-DIFORMYL-4-METHYLPHENOLATE

JIAN GAO[a], XING-YOU XU[a,b], JUN CHEN[b], SHU-AN LI[b],
XU-JIE YANG[a], LU-DE LU[a,]* and XIN WANG[a]

[a]*Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, P. R. China;* [b]*Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P. R. China*

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$[Cd_2L](ClO_4)(CH_3OH)$, the first bicadmium(II) cryptate derived from weak nucleophilic addition to $[Cd_2L']$, which was synthesized by [2+3] Schiff-base condensation of 2-aminoethyl-bi(3-aminopropyl)amine (ppe) with sodium 2,6-diformyl-4-methylphenolate (sdmp) in the presence of $Cd(ClO_4)_2 \cdot 6H_2O$, has been synthesized and characterized by single-crystal X-ray diffraction. The complex crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 11.8143(3)$, $b = 13.6117(4)$, $c = 15.9894(4)$ Å, $\alpha = 103.10$, $\beta = 91.6600(10)$, $\gamma = 104.1770(10)°$, $V = 2418.40(11)$ Å$^3$, $F(000) = 1144$, $D_{calc} = 1.536\,g\,cm^{-3}$, $Z = 2$, $R = 0.0749$, $wR = 0.1846$. Cd(1) is in an N4O2 coordination environment and forms a distorted tetragonal bipyramid; Cd(2) lies in an N4O3 coordination environment and possesses a monocapped-octahedral geometry.

*Keywords:* Bicadmium(II) cryptate; Hydrolysis; Crystal structure

## INTRODUCTION

There has been growing interest in macrocyclic chemistry due to strong coordination ability to, and recognition functions for, transition metal ions [1–4]. Macrocyclic ligands provide suitable frameworks and well-defined stereochemical environments for bound metal ions influencing physicochemical properties [5]. Binuclear cadmium(II) Schiff-base macrocyclic complexes involving tris(2-aminoethyl)amine (tren) or tris(2-aminopropyl)amine (trpn) have been reported [6–13]. Most of these complexes are very stable in air and solution. However, there are fewer reports on bicadmium(II) cryptates condensed from an asymmetrical tetraamine. In order to study

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*Corresponding author. Fax: +86-25-84315518. E-mail: mclnjust@sohu.com

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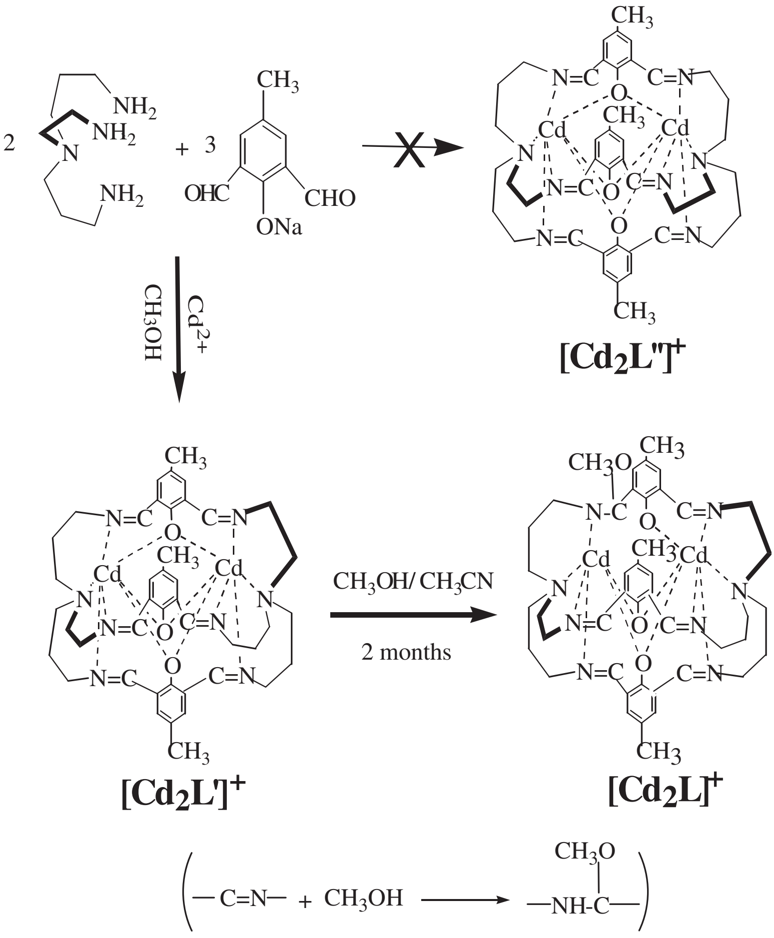

SCHEME 1

the influence of the asymmetrical structure of a tripodal tetraamine on the cryptate's framework, coordination geometry and stability, we synthesized a cryptate condensed from 2-aminoethyl-bi(3-aminopropyl)amine (ppe) and 2,6-diformyl-4-methylphenolate (sdmp) in the presence of $Cd^{2+}$. Two kinds of products, $[Cd_2L']$ and $[Cd_2L'']$, can be obtained in this condensation; however, only $[Cd_2L']$ was found. $[Cd_2L]$ was obtained by nucleophilic addition of methanol to $[Cd_2L']$ and its structure was determined by single-crystal X-ray diffraction. The entire process is shown in Scheme 1.

## EXPERIMENTAL

### Materials and Instrumentation

All starting materials were of chemical purity and the solvents used in the physical measurements were of analytical purity. 2-Aminoethyl-bi(3-aminopropyl)amine and 2,6-diformyl-4-methylphenolate were prepared by methods described in the literature [14,15].

Elemental analysis was performed with a Perkin-Elmer 240c instrument. IR spectra were measured as KBr disks using a Nicolet 5DX FT-IR spectrophotometer. An electronic spectrum was recorded on a Shimadzu UV-240 spectrophotometer. Solution electrical conductivity was measured with a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of *ca* $1.0 \times 10^{-3}$ mol dm$^{-3}$ in acetonitrile. The ES mass spectral measurement was carried out on an LCQ System (Finngann MAT, USA) using acetonitrile and methanol as the mobile phase. The quoted *m*/*z* values represent the major peaks in the isotopic distribution.

### Preparation of $[Cd_2L'](ClO_4)(CH_3OH)$

To a stirred solution of sodium 2,6-diformyl-4-methylphenolate (0.1395 g, 0.75 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (0.2621 g, 0.625 mmol) in 30 cm$^3$ absolute methanol was added dropwise a solution of 2-aminoethyl-bi(3-aminopropyl)amine (0.087 g, 0.5 mmol) in 10 cm$^3$ absolute methanol at 0°C. After stirring for 3 h at 45°C, the yellow product precipitated and was filtered off, washed with methanol and dried in vacuo. Yield 76%. Anal. Calcd. for $C_{44}H_{57}Cd_2ClN_8O_8$(%): C, 48.66; H, 5.25; N, 10.32. Found: C, 48.53; H, 5.12; N, 10.67. ES-MS, *m*/*z* (%): 954.3 (100), 478.3 (92). IR (cm$^{-1}$): 3436s, $\nu$(OH); 1636s, $\nu$(C=N); 1094s, $\nu(ClO_4^-)$. UV–Vis [$\lambda_{max}$ (nm), $CH_3CN$]: 397 (3856 M$^{-1}$ cm$^{-1}$); 241 (12 860 M$^{-1}$ cm$^{-1}$). $\Lambda_M$ ($CH_3CN$, 279 K): 106 S cm$^2$ mol$^{-1}$.

### Preparation of $[Cd_2L](ClO_4)(CH_3OH)$

A mixture of the above filtrate and 10 cm$^3$ acetonitrile was placed in an ambient environment. After two months, yellowish single crystals suitable for X-ray structure determination were obtained by slow evaporation. Yield 36%. Anal. Calcd. for $C_{45}H_{61}Cd_2ClN_8O_9$(%): C, 48.29; H, 5.45; N, 10.01. Found: C, 48.71; H, 5.31; N, 10.54. IR (cm$^{-1}$): 3436s $\nu$(OH); 3210m $\nu$(NH); 1634s $\nu$(C=N); 1098s $\nu(ClO_4)$. *m*/*z* (%): 982.1 (100).

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

### X-ray Crystallography

A yellow single crystal of dimensions $0.36 \times 0.30 \times 0.30$ mm was mounted on a glass fiber. The crystal data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) over the range $1.31° \leq \theta \leq 25.09°$ with an $\omega$-scan mode. Data reductions and cell refinements were performed with Smart-CCD software. An absorption correction using SADABS software was applied. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using SHELXL-97 [16]. The oxygen atoms of the perchlorate and the solvent $CH_3OH$ molecule were found disordered, the site occupancy factors for O11, O12, O13, O14; O11′, O12′, O13′, O14′; C51, O51 and C52, O52 were fixed

TABLE I Crystal data collection parameters for $[Cd_2L](ClO_4)(CH_3OH)$

| | |
|---|---|
| Empirical formula | $C_{45}H_{61}Cd_2ClN_8O_9$ |
| Formula weight | 1118.27 |
| Radiation (Å) | Mo Kα, 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 11.8143(3) |
| $b$ (Å) | 13.6117(4) |
| $c$ (Å) | 15.9894(4) |
| $\alpha$ (°) | 103.10 |
| $\beta$ (°) | 91.6600(10) |
| $\gamma$ (°) | 104.1770(10) |
| $V$ (Å$^3$) | 2418.40(11) |
| $Z$ | 2 |
| $D_{calc}$ (Mg m$^{-3}$) | 1.536 |
| Absorption coefficient (mm$^{-1}$) | 0.996 |
| $\theta$ range (°) | 1.31 to 25.09 |
| Index ranges | $-13 \leq h \leq 14$; $-10 \leq k \leq 16$; $-18 \leq l \leq 19$ |
| Reflections collected | 12 725 |
| Independent reflections | 8495 [$R$(int) = 0.0330] |
| Independent reflections ($> 2\sigma$) | 7085 |
| Absorption correction | Semiempirical from equivalents |
| Max/min transmissions | 1.0000 and 0.6255 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 8495/55/641 |
| Goodness-of-fit on $F^2$ | 1.220 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0749$, $wR2 = 0.1846$ |
| $R$ indices (all data) | $R1 = 0.0936$, $wR2 = 0.2053$ |
| Largest diff. peak and hole | 1.268 and −1.200 e Å$^{-3}$ |

at 0.5 and refined isotropically. All H atoms were placed in the calculated positions. Data collection, refinement and crystallographic data are summarized in Table I.

## RESULTS AND DISCUSSION

### Spectroscopic Characterization

The structure of $[Cd_2L']$ was confirmed by elemental analysis, IR, ES-MS, electronic spectroscopy and electrical conductivity. Condensation of all primary amine groups and carbonyl groups was confirmed by the lack of N–H double stretching bands in the IR region 3150–3450 cm$^{-1}$ and the presence of strong C=N stretching bands at 1636 cm$^{-1}$. The presence of a broad band at 3436 cm$^{-1}$ characteristic of the OH group of $CH_3OH$ showed that $CH_3OH$ exists in the complex, in agreement with the elemental analysis. The strong peak at 1094 cm$^{-1}$ without splitting showed that the $ClO_4^-$ ion did not take part in coordination with the Cd atom. This is also confirmed by the molar conductivity of the complex [$\Lambda_M$ ($CH_3CN$, 289 K) = 106 S cm$^2$ mol$^{-1}$], which is attributable to a 1 : 1 electrolyte and indicates that the phenoxy oxygens also coordinate to cadmium. The two strong peaks in the UV region were designated as $\pi$–$\pi^*$ transitions of benzene rings and C=N groups. The main peaks at $m/z$ 954.3 and 478.3 (Fig. 1a) correspond to $[Cd_2L']^+$ and $[Cd_2L'+H]^{2+}$, respectively. The two species were confirmed by good agreement between the observed and calculated isotopic distributions. Figure 1b shows typical examples for comparison between the experimental and calculated isotopic distribution for the peaks at $m/z$ 954.3. The hydrolysis

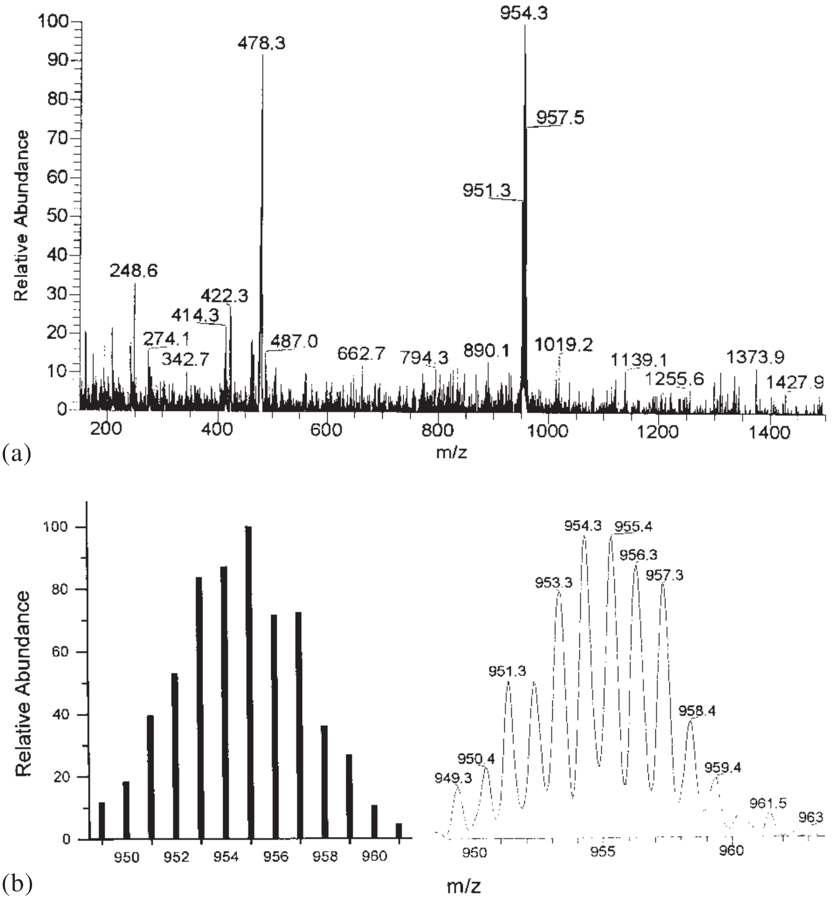

FIGURE 1 (a) The ES mass spectrum of $[Cd_2L']$. (b) The observed (traces) and calculated (bar) isotopic distributions for the peak at *m*/*z* 954.3.

reaction towards $[Cd_2L']$ was first observed from IR and ES-MS spectra at two months. A vibration at about 3210 $cm^{-1}$ indicates N–H stretching, while the main peak at *m*/*z* 982.1 corresponds to the species $[Cd_2L\text{-}5H^\bullet]^+$. The hydrolysis of cryptate $[Cd_2L']$ proceeds more slowly in methanol at ambient temperature. Under these conditions only one imine function of $[Cd_2L']$ was hydrolyzed with solvent addition, and no ring opening occurred to yield cryptate $[Cd_2L]$, which can be crystallized out.

## Description of the Structure of $[Cd_2L](ClO_4)(CH_3OH)$

The crystal structure of the bicadmium(II) cryptate $[Cd_2L](ClO_4)(CH_3OH)$ consists of cationic $[Cd_2L]^+$, noncoordinated perchlorate ion and methanol molecule. The structure of $[Cd_2L]^+$ showing the atom numbering scheme is indicated in Fig. 2 and bond distances and angles are shown in Table II. Each Cd(II) atom is enclosed within the polyaza macrocycle. Cd(1) is in an N4O2 coordination environment with coordination number six and forms a distorted tetragonal bipyramid. Cd(2) is in an N4O3 coordination environment with coordination number seven and forms a

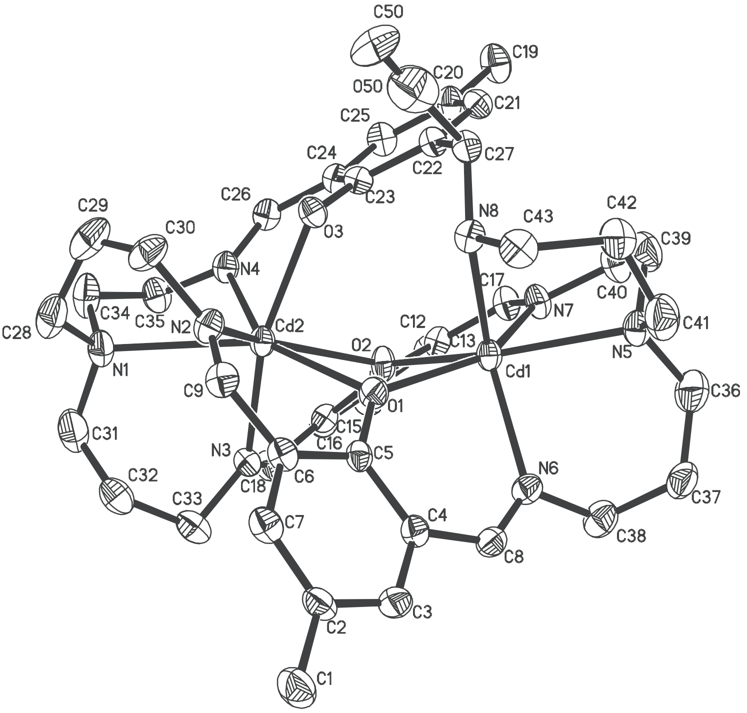

FIGURE 2 A stereoview of [$Cd_2L$] with the atom numbering scheme (ellipsoids at 30% probability).

monocapped-octahedral geometry. The dihedral angles of the three aromatic rings are 87.1, 17.5 and 72.8°, respectively, indicating that one aromatic ring is approximately vertical to, and almost parallel to, the other aromatic rings. The centroid–centroid distance of the two parallel aromatic rings is 4.831 Å, indicating a very weak interaction between them. Cd(1)–O(1), Cd(1)–O(2) and Cd(2)–O(phenoxy oxygen) are in the range 2.269–2.430 Å, close to that of a similar cryptate [$Cd_2L_A$] [6] derived from tris(2-aminoethyl)amine (tren) and cryptate [$Cd_2L_B$] [7] derived from tris(2-aminopropyl)amine (trpn). The long Cd(1)–O(3) distance of 3.667 Å indicates that there is no coordination between the two atoms. The six Cd(1)–N(imino) and Cd(2)–N(imino) bond distances lie in the range 2.300–2.390 Å, most of which are close to the standard Cd–N bond distance of 2.33 ± 0.005 Å [9], indicating normal coordination of the imino groups to Cd(II). The two Cd(1)–N(5) and Cd(2)–N(1) bond distances are 2.437 and 2.680 Å, respectively, shorter than those in [$Cd_2L_A$] and [$Cd_2L_B$], implying a stronger interaction between Cd(II) and the bridgehead nitrogen atoms in [$Cd_2L$]. The distance between the two bridgehead nitrogen atoms N(1) and N(5) is 8.742 Å, longer than in [$Cd_2L_B$] (8.71 Å). In addition, the long Cd(1)–Cd(2) distance of 3.687 Å is much greater than that of [$Cd_2L_A$] 3.436 Å and [$Cd_2L_B$] 3.472 Å, indicating that a larger framework is formed in the title cryptate. The N(8)–C(27) bond distance is 1.484 Å, and all the other imino amines are in the normal range of 1.276–1.298 Å, demonstrating that an addition reaction has occurred as indicated in Scheme 1.

Schiff-base condensation of tris(2-aminoethyl)amine with isophthaldehyde in the presence of Cu(II) is unstable and easily hydrolyzed with ring opening to give a terminal acetyl function [17]. These phenomena have been attributed to the Cu(II) in the

TABLE II Selected bond distances (Å) and angles (°) for $[Cd_2L](ClO_4)(CH_3OH)$

| | | | |
|---|---|---|---|
| Cd(1)–O(1) | 2.307(6) | Cd(2)–O(1) | 2.430(6) |
| Cd(1)–O(2) | 2.230(6) | Cd(2)–O(2) | 2.362(5) |
| Cd(1)–N(5) | 2.437(8) | Cd(2)–O(3) | 2.269(6) |
| Cd(1)–N(6) | 2.301(8) | Cd(2)–N(1) | 2.680(8) |
| Cd(1)–N(7) | 2.303(7) | Cd(2)–N(2) | 2.336(7) |
| Cd(1)–N(8) | 2.390(7) | Cd(2)–N(3) | 2.333(7) |
| Cd(2)–N(4) | 2.379(7) | N(3)–C(18) | 1.298(11) |
| N(4)–C(26) | 1.276(11) | N(6)–C(8) | 1.282(11) |
| N(7)–C(17) | 1.276(11) | N(8)–C(27) | 1.484(12) |
| O(2)–Cd(1)–N(6) | 107.6(3) | O(3)–Cd(2)–N(3) | 157.1(2) |
| O(2)–Cd(1)–N(7) | 78.6(2) | O(3)–Cd(2)–N(2) | 82.4(2) |
| N(6)–Cd(1)–N(7) | 119.7(3) | N(3)–Cd(2)–N(2) | 120.0(3) |
| O(2)–Cd(1)–O(1) | 72.7(2) | O(3)–Cd(2)–O(2) | 85.9(2) |
| N(6)–Cd(1)–O(1) | 79.4(2) | N(3)–Cd(2)–O(2) | 73.4(2) |
| N(7)–Cd(1)–O(1) | 149.5(2) | N(2)–Cd(2)–O(2) | 140.4(2) |
| O(2)–Cd(1)–N(8) | 108.9(2) | O(3)–Cd(2)–N(4) | 75.5(2) |
| N(6)–Cd(1)–N(8) | 126.2(3) | N(3)–Cd(2)–N(4) | 92.6(3) |
| N(7)–Cd(1)–N(8) | 105.2(3) | N(2)–Cd(2)–N(4) | 127.3(3) |
| O(1)–Cd(1)–N(8) | 75.5(2) | O(2)–Cd(2)–N(4) | 85.3(2) |
| O(2)–Cd(1)–N(5) | 152.0(2) | O(3)–Cd(2)–O(1) | 86.5(2) |
| N(6)–Cd(1)–N(5) | 82.5(3) | N(3)–Cd(2)–O(1) | 94.7(2) |
| N(7)–Cd(1)–N(5) | 73.8(3) | N(2)–Cd(2)–O(1) | 73.4(2) |
| O(1)–Cd(1)–N(5) | 135.4(2) | O(2)–Cd(2)–O(1) | 68.3(2) |
| N(8)–Cd(1)–N(5) | 83.3(3) | N(4)–Cd(2)–O(1) | 149.1(2) |
| C(5)–O(1)–Cd(1) | 132.6(5) | O(3)–Cd(2)–N(1) | 115.0(2) |
| Cd(1)–O(1)–Cd(2) | 102.2(2) | N(3)–Cd(2)–N(1) | 77.2(3) |
| C(31)–N(1)–Cd(2) | 112.8(7) | N(2)–Cd(2)–N(1) | 79.2(3) |
| C(28)–N(1)–Cd(2) | 108.0(7) | O(2)–Cd(2)–N(1) | 139.3(2) |
| C(34)–N(1)–Cd(2) | 108.5(6) | N(4)–Cd(2)–N(1) | 68.6(2) |
| C(5)–O(1)–Cd(2) | 119.7(5) | O(1)–Cd(2)–N(1) | 142.4(2) |

Schiff-base complex being able to catalyze the hydrolysis of the C=N bond, and the solvent MeCN or $CH_2Cl_2$ are related to the reaction [17]. In general, Cd(II) has no such strong catalytic ability [9]. However, in our complex, Cd(II) has weak catalytic ability towards the hydrolysis of the C=N bond, perhaps attributed to the asymmetrical structure, which can lead to distorted geometry, increased Cd(1)–O(3) distance and reduced coordination number, weakening the C=N bond. A detailed reaction mechanism will be discussed in a later publication.

## Acknowledgments

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## Supplementary Data

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 223715 for complex $[Cd_2L]$. Copies of the data can be obtained free from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## References

[1] P.S. Marchetti, S. Bank, T.W. Bell, M.A. Kennedy and P.D. Ellis, *J. Am. Chem. Soc.* **111**, 2063 (1989).

[2] D. Dakternicks, *Coord. Chem. Rev.* **98**, 288 (1990).

[3] K.R. Adam, S.P.H. Arshad, D.S. Baldwin, P.A. Duckworth, A.J. Leong, L.F. Lindoy, B.J. McCool, M. McPartlin, B.A. Tailor and P.A. Tasker, *Inorg. Chem.* **33**, 1194 (1994).

[4] K.R. Adam, K.P. Dancey, A.J. Leong, L.F. Lindoy, B.J. McCool, M. McPartlin and P.A. Tasker, *J. Am. Chem. Soc.* **110**, 8471 (1988).

[5] J.F. Endicott and B. Durham, *Coordination Chemistry of Macrocyclic Compounds* (Plenum Press, New York, 1979), p. 393.

[6] M.G.B. Drew, O.W. Howarth, G.G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.* 3149 (1994).

[7] X.Y. Xu, J.L. Chen, Q.H. Luo and M.C. Shen, *Polyhedron* **16**, 223 (1997).

[8] X.Y. Xu, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *Polyhedron* **16**, 1301 (1997).

[9] W. Jun, X.Y. Xu, J.L. Chen, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *Inorg. Chim. Acta* **256**, 121 (1997).

[10] X.Y. Xu, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *J. Coord. Chem.* **42**, 25 (1997).

[11] X.Y. Xu, Z.L. Wang, Q.H. Luo, M.C. Shen, N.X. Zhang, X.G. Zhou and Z.Y. Zhou, *J. Coord. Chem.* **43**, 81 (1998).

[12] X.Y. Xu, Z.L. Wang, Q.H. Luo, M.C. Shen, N.X. Zhang, X.G. Zhou and Z.Y. Zhou, *J. Coord. Chem.* **43**, 281 (1998).

[13] X.Y. Xu, W.X. Ma, H. Cheng, W.W. Liu, M.X. Zhang, Q.L. Liu and Z.D. Zhang, *J. Coord. Chem.* **48**, 1 (1999).

[14] A.M. Dittler-Klingemann and F. Ekkehardt Hahn, *Inorg. Chem.* **35**, 1996 (1996).

[15] S. Taniguch, *Bull. Chem. Soc. Jpn.* **57**, 268 (1984).

[16] G.M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1997).

[17] C.J. Harding, Q. Lu, J.F. Malone, D.J. Marrs, N. Martin, V. McKee and J. Nelson, *J. Chem. Soc., Dalton Trans.* 1739 (1995).