

Syntheses, Structures, and Luminescent Properties of [Bis(iminoalkyl)pyridine]cadmium(II) Complexes

Rui-Qing Fan,^[a] Dong-Sheng Zhu,^[a] Ying Mu,^{*,[a]} Guang-Hua Li,^[b] Yu-Lin Yang,^[b] Qing Su,^[a] and Shou-Hua Feng^[b]

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Four new Cd^{II} complexes of 2,6-bis[1-(phenylimino)ethyl]pyridine (**L**¹), 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (**L**²), 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (**L**³), 2,6-bis[1-(2-methylphenylimino)ethyl]pyridine (**L**⁴) have been synthesized. These complexes have the formulas [Cd(**L**¹)Cl₂]·1.5CH₃CN (**1**), [Cd(**L**²)Cl₂] (**2**), [Cd(**L**³)Cl₂]·CH₃CN (**3**), and [Cd(**L**⁴)Cl₂]·CH₃CN (**4**). The molecular structures of complexes **1–4** were determined by single-crystal X-ray diffraction. Crystallographic studies of **1–4** reveal all four complexes to be five-coordinate with geo-

metries that can be best described as distorted trigonal-bipyramidal. All eight compounds (**L**^{1–4} and **1–4**) are luminescent at room temperature in solution and the solid state. At 298 K in dichloromethane solution, all compounds have fluorescent emissions at about 368–409 nm. The fluorescent emission of these compounds originates from ligand-centered $\pi^*-\pi$ transitions. The Cd^{II} centers play a key role in enhancing the fluorescent emission of the ligands.

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Introduction

Luminescent coordination compounds with pyridine-type ligands have attracted much attention recently due to their good performance in sensor technologies and electroluminescent devices.^[1–7] Several d¹⁰ metal complexes with pyridine-type ligands have been synthesized and their luminescence behavior studied.^[1–3] Among these, luminescent cadmium complexes have been widely investigated as potential luminescent materials.^[1b,1d,2a,2b,2d] [Bis(iminoalkyl)pyridine]metal complexes have also been the subject of intense research due to their interesting coordination chemistry and applications in catalysis.^[8–17] Many complexes containing one or two bis(iminoalkyl)pyridine ligands with small aryl substituents have been synthesized and characterized.^[8–9] Recently, iron and cobalt complexes with bulky aryl-substituted bis(iminoalkyl)pyridine ligands were reported by Brookhart and Gibson et al.^[10–12] These complexes exhibit high activity for olefin polymerization. Brookhart et al. have also reported [bis(iminoalkyl)pyridine]ruthenium com-

plexes that can catalyze the epoxidation of olefins.^[17] To the best of our knowledge, no investigation has been carried out on the luminescent properties of [bis(iminoalkyl)pyridine]metal complexes. We explored this possibility and selected four [bis(iminoalkyl)pyridine]cadmium complexes for the present study. Herein we report the syntheses, crystal structures, and luminescent properties of a series of Cd^{II} complexes of ligands **L**^{1–4}.

Results and Discussion

Synthesis and Characterization

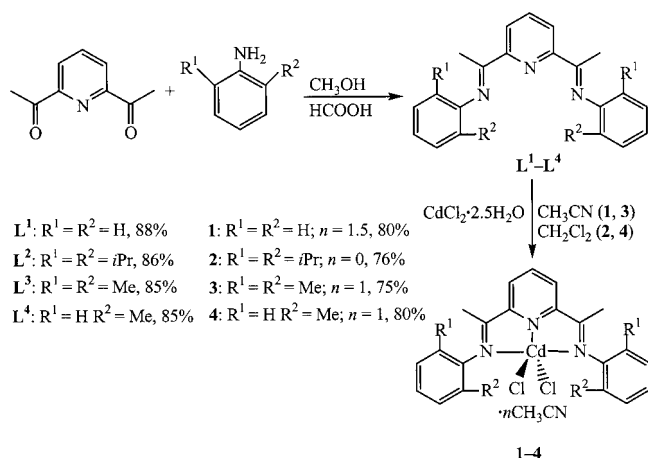
2,6-Bis[1-(phenylimino)ethyl]pyridine (**L**¹), 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (**L**²), 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (**L**³), and 2,6-bis[1-(2-methylphenylimino)ethyl]pyridine (**L**⁴) were synthesized according to modified published procedures in good yield by condensation of 2,6-diacetylpyridine with the corresponding aniline in refluxing absolute methanol in the presence of a catalytic amount of formic acid (Scheme 1).^[8a,10] Cadmium complexes of these ligands were prepared by reaction of CdCl₂·2.5H₂O with a stoichiometric amount of the corresponding 2,6-bis(iminoalkyl)pyridine ligand in acetonitrile (complexes **1** and **3**) or in dichloromethane (complexes **2** and **4**) at room temperature (Scheme 1). Complexes **1–4** were obtained as yellowish crystals in good yield.

^[a] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, Changchun 130012, People's Republic of China

^[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, People's Republic of China
Fax: + 86-431-519-3421

E-mail: ymu@mail.jlu.edu.cn

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Scheme 1

All compounds were characterized by 1H NMR, UV/Vis, and IR spectroscopy, and elemental analysis. Complexes 1–4 were also studied by single-crystal X-ray diffraction.

Structures

Crystals of 1–4 suitable for X-ray structural determination were grown from acetonitrile/dichloromethane (2:1) solution (1, 3, and 4), or from a concentrated dichloromethane solution (2). The molecular structures of complexes 1–4 are shown below, and selected bond lengths and angles are presented in Table 1.

There are two independent complex molecules and three acetonitrile molecules in the asymmetric unit in the cadmium complex 1 (Figure 1); the two molecules show an approximate C_s symmetry about a plane containing the cadmium atom, two chlorine atoms, and the pyridine nitrogen atom. The dihedral angles between the phenyl rings and the plane formed by three coordinated nitrogen atoms are

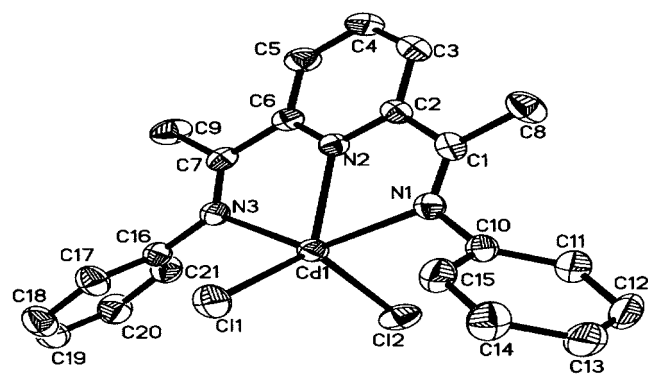


Figure 1. Molecular structure of complex 1 (the other molecule and CH_3CN molecules have been omitted for clarity)

$75.23(17)^\circ$ and $82.09(20)^\circ$ in one of these molecules; these values are larger than those in the other molecule [$62.86(17)^\circ$ and $67.23(14)^\circ$, respectively]. The dihedral angles between the two phenyl rings are $83.98(18)^\circ$ and $74.49(15)^\circ$, respectively, in the two molecules. The cadmium atom deviates by $0.077 \text{ \AA}$ from the coordination plane in one molecule, while in the other the metal atom is displaced by $0.084 \text{ \AA}$. For both molecules the central cadmium atom is coordinated to five atoms and the geometry about the cadmium atom is distorted trigonal-bipyramidal, with the equatorial plane defined by the N(2)(pyridine), Cl(1) and Cl(2) atoms and the N(1) and N(3)(imino) atoms in the axial positions. The mean deviation of the cadmium atom from the equatorial plane in one molecule is only $0.019 \text{ \AA}$, while in the other the metal atom is displaced by $0.009 \text{ \AA}$. In the two molecules, the angles in the equatorial plane range between $113.36(8)^\circ$ and $128.50(8)^\circ$, and the axial Cd–N(imino) bonds subtend an angle of $137.99(11)^\circ$ [in the other this angle is $137.92(11)^\circ$]. The Cd–N(imino) bonds [$2.407(3)$ and $2.419(3) \text{ \AA}$] are longer than the Cd–N(pyridine) bonds [$2.310(3) \text{ \AA}$], as is the case in the other molecule. The imino C=N bonds in 1 have a distinc-

Table 1. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for complexes 1–4

	1		2	3	4	
	Molecule 1	Molecule 2			Molecule 1	Molecule 2
Cd–N(2)	2.310(3)	2.313(3)	2.331(5)	2.300(6)	2.316(12)	2.330(11)
Cd–N(1)	2.407(3)	2.378(3)	2.480(5)	2.426(6)	2.359(12)	2.420(10)
Cd–Cl(1)	2.417 (1)	2.411(1)	2.411(2)	2.420(2)	2.450(4)	2.436(5)
Cd–N(3)	2.419(3)	2.390(3)	2.467(5)	2.431(5)	2.438(10)	2.420(11)
Cd–Cl(2)	2.434(1)	2.436 (1)	2.451(2)	2.434(2)	2.422(5)	2.458(4)
N(1)–C(1)	1.271(5)	1.278(5)	1.307(8)	1.282(8)	1.270(20)	1.262(16)
N(3)–C(7)	1.279(5)	1.271(5)	1.299(8)	1.275(8)	1.289(17)	1.263(18)
N(2)–Cd–N(1)	69.25(11)	68.79(11)	68.14(16)	69.50(20)	71.00(40)	68.50(40)
N(2)–Cd–Cl(1)	128.50(8)	126.81(9)	139.19(14)	118.52(15)	116.60(30)	125.70(30)
N(1)–Cd–Cl(1)	101.16(8)	103.49(9)	100.81(13)	99.62(16)	98.10(30)	102.90(30)
N(2)–Cd–N(3)	68.82(11)	69.20(11)	68.29(17)	69.00(20)	68.30(40)	68.80(40)
N(1)–Cd–N(3)	137.99(11)	137.92(11)	131.99(16)	138.40(20)	139.20(40)	137.30(40)
Cl(1)–Cd–N(3)	102.57(8)	103.24(9)	99.01(14)	102.15(14)	101.00(30)	102.50(30)
N(2)–Cd–Cl(2)	113.43(8)	113.36(8)	98.71(14)	124.25(15)	121.30(30)	117.60(30)
N(1)–Cd–Cl(2)	99.25(9)	95.79(9)	103.80(13)	102.69(16)	99.90(40)	98.70(30)
Cl(1)–Cd–Cl(2)	118.07(5)	119.81(5)	122.05(9)	117.22(8)	122.12(17)	116.72(16)
N(3)–Cd–Cl(2)	99.44(8)	98.38(10)	101.71(13)	98.16(14)	99.90(30)	99.80(30)

tive double-bond character, with C=N distances in the range 1.271(5)–1.279(5) Å.

Complexes **2** (Figure 2) and **3** (Figure 3) possess structures with approximate C_s symmetry about a plane

bisecting the central pyridine ring and containing the cadmium atom and two chlorine atoms, while complex **4** (Figure 4) adopts C_2 symmetry. The central cadmium atom in **2–4** is coordinated to five groups and the geometry about

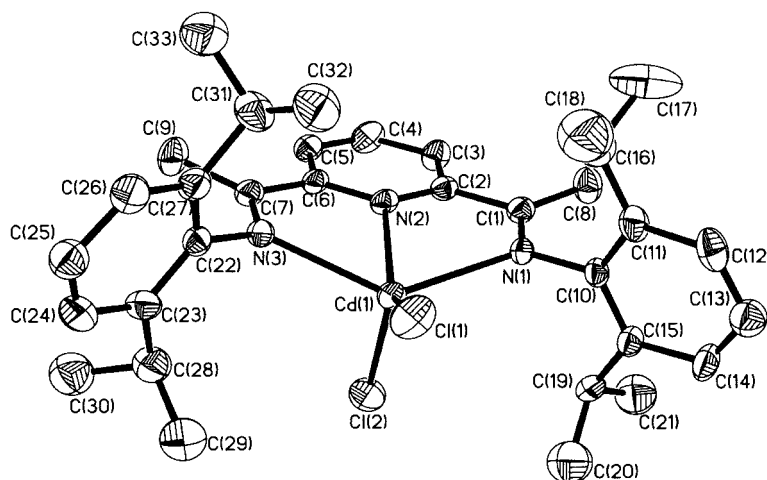


Figure 2. Molecular structure of complex **2**

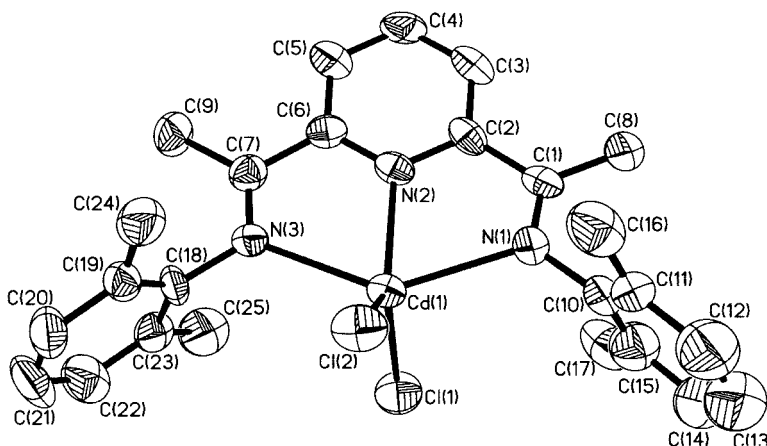


Figure 3. Molecular structure of complex **3** (the CH_3CN molecule has been omitted for clarity)

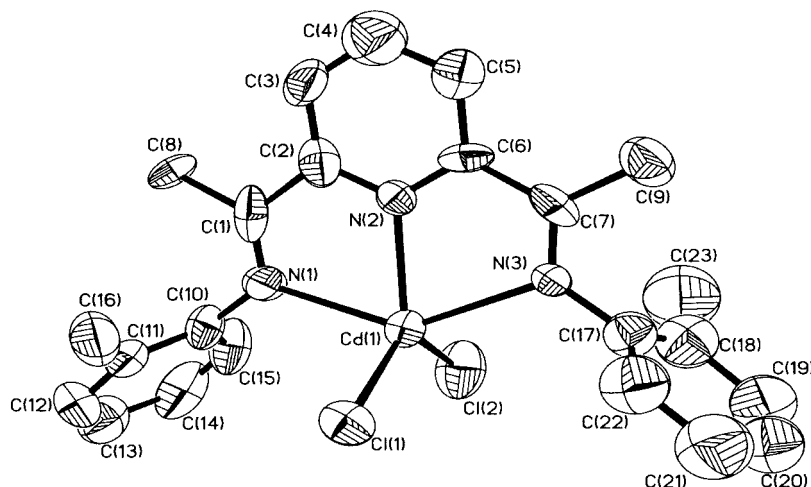


Figure 4. Molecular structure of complex **4** (the other molecule and CH_3CN molecules have been omitted for clarity)

the cadmium atom is a distorted trigonal bipyramid, with the equatorial plane defined by the N(2)(pyridine), Cl(1) and Cl(2) atoms and the N(1) and N(3)(imino) atoms in the axial positions. Complex **3** contains one independent molecule and one acetonitrile molecule, where as there are two independent molecules and two acetonitrile molecules in the asymmetric unit in the cadmium complex **4**. The mean deviation of the cadmium atoms in **2–4** from the equatorial planes is 0.027, 0.020 and 0.002 Å (0.007 Å for the other molecule in **4**), respectively, and the axial Cd–N(imino) bonds subtend angles of 131.99(16)°, 138.40(20)° and 139.20(40)° [137.30(40)° for the other molecule in **4**], respectively. The cadmium atoms in **2–4** deviate by 0.652, 0.087 and 0.040 Å (0.037 Å for the other molecule in **4**), respectively, from the coordination plane. The Cd–N(pyridine) bonds in **2–4** range from 2.300(6)–2.331(5) Å, while the distances between the cadmium atom and the imino nitrogen atoms in the three complexes are almost the same [2.467(5) and 2.480(5) Å in **2**, [2.426(6) and 2.431(5) Å] in **3** and [2.359(12) and 2.438(10) Å] in **4** [2.420(10) and 2.420(11) Å for the other molecule in **4**]. The planes of the phenyl rings in **2–4** are oriented essentially orthogonal to the coordination plane [ranging between 75.62(46)° and 89.59(52)°]. In each complex the Cd–N(pyridine) bond is significantly shorter than the Cd–N(imino) bonds, with the formal double-bond character of the imino linkages N(1)–C(1) and N(3)–C(7) being retained [C=N distances in range 1.262(16)–1.307(8) Å]. There are no intermolecular packing features of interest in any of the four complexes.

Luminescence Properties

Table 2 presents the absorption and emission data for the new complexes **1–4** in dichloromethane solution and in the solid state at room temperature, together with those for ligands **L¹–L⁴**. The four complexes show two main absorp-

Table 2. Photoluminescent data for ligands **L¹–L⁴** and complexes **1–4**^[a]

	Absorption [nm] (ϵ [dm ³ mol ⁻¹ cm ⁻¹])	Emission λ_{max} [nm]	Conditions
L¹	281 (16025), 329 (7485)	368	CH ₂ Cl ₂ , 298K
L²	284 (16180), 334 (7640)	471	solid, 298K
L³	291 (16528), 340 (7998)	381	CH ₂ Cl ₂ , 298K
L⁴	287 (16335), 337 (7843)	480	solid, 298K
1	301 (16944), 339 (7950)	397	CH ₂ Cl ₂ , 298K
2	305 (17195), 343 (8153)	482	solid, 298K
3	313 (17456), 350 (8511)	399	CH ₂ Cl ₂ , 298K
4	309 (17253), 347 (8259)	485	solid, 298K
		488	CH ₂ Cl ₂ , 298K
		486	solid, 298K

^[a] Concentration ca. 10⁻⁵ M.

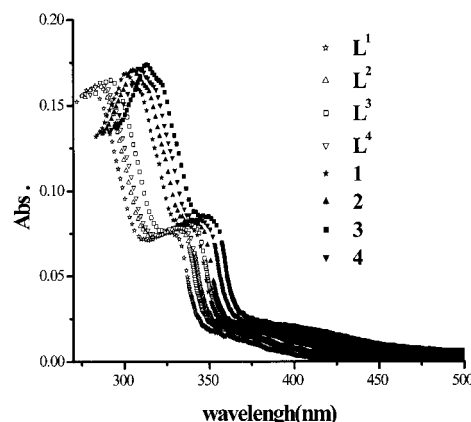


Figure 5. UV/Vis absorption spectra of ligands **L¹–L⁴** and complexes **1–4**

tion bands, which are similar to ligands **L¹–L⁴** in the UV region, as shown in Figure 5. The electronic absorption spectra of the complexes show low-energy absorption bands at about 339–350 nm (329–340 nm for ligands **L¹–L⁴**), and higher energy absorption bands at about 301–313 nm (281–291 nm for ligands **L¹–L⁴**), attributed to ligand-centered π – π^* transitions. The electronic absorption spectra of the complexes are red-shifted relative to the ligands due to perturbation of the intraligand π – π^* transition of the bis(iminoalkyl)pyridine unit by the metal atom. The energy trends of this band for the series **1–4** and **L¹–L⁴** are found to follow the order **3** < **4** < **2** < **1** and **L³** < **L⁴** < **L²** < **L¹**, which is in line with the electron-donating ability of the alkyl group (2,6-dimethylphenyl > 2-methylphenyl > 2,6-diisopropylphenyl > phenyl).

Complexes **1–4** have broad fluorescent emission bands in degassed CH₂Cl₂ solution at room temperature, with maxima at 397, 399, 409, and 402 nm for **1–4**, respectively (λ_{max} = 368, 375, 381, and 378 nm for **L¹–L⁴**; Figure 6). Similar to the electronic absorption data, the emission energies are found to depend on the bis(iminoalkyl)pyridine ligand. For complexes **1–4** and ligands **L¹–L⁴**, emission-energy trends in the order **3** < **4** < **2** < **1** and **L³** < **L⁴** < **L²**

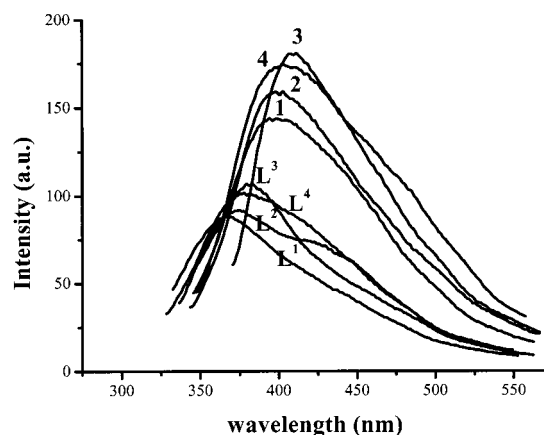


Figure 6. Emission spectra of ligands **L¹–L⁴** and complexes **1–4** in solution at room temperature

$< \mathbf{L}^1$ are observed, again in line with the electron-donating ability of the alkyl group. The Cd^{II} centers in complexes **1–4** play a key role in enhancing the fluorescent emission of the ligands. The chelation of the ligands to the metal center also contributes to the enhancement of the fluorescent emission by increasing the rigidity of the ligands, thus reducing the loss of energy by thermal vibrational decay. However, in the solid state at room temperature complexes **1–4** exhibit a bright, greenish-blue emission band with maxima at 482, 485, 488, and 486 nm, respectively ($\lambda_{\text{max}} = 471, 475, 480, \text{ and } 476 \text{ nm}$ for $\mathbf{L}^1\text{--}\mathbf{L}^4$); these values are red-shifted by about 80 nm (100 nm for $\mathbf{L}^1\text{--}\mathbf{L}^4$) from the emission in solution. This dramatic red-shift of the emission energy for complexes **1–4** and ligands $\mathbf{L}^1\text{--}\mathbf{L}^4$ from solution to the solid state is probably caused by intermolecular interactions in the solid state that effectively decrease the energy gap.

Conclusion

A series of [bis(iminoalkyl)pyridine]cadmium(II) complexes have been synthesized and characterized. Complexes **1–4** and ligands $\mathbf{L}^1\text{--}\mathbf{L}^4$ have fluorescent emission at 368–409 nm in dichloromethane solution at room temperature. Complexes **1–4** and ligand $\mathbf{L}^1\text{--}\mathbf{L}^4$ have broad fluorescent emission bands in the solid state at room temperature, with $\lambda_{\text{max}} = 482, 485, 488, 486 \text{ nm}$ for **1–4**, and 471, 475, 480, 476 nm for $\mathbf{L}^1\text{--}\mathbf{L}^4$, respectively. Their luminescent properties show that they are a new class of luminescent metal compounds with potential applications in optoelectronic devices.

Experimental Section

General: All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Elemental analyses were performed with a Perkin–Elmer 240c elemental analyzer. IR spectra were obtained with a Nicolet Impact 410 FTIR spectrometer using KBr pellets. NMR spectra were recorded with a Varian Mercury 300 MHz spectrometer. UV/Vis spectra were obtained with a Perkin–Elmer Lambda 20 spectrometer. Luminescence spectra were measured with a Perkin–Elmer LS55 Luminescence spectrometer at room temperature. Aniline, 2,6-diisopropylaniline, 2,6-dimethylaniline, and 2-methylaniline were purchased from Aldrich Chemical Co. and used as received. Solvents were refluxed in the presence of an appropriate drying agent, and distilled and degassed prior to use. For methanol, Mg ribbon was used as drying agent, whereas acetonitrile and dichloromethane were dried with calcium hydride. 2,6-Diacetylpyridine was prepared according to a published procedure.^[18]

Preparation of 2,6-Bis[1-(phenylimino)ethyl]pyridine ($\mathbf{L}^1$): Aniline (2.8 mL, 31.0 mmol) was added to a solution of 2,6-diacetylpyridine (1.70 g, 10.4 mmol) in absolute methanol (30 mL). After the addition of several drops of formic acid, the reaction mixture was refluxed for 8 h and then allowed to cool down to room temperature. The crude product precipitated as a yellow powder. Pure $\mathbf{L}^1$ was obtained in 88% yield (2.87 g) upon recrystallization from methanol. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.36$ (d, $J = 7.8 \text{ Hz}$,

2 H, Py- H_m), 7.89 (t, $J = 7.8 \text{ Hz}$, 1 H, Py- H_p), 7.42–6.85 (m, 10 H, Ar- H), 2.42 (s, 6 H, $\text{N}=\text{CMe}$) ppm. IR (KBr): $\tilde{\nu} = 3059$ (w), 2919 (w), 2860 (w), 1638 (vs), 1594 (m), 1574 (m), 1482 (s), 1445 (m), 1417 (w), 1361 (s), 1319 (m), 1294 (w), 1255 (w), 1220 (s), 1173 (m), 1150 (w), 1118 (m), 1091 (m), 1076 (m), 1027 (m), 992 (w), 969 (w), 912 (w), 874 (w), 823 (s), 808 (m), 774 (s), 762 (m), 743 (m), 707 (s), 697 (m), 658 (w), 645 (w), 551 (w), 520 (m), 468 (w), 443 (w) cm^{-1} . $\text{C}_{21}\text{H}_{19}\text{N}_3$ (313.4): calcd. C 80.48, H 6.11, N 13.41; found C 80.28, H 6.00, N 13.32.

Preparation of 2,6-Bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine ($\mathbf{L}^2$): 2,6-Diisopropylaniline (8.7 mL, 46.1 mmol) was added to a solution of 2,6-diacetylpyridine (2.5 g, 15.3 mmol) in absolute methanol (50 mL). After the addition of several drops of formic acid, the reaction mixture was refluxed for 24 h and then allowed to cool down to room temperature. The crude product precipitated as yellow powder. Pure $\mathbf{L}^2$ was obtained in 86% yield (6.35 g) upon recrystallization from methanol. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.60$ (d, $J = 7.8 \text{ Hz}$, 2 H, Py- H_m), 7.98 (t, $J = 7.8 \text{ Hz}$, 1 H, Py- H_p), 7.21–7.13 (m, 6 H, Ar- H), 2.78 (sept, $J = 6.8 \text{ Hz}$, 4 H, CHMe_2), 2.30 (s, 6 H, $\text{N}=\text{CMe}$), 1.19 (dd, $J = 6.8 \text{ Hz}$, 24 H, CHMe_2) ppm. IR (KBr): $\tilde{\nu} = 3068$ (w), 2960 (s), 2925 (w), 2870 (w), 1646 (vs), 1588 (w), 1571 (w), 1455 (m), 1438 (m), 1406 (w), 1383 (w), 1368 (s), 1321 (w), 1301 (w), 1255 (w), 1240 (m), 1195 (m), 1121 (m), 1103 (w), 1079 (w), 1059 (w), 1041 (w), 994 (w), 961 (w), 936 (w), 886 (w), 829 (m), 801 (w), 770 (s), 758 (w), 744 (w), 691 (w), 634 (w), 533 (w), 443 (w) cm^{-1} . $\text{C}_{33}\text{H}_{43}\text{N}_3$ (481.7): calcd. C 82.28, H 9.00, N 8.72; found C 82.50, H 8.91, N 8.65.

Preparation of 2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine ($\mathbf{L}^3$): 2,6-Dimethylaniline (6.4 mL, 51.7 mmol) was added to a solution of 2,6-diacetylpyridine (2.81 g, 17.2 mmol) in absolute methanol (50 mL). After the addition of several drops of formic acid, the reaction mixture was refluxed for 24 h and then allowed to cool down to room temperature. The crude product precipitated as a yellow powder. Pure $\mathbf{L}^3$ was obtained in 85% yield (5.4 g) upon recrystallization from methanol. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.56$ (d, $J = 7.8 \text{ Hz}$, 2 H, Py- H_m), 7.95 (t, $J = 7.8 \text{ Hz}$, 1 H, Py- H_p), 7.11–6.95 (m, 6 H, Ar- H), 2.27 (s, 6 H, $\text{N}=\text{CMe}$), 2.07 (s, 12 H, CMe) ppm. IR (KBr): $\tilde{\nu} = 3068$ (w), 3019 (w), 2970 (w), 2944 (w), 2915 (w), 2851 (w), 2727 (w), 1646 (vs), 1594 (m), 1567 (m), 1468 (s), 1437 (m), 1366 (s), 1324 (w), 1297 (m), 1247 (m), 1203 (s), 1160 (w), 1148 (w), 1126 (s), 1093 (s), 1071 (w), 1029 (w), 991 (w), 972 (w), 920 (w), 886 (w), 875 (w), 826 (s), 817 (s), 804 (w), 777 (s), 762 (vs), 744 (w), 692 (m), 623 (m), 576 (w), 541 (w), 530 (w), 493 (w), 422 (w) cm^{-1} . $\text{C}_{25}\text{H}_{27}\text{N}_3$ (369.5): calcd. C 81.26, H 7.37, N 11.37; found C 80.98, H 7.40, N 11.56.

Preparation of 2,6-Bis[1-(2-methylphenylimino)ethyl]pyridine ($\mathbf{L}^4$): 2-Methylaniline (2.2 mL, 20.5 mmol) was added to a solution of 2,6-diacetylpyridine (1.1 g, 6.7 mmol) in absolute methanol (25 mL). After the addition of several drops of formic acid, the reaction mixture was refluxed for 24 h and then allowed to cool down to room temperature. The crude product precipitated as a yellow powder. Pure $\mathbf{L}^4$ was obtained in 85% yield (1.96 g) upon recrystallization from methanol. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.42$ (d, $J = 7.6 \text{ Hz}$, 2 H, Py- H_m), 7.92 (t, $J = 7.6 \text{ Hz}$, 1 H, Py- H_p), 7.23–6.69 (m, 8 H, Ar- H), 2.34 (s, 6 H, $\text{N}=\text{CMe}$), 2.14 (s, 6 H, CMe) ppm. IR (KBr): $\tilde{\nu} = 3068$ (w), 3019 (w), 2920 (w), 2856 (w), 1648 (vs), 1601 (m), 1569 (m), 1480 (s), 1450 (m), 1363 (s), 1321 (m), 1294 (w), 1255 (w), 1220 (s), 1187 (w), 1155 (w), 1118 (s), 1095 (w), 1073 (m), 1041 (m), 964 (w), 933 (w), 880 (w), 851 (w), 817 (s), 780 (s), 740 (s), 727 (s), 651 (w), 642 (w), 567 (w), 533 (w), 446 (m), 405 (w) cm^{-1} . $\text{C}_{23}\text{H}_{23}\text{N}_3$ (341.5): calcd. C 80.90, H 6.79, N 12.31; found C 80.89, H 6.82, N 12.27.

Preparation of {2,6-Bis[1-(phenylimino)ethyl]pyridine}dichlorocadmium(II)-1.5CH₃CN (1): A mixture of **L**¹ (124 mg, 0.39 mmol) and CdCl₂·2.5H₂O (90 mg, 0.39 mmol) in acetonitrile (30 mL) was stirred under nitrogen at room temperature for 12 h. Evaporation of the solvent gave the crude product as a yellowish powder. Pure **1** was obtained in 80% yield (174 mg) upon recrystallization from acetonitrile/dichloromethane (2:1). ¹H NMR (300 MHz, CD₃CN): δ = 8.50 (quint, J = 7.2 Hz, 3 H, Py-*H*), 7.52–7.17 (m, 10 H, Ar-*H*), 2.52 (s, 6 H, N=CMe) ppm. ¹³C NMR (CD₃CN, ¹H gated decoupled): δ = 166.30 (N=C), 148.41 (Py-*C*_o), 147.39 (Ar-*C*_i), 143.44 (Ar-*C*_o), 129.27 (Ar-*C*_p), 128.09 (Py-*C*_p), 126.37 (Py-*C*_m), 121.66 (Ar-*C*_m), 17.46 (N=CMe) ppm. IR (KBr): $\tilde{\nu}$ = 3089 (w), 3029 (w), 2960 (w), 2915 (w), 2247 (w), 1631 (s), 1591 (s), 1487 (s), br 1450 (m), 1371 (s), 1309 (w), 1284 (w), 1252 (s), 1227 (s), 1185 (w), 1148 (w), 1103 (w), 1071 (w), 1019 (m), 981 (w), 909 (w), 859 (w), 820 (s), 777 (s), 758 (m), 743 (m), 725 (m) 697 (s), 674 (w), 654 (w), 576 (w), 552 (w), 533 (m), 468 (w), 407 (w) cm⁻¹. C₂₁H₁₉CdCl₂N₃·1.5CH₃CN (558.1): calcd. C 51.63, H 4.24, N 11.29; found C 51.60, H 4.31, N 11.25.

Preparation of {2,6-Bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine}dichlorocadmium(II) (2): A mixture of **L**² (169 mg, 0.35 mmol) and CdCl₂·2.5H₂O (80 mg, 0.35 mmol) in dichloromethane (40 mL) was stirred under nitrogen at room temperature for 12 h. The volume of the reaction mixture was reduced to about 10 mL and the mixture left to stand at 0 °C for several days. Yellowish crystals of **2** formed and were separated from the solution. Yield: 177 mg (76%). ¹H NMR (300 MHz, CD₃CN): δ = 8.51 (quint, J = 6.9 Hz, 3 H, Py-*H*), 7.27–7.18 (m, 6 H, Ar-*H*), 2.89 (sept, J = 6.6 Hz, 4 H, CHMe₂), 2.40 (s, 6 H, N=CMe), 1.22 (dd,

J = 6.6 Hz, 24 H, CHMe₂) ppm. IR (KBr): $\tilde{\nu}$ = 3084 (w), 3063 (w), 2965(s), 2925 (m), 2870 (w), 1636 (s), 1584 (s), br 1457 (m), 1371 (s), 1329 (w), 1306 (w), 1249 (s), 1203 (m), 1106 (m), 1054 (w), 1039 (w), 1017 (w), 979 (w), 937 (w), 819 (m), 796 (m), 775 (m), 758 (w), 744 (w), 716 (w), 697 (w), 637 (w), 529 (w), 468 (w), 445 (w), 432 (w) cm⁻¹. C₃₃H₄₃CdCl₂N₃ (664.7): calcd. C 59.60, H 6.52, N 6.32; found C 59.99, H 6.85, N 6.68.

Preparation of {2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine}dichlorocadmium(II)-CH₃CN (3): A mixture of **L**³ (137 mg, 0.37 mmol) and CdCl₂·2.5H₂O (85 mg, 0.37 mmol) in acetonitrile (30 mL) was stirred under nitrogen at room temperature for 12 h. Evaporation of the solvent gave the crude product as a yellowish powder. Pure product **3** was obtained in 75% yield (165 mg) upon recrystallization from acetonitrile/dichloromethane (2:1). ¹H NMR (300 MHz, CD₃CN): δ = 8.53 (quint, J = 6.3 Hz, 3 H, Py-*H*), 7.25–7.08 (m, 6 H, Ar-*H*), 2.41 (s, 6 H, N=CMe), 2.20 (s, 12 H, CMe) ppm. IR (KBr): $\tilde{\nu}$ = 3084 (w), 3024 (w), 2969 (w), 2920 (w), 2742 (w), 2247 (w), 1928 (w), 1854 (w), 1633 (s), 1584 (s), 1470 (s), 1443 (s), 1371(s), 1304 (m), 1255 (s), 1215 (s), 1163 (w), 1105 (m), 1093 (m), 1036 (m), 1022 (s), 980 (m), 966 (w), 917 (m), 902 (w), 823 (s), 814 (s), 782 (s), 768 (s), 740 (m), 695 (m), 633 (m), 582 (m), 554 (m), 530 (w), 516 (w), 495 (w), 419 (w) cm⁻¹. C₂₅H₂₇CdCl₂N₃·CH₃CN (593.6): calcd. C 54.61, H 5.09, N 9.43; found C 54.83, H 5.21, N 9.03.

Preparation of {2,6-Bis[1-(2-methylphenylimino)ethyl]pyridine}dichlorocadmium(II)-CH₃CN (4): A mixture of **L**⁴ (131 mg, 0.38 mmol) and CdCl₂·2.5H₂O (86 mg, 0.38 mmol) in dichloromethane (30 mL) was stirred under nitrogen at room temperature

Table 3. Crystallographic data and structure refinement for complexes **1–4**

	1	2	3	4
Empirical formula	C ₂₄ H _{23.5} CdCl ₂ N _{4.5}	C ₃₃ H ₄₃ CdCl ₂ N ₃	C ₂₇ H ₃₀ CdCl ₂ N ₄	C ₂₅ H ₂₆ CdCl ₂ N ₄
Formula mass	558.08	664.67	593.61	565.59
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.048 (2)	8.884 (2)	13.418(4)	9.455(9)
<i>b</i> [Å]	12.686(3)	9.967(2)	14.941(4)	13.035(8)
<i>c</i> [Å]	22.661(5)	21.213(4)	14.547(4)	21.739(16)
α [°]	91.95(3)	81.02(3)	90	93.71(7)
β [°]	97.52(3)	88.52(3)	108.36(1)	90.31(7)
γ [°]	93.68(3)	66.52(3)	90	98.09(8)
Volume [Å ³]	2571.0(9)	1700.3(6)	2768.2(13)	2647.0(40)
<i>Z</i>	4 ^[a]	2	4	4 ^[a]
<i>D</i> _{calcd} [g m ⁻³]	1.432	1.969	3.042	1.379
μ [mm ⁻¹]	1.075	2.805	6.170	1.044
<i>F</i> (000)	1108	960	2291	1080
θ range for data collection [°]	0.91–27.46	2.26–27.48	1.80–24.96	2.36–25.11
Limiting indices	–11 ≤ <i>h</i> ≤ 11 –16 ≤ <i>k</i> ≤ 16 –29 ≤ <i>l</i> ≤ 29	–11 ≤ <i>h</i> ≤ 11 –12 ≤ <i>k</i> ≤ 12 –27 ≤ <i>l</i> ≤ 27	–15 ≤ <i>h</i> ≤ 15 –17 ≤ <i>k</i> ≤ 17 –17 ≤ <i>l</i> ≤ 8	–5 ≤ <i>h</i> ≤ 10 –15 ≤ <i>k</i> ≤ 12 –25 ≤ <i>l</i> ≤ 16
Absorption correction	semi-empirical	semi-empirical	empirical	empirical
Data/restraints/parameters	11565/9/668	7213/78/352	4826/24/307	6225/106/577
Goodness-of-fit on <i>F</i> ²	1.053	1.019	0.949	1.047
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> ₁ ^[b]	0.0429	0.0736	0.0502	0.0756
<i>wR</i> ₂ ^[c]	0.1251	0.1603	0.0982	0.1791
<i>R</i> indices (all data)				
<i>R</i> ₁ ^[b]	0.0525	0.1131	0.1209	0.1490
<i>wR</i> ₂ ^[c]	0.1368	0.1813	0.1104	0.2159
Largest difference peak/hole [e·Å ⁻³]	0.649/–1.231	1.160/–0.877	0.741/–0.376	1.296/–0.609

^[a] There are two crystallographically independent molecules in the asymmetric unit. ^[b] $R_1 = \|F_o\| - \|F_c\|/\|F_o\|$. ^[c] $wR_2 = \{[w(F_o^2 - F_c^2)]/[w(F_o^2)]\}^{1/2}$.

for 12 h. Evaporation of the solvent gave the crude product as yellowish powder. Pure product **4** was obtained in 80% yield (172 mg) upon recrystallization from acetonitrile/dichloromethane (2:1). ¹H NMR (300 MHz, CD₃CN): δ = 8.49 (quint, J = 6.6 Hz, 3 H, Py-*H*), 7.33–6.97 (m, 8 H, Ar-*H*), 2.38 (s, 6 H, N=CMe). 2.18 (s, 6 H, CMe) ppm. IR (KBr): $\tilde{\nu}$ = 3079 (w), 3029 (w), 2975 (w), 2920 (w), 2947 (w), 1638 (s), 1599 (m), 1584 (s), 1487 (s), br 1463 (m), 1368 (s), 1311 (w), 1255 (s), 1230 (s), 1200 (s), 1148 (w), 1113 (m), 1041 (m), 1019 (s), 982 (w), 941 (w), 863 (m), 817 (s), 795 (s), 786 (s), 755 (s), 731 (m), 716 (m), 704 (w), 667 (w), 652 (w), 594 (w), 568 (w), 547 (w), 527 (w), 446 (m), 413 (w) cm⁻¹. C₂₃H₂₃CdCl₂N₃·CH₃CN (565.6): calcd. C 53.07, H 4.63, N 9.90; found C 53.43, H 4.91, N 9.65.

X-ray Crystallography of 1–4: The data were collected with a Rigaku R-Axis RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) at 293 ± 2 K. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package.^[19] The cadmium and chlorine atoms were located first, and the carbon and nitrogen atoms were found in difference Fourier maps. The hydrogen atoms residing on the carbon atoms were located geometrically. All non-hydrogen atoms were refined anisotropically. Crystallographic data are given in Table 3. CCDC-232412 (**1**), -232417 (**2**), -232418 (**3**) and -232413 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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; E-mail: deposit@ccdc.cam.ac.uk].

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