

Cd(II), Zn(II), and Pd(II) Complexes of an Isoindoline Pincer Ligand: Consequences of Steric Crowding

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Received May 3, 2005

The sterically crowded isoindoline pincer ligand, 6'-MeLH, prepared by condensation of 4-methyl-2-aminopyridine and phthalonitrile, exhibits very different reaction chemistry with Cd²⁺, Zn²⁺, and Pd²⁺. Three different ligand coordination modes are reported, each dependent upon choice of metal ion. This isoindoline binds to Cd²⁺ as a charge-neutral, zwitterionic, bidentate ligand using imine and pyridine nitrogen atoms to form the eight-coordinate fluxional complex, Cd(6'-MeLH)₂(NO₃)₂. In the presence of Zn²⁺, however, loss of a pyridine arm occurs through solvolysis and tetrahedrally coordinated complexes are formed with coordination of pyrrole and pyridine nitrogen atoms. Reaction with Pd²⁺ produces the highly distorted, square planar complex Pd(6'-MeL)Cl in which a deprotonated isoindoline anion coordinates as a tridentate pyridinium NNC pincer ligand.

Introduction

Pyridine-arm isoindolines are known to coordinate to metal ions as tridentate pincer ligands either as deprotonated anions, n'-RL⁻, or (in one instance) as the charge-neutral iminium zwitterion, n'-RLH. Complexes synthesized previously have in almost all cases contained the unsubstituted, deprotonated isoindoline anion (L⁻) or its alkyl-substituted pyridine derivatives, n'-RL⁻, with substituents in the 3, 4, or 5 positions.¹ The first systematic investigation was reported by Gagné and co-workers,^{1b} who prepared a series of first-row transition-metal complexes, M(4'-MeL)₂, M = Mn–Zn. In these octahedral complexes the isoindoline anion coordinates meridionally as a NNN tridentate pincer ligand.

We have been interested in elucidating the different coordination modes of isoindoline pincer ligands with respect to choice of metal ion and the size, position, and electron-donating ability of the substituent R. In this context, we previously showed that bidentate isoindoline coordination is feasible and occurs when Zn(ClO₄)₂·6H₂O reacts with 4'-RL⁻ in a 1:1 molar ratio in methanol to form the trinuclear complex [Zn₃(4'-MeL)₄](ClO₄)₂.² However when this reaction is carried out with Cu(ClO₄)₂·6H₂O, the trigonal bipyramidal complex [Cu(4'-MeL)(H₂O)₂](ClO₄) is formed.² We also demonstrated that 4'-MeLH reacts *without* deprotonation with Cd(NO₃)₂ to form Cd(4'-MeLH)(NO₃)₂, which was the first structurally characterized complex containing a charge-neutral, isoindoline zwitterionic pincer ligand, Chart 1.³

Given the recent interest in sterically crowded ligands and their ability to enforce unusual coordination geometries or ligand distortions,^{4–6} we chose to investigate the donor

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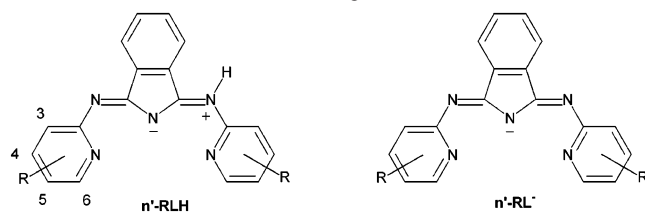
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Chart 1. Structures of Isoindoline Ligands



properties of 6'-MeLH. This pincer ligand should be incapable of forming undistorted square planar or octahedral complexes because of the blocking effect of the two methyl groups with respect to coordination of an ancillary ligand trans to the pyrrole nitrogen. We focus our attention here on the reaction of 6'-MeLH with three metal ions: Cd²⁺, which prefers octahedral coordination; Zn²⁺, which prefers tetrahedral coordination; and Pd²⁺, which exclusively favors square planar coordination. While the "normal" expectation is that the sterically congested 6'-MeLH isoindoline will coordinate as an anion via pyrrole and pyridine nitrogen atoms, there is the added possibility that coordination can occur through an imine nitrogen as reported in a Mo(II) isoindoline complex.⁷ Furthermore, it is also possible that 6'-MeLH can coordinate as a charge-neutral, tridentate iminium zwitterion as found in Cd(4'-MeLH)(NO₃)₂.³

We anticipated that 6'-MeLH might coordinate to metal ions as a charge-neutral, tridentate zwitterionic or deprotonated anion via pyrrole and pyridine nitrogen atoms and form either (a) severely distorted square planar complexes with Pd²⁺ in which an ancillary ligand would bind strongly out of plane or (b) 5-coordinate trigonal bipyramidal complexes with Zn²⁺ and Cd²⁺ in which the isoindoline coordinates meridionally. As recently reported by Addison and co-workers,⁸ both coordination modes have been validated in the unusual, sterically encumbered, trinuclear complex [Cu₃(4',6'-MeL)₃F₂]PF₆. In this complex the central Cu²⁺ ion has a trigonal bipyramidal conformation with equatorially bonded fluorides, while the outer Cu²⁺ ions are in a severely distorted square planar environment with bridging fluoride coordinated trans to the pyrrole nitrogen. Expanding upon the discovery of Addison's work, which demonstrates the ability of 4',6'-MeL⁻ to coordinate to Cu²⁺ as a pincer ligand when the ancillary ligand is the small fluoride ion,⁸ we report here the reactions of the d⁸ metal ion Pd²⁺ and the d¹⁰ metal ions Cd²⁺ and Zn²⁺ with 6'-MeLH and the surprisingly different products that are formed.

Experimental Section

The ligand 6'-MeLH was prepared using a published procedure given for 4'-MeLH.⁹ The complex Pd(COD)Cl₂ (COD = 1,5-cyclooctadiene) was prepared following a published procedure.¹⁰ All other chemicals were obtained commercially and used as

received. ¹H NMR spectra were recorded on Varian Inova 500 MHz and Bruker DMX 750 MHz spectrometers. Chemical shifts were referenced to the residual protic solvent peak. Infrared spectra were recorded on a Mattson Gemini spectrometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, Georgia.

Caution! Metal complexes containing organic ligands and perchlorate ion are potentially explosive and should be handled with care.

Cd(6'-MeLH)₂(NO₃)₂·2CH₃OH (1). Solid Cd(NO₃)₂·4H₂O (0.155 g, 0.502 mmol) was added with stirring to a solution of 6'-MeLH (0.327 g, 1.00 mmol) in warm methanol (30 mL). Upon cooling of the apricot-colored solution, the yellow crystals which formed were collected, washed with ice-cold methanol (3 × 5 mL), and vacuum dried. Lattice methanol is lost upon drying and replaced by one molecule of water. Yield: 0.212 g, 47%. IR (KBr): ν(N-H) 3084, ν(C=N/C=C) 1631, 1591, 1557, 1491, 1456, 1407, ν(NO₃⁻) 1296 cm⁻¹. ¹H NMR (750 MHz, CD₂Cl₂, 230K): δ 2.64 (s, 12H), 7.14 (d, 4H), 7.17 (d, 4H), 7.29 (s, 4H), 7.43 (s, 4H), 7.78 (t, 4H), 12.60 (s, NH, 2H). Anal. Calcd for C₄₀H₃₆N₁₂CdO₇: C, 52.83; H, 3.99; N, 18.49. Found: C, 52.88; H, 3.94; N, 18.47.

[Zn(6'-L1H)₂](ClO₄)₂ (2). Solid Zn(ClO₄)₂·6H₂O (0.372 g, 1.0 mmol) was added with stirring to a solution of 6'-MeLH (0.327 g, 1.0 mmol) in 30 mL of warm methanol. After filtration to remove traces of undissolved solid, the solution was allowed to evaporate for a few days until crystallization occurred. The resulting thin, yellow needles were collected, washed with ice-cold methanol (3 × 5 mL), and air dried. Yield: 0.137 g, 33%. IR (KBr): ν(C=N/C=C) 1633, 1555, 1463, ν(ClO₄⁻) 1065 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂, 293K): δ 10.1 (s, NH, 2H), 8.36 (m, 1H), 8.34 (t, 1H), 7.89 (m, 2H), 7.82 (d, 1H), 7.77 (m, 1H), 7.60 (d, 1H), 3.15 (s, 3H), 3.06 (s, 3H), 2.83 (s, 3H). Anal. Calcd for C₃₂H₃₄N₆O₁₂·Cl₂Zn: C, 48.74; H, 4.77; N, 9.48. Found: C, 48.69; H, 4.91; N, 9.57.

Zn(6'-L2)₂ (3). The filtrate from the preparation of 2, after being allowed to evaporate for a few days, produced orange crystals which were collected, washed with ice-cold methanol (3 × 5 mL), and air dried. Upon air drying, the hemihydrate was formed. Yield: 0.048 g, 18%. IR (KBr) ν(C=O) 1704, ν(C=N/C=C) 1617, 1595, 1544, 1448 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂, 293K): δ 7.97 (d, 1H), 7.79 (t, 1H), 7.70 (d, 1H), 7.60 (dt, 1H), 7.56 (d, 1H), 7.53 (dt, 1H), 6.92 (d, 1H), 2.37 (s, 3H). Anal. Calcd for C₂₈H₂₁N₆O_{2.5}Zn (hemihydrate): C, 61.50; H, 3.87; N, 15.37. Found: C, 61.94; H, 3.85; N, 15.29.

Pd(6'-MeL)Cl·THF (4). Solid Pd(COD)Cl₂ (0.1427 g, 0.500 mmol) was added with stirring to a warm solution of 6'-MeLH (0.1638 g, 0.500 mmol) in 15 mL of methanol, and the resulting solution was refluxed for 6 h. The red microcrystalline product was recrystallized from THF by layering with diethyl ether and produced crystals of the THF solvate suitable for X-ray diffraction studies. Yield: 20.9 mg, 7.7%. IR (KBr) ν(N-H) 3400 (br), ν(C=N/C=C) 1580, 1523, 1440 cm⁻¹. ¹H NMR (500 MHz, THF-d₈, 293 K): δ 12.3 (s, NH), 9.53 (d, 1H), 8.02 (m, 1H), 7.94 (m, 1H), 7.78 (t, 1H), 7.61 (m, 1H), 7.59 (m, 1H), 7.38 (d, 1H), 7.10 (d, 1H), 6.93 (d, 1H), 3.20 (s, 3H), 2.61 (s, 3H). Anal. Calcd for C₂₄H₂₄N₅ClO₂Pd: C, 53.35; H, 4.48; N, 12.96. Found: C, 53.29; H, 4.36; N, 12.76.

X-ray Crystal Structure Determinations. X-ray diffraction data were recorded on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Standard Bruker control (SMART) and integration (SAINT) programs were employed, and Bruker SHELXTL¹¹ software was used for structure

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Table 1. Crystallographic Data for Compounds **1**, **3**, and **4**

compound	1	3	4
chemical formula	C ₄₀ H ₃₈ CdN ₁₂ O ₆	C ₂₈ H ₂₀ N ₆ O ₂ Zn	C ₂₄ H ₂₄ ClN ₅ OPd
fw	895.22	537.87	540.33
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P1</i>
<i>a</i> , Å	14.055(4)	13.969(2)	7.4036(8)
<i>b</i> , Å	20.270(5)	12.547(2)	11.0386(11)
<i>c</i> , Å	15.082(4)	15.301(3)	14.1390(15)
α , deg	90	90	73.811(2)
β , deg	101.748(5)	116.096(3)	79.324(2)
γ , deg	90	90	79.795(2)
<i>V</i> , Å ³	4206.7(19)	2408.4(7)	1080.8(2)
<i>Z</i>	4	4	2
<i>T</i> , °C	173(2)	273(2)	173(2)
λ , Å	0.7107	0.7107	0.7107
<i>D</i> _{calcd} , g cm ⁻³	2.83	1.48	1.66
μ , mm ⁻¹	1.159	1.059	1.010
<i>R</i> (<i>F</i> _o) ^a	0.0425	0.0440	0.0419
<i>R</i> _w (<i>F</i> _o ²) ^a	0.112	0.112	0.111
GOF	0.984	0.936	1.079

^a Refinement by full-matrix least-squares on *F*² (all data); *R*_w for all data, *R* for *I* > 2 σ (*I*); $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (LP)^2 + MP$, $P = (F_o^2 + 2F_c^2)/3$.

solution, refinement, and graphics. Selected crystallographic results and details of the X-ray diffraction experiments are listed in Table 1. The unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. Intensities were integrated from a series of frames (ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.¹² The structures were solved by direct methods and refined (on *F*² using all data) by a full-matrix, weighted least-squares process. Molecular packing in each of the structures was examined for evidence of chemically significant intermolecular contacts; no such contacts were identified.

Results and Discussion

When 6'-MeLH reacts with Cd(NO₃)₂·4H₂O in methanol in either 1:1 or 2:1 stoichiometry, the eight-coordinate complex Cd(6'-MeLH)₂(NO₃)₂ (**1**) is isolated. The crystal structure of **1**, Figure 1, illustrates the unusual coordination of 6'-MeLH to Cd²⁺ via one pyridine and one imine nitrogen atom of each isoindoline ligand. This is quite different from the reaction of Cd(NO₃)₂·4H₂O with 4'-MeLH, where the product is Cd(4'-MeLH)(NO₃)₂,³ a seven-coordinate complex with 4'-MeLH coordinating via a pyrrole and pyridine nitrogen atom as a tridentate, charge-neutral, iminium zwitterionic ligand. Coordination of the isoindoline in normal tridentate fashion, whether as a charge-neutral iminium zwitterion or as a deprotonated anion, does not occur in **1** due to the bulk of the 6'-methyl groups and their interference with coordination of a fourth ligand trans to the pyrrole nitrogen.

The pyrrole nitrogen atoms, N3 and N8, in **1** remain protonated and are not coordinated to Cd. The protons on N3 and N8 were located in the difference electron density map and refined independently with satisfactory results. These protons are hydrogen bonded to pyridine N5 (N···H = 2.09(5) Å) and N10 (N···H = 1.98(5) Å) atoms, respectively. Each isoindoline ligand is nonplanar, with the

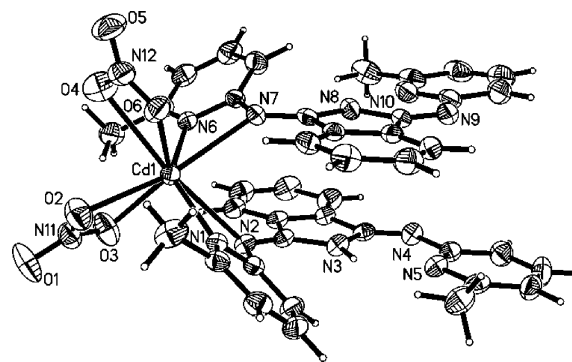


Figure 1. Thermal ellipsoid plot (50% probability) showing the structure and partial numbering scheme for **1**. Selected bond lengths (Å): Cd–N1, 2.324(3); Cd–N2, 2.655(3); Cd–N6, 2.340(3); Cd–N7, 2.550(3); Cd–O2, 2.511(3); Cd–O3, 2.342(3); Cd–O4, 2.676(3); Cd–O6, 2.343(3). Selected bond angles: N1–Cd–N2, 54.00(11)°; N6–Cd–N7, 54.89(11)°.

coordinated pyridine rings rotated 38.9° and 35.2° relative to their respective central isoindoline rings. The nonbonded pyridine arms extend into space away from each other and are separated by approximately 3.45 Å at the distance of closest approach. The nitrate ions coordinate as bidentate ligands, and as a consequence Cd²⁺ is eight-coordinate. The site symmetry about Cd is irregular, but the complex does possess approximate C₂ symmetry. Nitrate O3 and O6 atoms and pyridine N1 and N6 atoms are the “primary” donor atoms. The Cd–X bonds in this donor set vary in length between 2.32 and 2.34 Å. The “secondary” donor atoms are the imine N2 and N7 atoms and the nitrate O2 and O4 atoms, and bonds to these donor atoms vary from 2.51 to 2.68 Å. The average Cd–N(py) distances of 2.33(1) Å in **1** and 2.30(1) Å in Cd(4'-MeLH)(NO₃)₂ are quite similar, whereas the Cd–N(imine) bond lengths in **1** are 0.2–0.3 Å longer. The Cd–N(imine) distances are substantially longer because steric constraints on the isoindoline ligand keep the lone pair of the imine nitrogen from pointing directly at Cd. There has been only one previously reported structure of an isoindoline complex with a metal–N(imine) bond. The unusual binuclear Mo(II) complex, [Mo₂(OAc)₃(L)], L = unsubstituted isoindoline, has one Mo–N(imine) bond at 2.143 Å and one Mo–N(pyrrole) bond at 2.120 Å.⁷ The implication of this is that the imine nitrogen, although not as basic as the pyrrole nitrogen, can bind strongly to a metal ion when the orbitals are well matched for overlap.

The Cd–O primary bond distances in **1** are each 2.34 Å, while the average secondary Cd–O bond distances are 2.59(8) Å. A similar “short–long” pattern of Cd–O bond lengths is present in Cd(4'-MeLH)(NO₃)₂, a complex also containing two bidentate nitrate ligands.³ The four primary bonds in **1** form a distorted tetrahedral arrangement about Cd with the average of the six angles comprising these four primary bonds being 110(16)°. While tetrahedral coordination alone would not be especially unusual for Cd²⁺, the expanded 4 + 4 coordination sphere in **1** seemingly provides the stability that is required for product formation and isolation.

The presence of a broad methyl resonance at 2.6 ppm in the ¹H NMR spectrum of **1** in CD₂Cl₂ at 298 K, Figure 2a, signals that a fluxional process is occurring in solution. The aromatic proton resonances at 7.0–7.5 ppm are for the most

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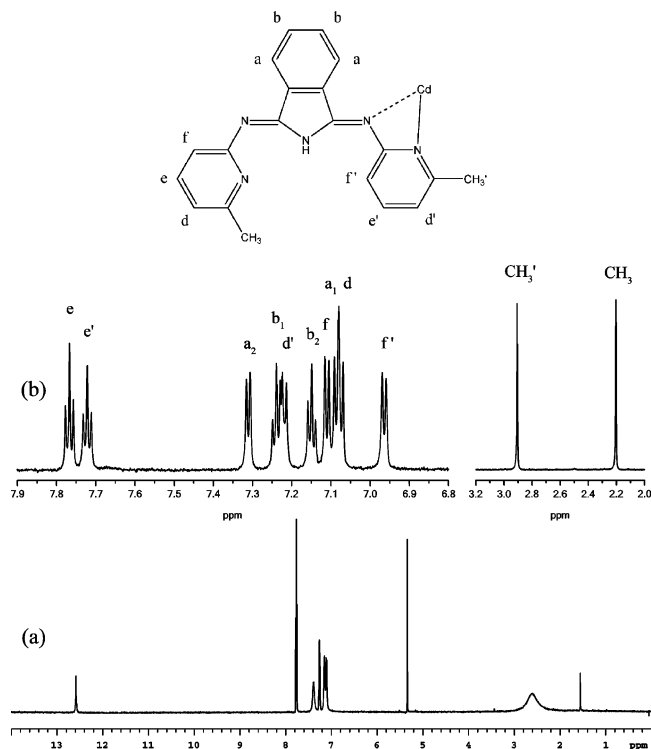


Figure 2. ^1H NMR spectra of **1** in CD_2Cl_2 at (a) 298 K, 500 MHz and (b) 230 K, 750 MHz.

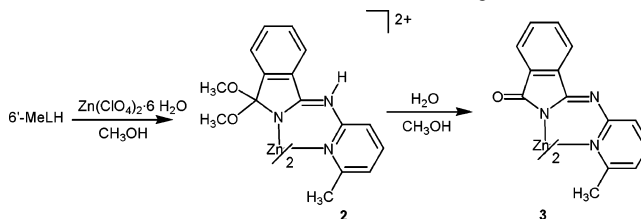
part well-resolved and postcoalescence, thus signifying that for these resonances $\Delta\nu \ll k$, where $\Delta\nu$ is the separation of the two peaks which are exchanging magnetic environments and k is the rate of exchange. Since addition of $6'$ -MeLH to the solution causes further broadening, it appears that ligand dissociation and reattachment is taking place such that both pyridine arms become equivalent under conditions of fast exchange. The long Cd–N(imine) bond distance does not argue well for the kinetic inertness of **1** in solution, and it is most likely that dissociation of $6'$ -MeLH is initiated by scission of the Cd–N(imine) bond.

The coordination site of the proton responsible for the sharp peak at 12.6 ppm is undoubtedly the pyrrole nitrogen, since $6'$ -MeLH also has its pyrrole proton resonance at 12.6 ppm. The NMR spectrum of **1** at 230 K is shown in Figure 2b with assignments obtained from 2D-COSY and 1D-NOESY spectra. At 230 K ligand exchange is very slow, all resonances are resolved and sharply defined, and the complex retains its C_2 symmetry in solution. Irradiation of the N–H resonance at 12.6 ppm produces NOE enhancement of the e' , f' , and CH_3 resonances and confirms that the spatial arrangement of the ligand in solution mirrors that found in the crystalline state.

The infrared spectrum of **1** contains a strong band at 1296 cm^{-1} which we attribute to an asymmetric N–O stretch of the nitrate ion.¹³ Bidentate nitrate should have a second vibrational band approximately $150\text{--}180\text{ cm}^{-1}$ higher in energy;¹³ however, positive identification was impossible because of the numerous ligand absorptions in this region

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Scheme 1. Reactions of Zn(II) with Isoindoline Ligand



of the spectrum. No nitrate combination bands in the $1700\text{--}1800\text{ cm}^{-1}$ region were observed.

We synthesized two other Cd(II) complexes of $6'$ -MeLH: $[\text{Cd}(6'\text{-MeLH})_2(\text{bipy})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$, bipy = 2,2'-bipyridine, and $[\text{Cd}(6'\text{-MeLH})_2(\text{ClO}_4)_2(\text{H}_2\text{O})]$.¹⁴ Both complexes contain bidentate imine–pyridine isoindoline coordination as found in **1**, although their respective coordination geometries are very different from that of **1**. The former complex is six-coordinate with a bidentate N_6 -octahedral environment about Cd. The latter complex is seven-coordinate and contains monodentate perchlorate and water as ancillary ligands. The NMR spectra of both in CD_2Cl_2 are highly fluxional as well and indicate rapid dissociation and reattachment of the $6'$ -MeLH ligand. Details concerning these related complexes will be reported elsewhere. With respect to Cd(II), it appears that bidentate imine–pyridine coordination is the “normal” coordination mode of $6'$ -MeLH. In the presence of ancillary ligands, this coordination mode allows Cd to bind to six, seven, or eight donor atoms for increased stability and avoids the steric problems associated with tridentate isoindoline coordination.

The reaction of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $6'$ -MeLH in methanol, however, does not yield an isoindoline complex (Scheme 1). Instead, when these components react in 1:1 or 1:2 molar stoichiometry in methanol and stand in solution for 2 days, a Zn(II) complex, $[\text{Zn}(6'\text{-L1H})_2](\text{ClO}_4)_2$ (**2**), with the unusual bidentate zwitterionic ligand, $6'$ -L1H, forms as yellow needles. This dimethylacetal-substituted ligand results from a solvolysis reaction in which one pyridine arm of $6'$ -MeLH is detached and presumably converted to 2-amino-6-methylpyridine. This solvolysis reaction appears to be unique and to the best of our knowledge has not been reported for any other isoindoline complex previously synthesized. Hydrolysis of $[\text{Zn}(6'\text{-L1H})_2]^{2+}$ remaining in the methanol filtrate slowly converts the dimethylacetal moiety into a ketone and produces deprotonated $\text{Zn}(6'\text{-L2})_2$ (**3**) as an orange crystalline product. A similar reaction between $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $6'$ -MeLH occurs in ethanol with formation of the analogous diethylacetal complex and the hydrolyzed ketone complex.

Although we were not able to grow high-quality crystals of **2**, a marginally satisfactory X-ray structural determination confirmed tetrahedral coordination about Zn as shown in Scheme 1. Given this tetrahedral arrangement, the $6'$ -methyl groups no longer represent a steric obstacle to metal coordination. The ^1H NMR spectrum of **2** (Figure 3) is consistent with this structure. A broad resonance at 10.1 ppm is due to the fluxional iminium proton which exchanges with

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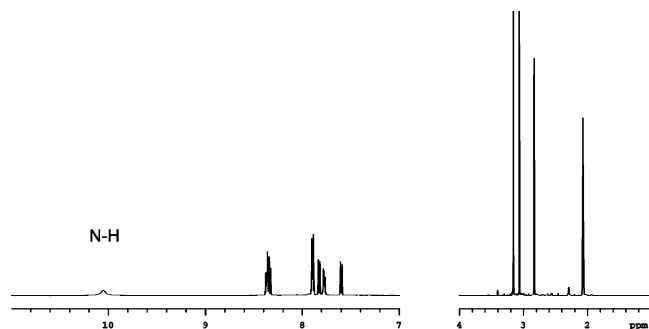


Figure 3. ^1H NMR spectrum of **2** in CD_3CN , 500 MHz.

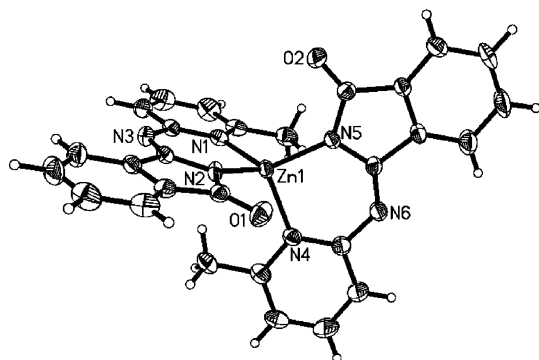


Figure 4. Thermal ellipsoid plot (50% probability) showing the structure and numbering scheme for **3**. Selected bond lengths (\AA): Zn–N1, 2.051(3); Zn–N2, 1.928(3); Zn–N4, 2.076(3); Zn–N5, 1.935(3). Selected bond angles: N1–Zn–N2, $93.86(11)^\circ$; N4–Zn–N5, $94.52(11)^\circ$.

adventitious water present in the solvent. The two methoxy proton resonances appear at 3.06 and 3.15 ppm.

The structure of **3**, Figure 4, is similar to that of **2** with tetrahedral coordination about Zn. The average Zn–N(pyridine) and Zn–N(pyrrole) bond lengths are 2.064(12) and 1.932(3) \AA , the latter being shorter because of the greater basicity of the pyrrole nitrogen. These distances are very similar to those found in the trinuclear complex $[\text{Zn}_3(4'\text{-MeL})_4](\text{ClO}_4)_2$, with its average Zn–N(pyridine) and Zn–N(pyrrole) bond lengths of 2.02(5) and 1.93(5) \AA , respectively, for *bidentate* $4'\text{-MeL}^-$.² The average N(pyridine)–Zn–N(pyrrole) bite angle in **3** is $94.2(3)^\circ$ and is not unusual for a six-membered chelate ring. The ^1H NMR spectrum of **3** in CDCl_3 and its chemical shift assignments are consistent with those of **2**.

The difference in behavior between Zn^{2+} and Cd^{2+} is striking but not unexpected as these d^{10} metal ions often exhibit different bonding preferences toward ligands. Commonly, the smaller Zn^{2+} ion prefers tetrahedral coordination, whereas the larger Cd^{2+} ion favors higher coordination numbers.^{15,16} We found this to be the case when Zn^{2+} , Cd^{2+} , and Hg^{2+} reacted with $4'\text{-MeL}^-$ in a 1:1 molar ratio. With Zn^{2+} and Hg^{2+} the tetrahedrally coordinated, trinuclear complexes $[\text{M}_3(4'\text{-MeL})_4]^{2+}$ were formed, whereas the reaction product with Cd^{2+} was the octahedral complex $\text{Cd}(4'\text{-MeL})_2$.¹⁴

For either Zn^{2+} or Cd^{2+} , mer-octahedral coordination, as would be the case with $[\text{M}(6'\text{-MeLH})_2]^{2+}$ or $\text{M}(6'\text{-MeL})_2$, is

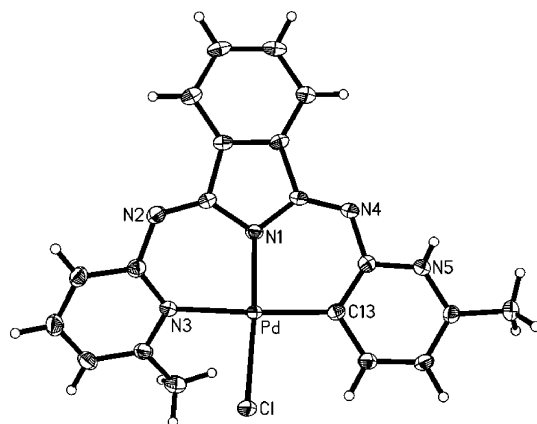


Figure 5. Thermal ellipsoid plot (50% probability) showing the structure and numbering scheme for **4**. Selected bond lengths (\AA): Pd–N1, 1.967(2); Pd–N3, 2.152(3); Pd–C13, 1.990(3); Pd–Cl, 2.3654(8). Selected bond angles: N3–Pd–C13, $171.65(11)^\circ$; N1–Pd–Cl, $165.13(8)^\circ$.

sterically impossible. While a highly distorted square planar geometry, as in the hypothetical $\text{M}(6'\text{-MeL})\text{X}$, might be possible for the divalent d^8 metal ions Pd^{2+} and Pt^{2+} , it represents a highly unlikely geometry for Cd^{2+} and Zn^{2+} . For the larger Cd^{2+} ion bidentate coordination of two $6'\text{-MeLH}$ ligands via pyridine and imine nitrogen atoms is seemingly the coordination mode of least steric strain, consistent with coordination number ≥ 6 . In contrast, the reaction of Zn^{2+} with $6'\text{-MeLH}$ is seemingly driven by the stability acquired by tetrahedral complex formation. Whereas the dimethylacetal fragment $6'\text{-L1H}$ coordinates as a charge-neutral, bidentate, iminium zwitterionic ligand in **2**, the ketone fragment $6'\text{-L2}$ coordinates as a deprotonated ligand in **3**. This nicely illustrates how imine basicity and zwitterion ligand complexation are related and may be selectively controlled by the appropriate choice of substituents. Whereas **2** is an iminium zwitterionic complex, the iminium proton is not retained in **3**, presumably due to the electron-withdrawing ability of the carbonyl group.

The reaction of $\text{Pd}(\text{COD})\text{Cl}_2$ with $6'\text{-MeLH}$ in refluxing methanol produces a complex with yet another coordination mode for this ligand. Deprotonation of the pyrrole nitrogen occurs *without* addition of base, and a severely distorted, square planar complex, $\text{Pd}(6'\text{-MeL})\text{Cl}\cdot\text{THF}$ (**4**), a palladacycle, is isolated after recrystallization from THF/ether. As shown in Figure 5, the isoindoline anion coordinates as a NNC pincer ligand with only one of its two methyl groups in the immediate vicinity of the Cl atom. Metal coordination at C13 and protonation of N5 transforms $6'\text{-MeL}^-$ into an unusual tridentate zwitterionic ligand with negative centers at N1 and C13 and a positive center at N5. The pyridinium proton attached to N5 is hydrogen bonded to the oxygen atom of THF at a distance of 2.075 \AA . This proton was located in a difference electron density map and refined independently with satisfactory results.

This complex is significantly distorted from square planar geometry as a consequence of the proximity of the $6'\text{-CH}_3$ group (adjacent to N3) to the fourth coordination site of the complex. The distortion manifests itself in the twisting of the N3-pyridine ring of $6'\text{-MeL}^-$ by 30.7° relative to the plane of the five-membered pyrrole ring such that N3 and

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the C atom of the 6'-CH₃ group are positioned 0.64 and 2.15 Å, respectively, above this reference plane. Whereas Pd lies within this plane, Cl is displaced by 0.60 Å below the plane such that the N1-Pd-Cl angle is 165°. The substantial twisting of the N3-pyridine ring creates space for chloride to occupy the fourth position in the coordination sphere about Pd, while the twisting of the C13-pyridine ring by -4.9° and the consequent proximity of 6'-H and Cl allow for an intermolecular C-H...Cl hydrogen bond of 2.48 Å.

Although the structure of **4** is highly irregular, the Pd-N and Pd-Cl bond distances are quite similar to those reported by Gade et al.^{1h} for Pd(5'-BrL)Cl, a complex with significantly less structural distortion and one in which the isoindoline coordinates in its normal fashion as a NNN pincer ligand. In all isoindoline pincer complexes the M-N(pyrrole) bond length is shorter than M-N(pyridine) by approximately 0.08–0.15 Å,^{1–3} albeit in **4** the difference in length is 0.185 Å. The Pd-C bond length of 1.99 Å in **4**, however, falls within the normal range of 1.99–2.01 Å expected for palladacycles¹⁷ and the Pd-Cl bond length differs by only 0.03 Å from the distance reported for Pd(5'-BrL)Cl.^{1h}

There are further similarities between the structures of **4** and Pd(5'-BrL)Cl. Both complexes, for example, are stabilized by intramolecular C-H...Cl hydrogen bonding. In the latter complex the relevant H...Cl distances are 2.46 and 2.40 Å, whereas in **4** the distance is 2.48 Å. These distances are consistent with N-H...Cl hydrogen bond distances of 2.45 and 2.47 Å recently reported for a bis(guanidine)-copper(I) chloride complex.¹⁸ Similarly, chloride is displaced by 0.60 Å below the pyrrole plane in Pd(5'-BrL)Cl, and the N1-Pd-Cl angle is 167.7°. The fact that the isoindoline anion in **4** is a NNC rather than a NNN pincer ligand as in Pd(5'-BrL)Cl is clearly the result of the energetically unfavorable steric requirements for chloride coordination in the presence of the two neighboring 6'-CH₃ groups. This fact coupled with the known special stability of the Pd-C bond accounts for the formation of **4** as the less sterically strained palladacycle complex.

Whereas the zwitterionic complex Cd(4'-MeLH)(NO₃)₂ is fluxional in CD₂Cl₂ solution, its iminium proton transported between imine nitrogens of the isoindoline by methanol solvate and adventitious water, it appears that **4** is not

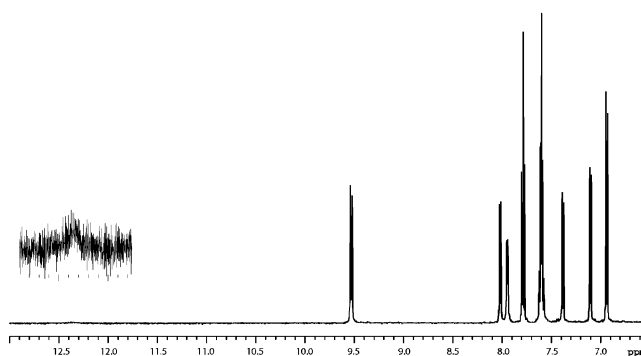


Figure 6. ¹H NMR spectrum of **4** in THF-*d*₈, 500 MHz.

fluxional. The absence of line broadening of the aromatic and methyl proton resonances in the ¹H NMR spectrum in THF-*d*₈ (Figure 6) suggests that the pyridinium proton in **4** is tightly held by N5. The very broad, barely detectable, peak at ca. 12.3 ppm is due to the pyridinium proton, its breadth and position being consistent with the spectra of pyridinium salts and the pyridinium complex [(η⁶-C₆H₆)Cr(η⁵-C₅H₅NH)⁺.¹⁹

In conclusion, the presence of the two bulky methyl groups in 6'-MeLH effectively prevents this ligand from coordinating as a deprotonated, anionic or charge-neutral, zwitterionic NNN pincer ligand to Cd(II), Zn(II), and Pd(II) in the reactions studied. In all three systems it is due to the inability of an ancillary ligand to coordinate trans to the pyrrole nitrogen. For Cd(II) and Pd(II) other coordination modes of this ligand are possible, whereas for Zn(II) loss of a pyridine arm through solvolysis and subsequent coordination of the remaining fragment is favored.

Acknowledgment. M.W. acknowledges the support of Research Corporation. We thank Nils Schlörer, University of Washington, for obtaining the 750 MHz spectrum and for helpful discussions and Lance Culnane for initial experimental assistance. The SMART X-ray diffractometer at Colorado State University was provided by a grant from the National Institutes of Health Shared Instrumentation Grant Program.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0506916

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