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Size Discrimination in the Coordination Chemistry of an Isoindoline Pincer Ligand with Cd(II) and Zn(II)

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The reactions of Cd^{2+} and Zn^{2+} with the pyridine-arm isoindoline ligand 4′-MeLH = 1,3-bis[2-(4-methylpyridyl)-imino]isoindoline produced the series of octahedrally coordinated complexes M(4′-MeL)$_2$, [M(4′-MeLH)$_2$]$^{2+}$, and [M(4′-MeL)(4′-MeLH)]$^+$. The complexes M(4′-MeL)$_2$ resulted from reactions of the respective metal perchlorates with deprotonated ligand, whereas the complexes [M(4′-MeLH)$_2$](ClO$_4$)$_2$ resulted from reactions with ligand in the absence of added base. The mixed-ligand complexes [M(4′-MeL)(4′-MeLH)]$^+$ were generated in solution by reactions of equimolar quantities of M(4′-MeL)$_2$ and [M(4′-MeLH)$_2$]$^{2+}$. Whereas [Cd(4′-MeL)(4′-MeLH)]$^+$ is stable in solution, [Zn(4′-MeL)(4′-MeLH)]$^+$ converts to and establishes equilibrium with the tetrahedrally coordinated, trinuclear complex [Zn$_3$(4′-MeL)$_4$]$^{2+}$. The complexes Cd(4′-MeL)$_2$ (**1**), Zn(4′-MeL)$_2$ (**2**), and [Cd(4′-MeL)(4′-MeLH)]ClO$_4$ (**5**) were characterized by single-crystal X-ray diffraction, with the latter complex being shown to contain 4′-MeLH coordinated as a protonated iminium zwitterionic ligand. The [M(4′-MeLH)$_2$]$^{2+}$ and [M(4′-MeL)(4′-MeLH)]$^+$ complexes are tautomeric in solution because of the shuttling of the iminium protons between imine N atoms. The rate of prototropic tautomerism in [Cd(4′-MeLH)$_2$]$^+$ was followed by ^{1}H NMR spectroscopy. Over the temperature range 276–312 K, a linear Eyring plot with the activation parameters $\Delta G^{\ddagger} = 16.0 \pm 0.1$ kcal/mol, $\Delta H^{\ddagger} = 2.9 \pm 0.1$ kcal/mol, and $\Delta S^{\ddagger} = -44.0 \pm 0.3$ cal/mol·K was obtained.

Introduction

1,3-Bis(2-pyridylamino)isoindolines and their alkyl-substituted derivatives, *n*′-RLH, shown below, are a family of N donor pincer ligands formed by the condensation reaction of 1,2-dicyanobenzene with various 2-aminopyridines. Upon deprotonation with a base, they coordinate as uninegative, tridentate ligands via pyrrole and pyridine N atoms, and this has been observed in numerous cases in reactions with transition-metal ions.[1]

As uninegative tridentate N donor ligands, these derivatized isoindolines are similar to the familiar pyrazolylborates,[2] although the distinction between the two is that pyrazolylborates coordinate facially, whereas isoindolines are restricted to coordinate meridionally. Isoindolines may also be classified as pincer ligands. In contrast to the well-known meridionally coordinated PCP and NCN analogues, however, the central pyrrole N atom of an isoindoline is substantially

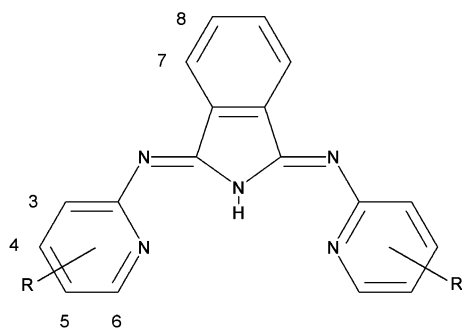less basic than the central C atom of PCP and NCN pincer ligands.

Over a period of approximately 20 years, there has been intermittent interest in the use of various metal complexes of deprotonated 1,3-bis(2-pyridylamino)isoindolines and its alkyl-substituted derivatives for the oxidation of substrates such as alcohols[3] and hydrocarbons[4] and most recently for the hydrogenation of alkenes.[5] In the latter case, it has been proposed that the square-planar palladium isoindoline com-

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(1) For example, see: (a) Gagné, R. R.; Gall, R. S.; Lisensky, G. S.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem* **1979**, *18*, 771. (b) Gagné, R. R.; Marritt, W. A.; Marks, D. N.; Siegl, W. O. *Inorg. Chem.* **1981**, *20*, 3260. (c) Addison, A. W.; Burke, P. J.; Henrick, K. *Inorg. Chem.* **1982**, *21*, 60. (d) Domaille, P. J.; Harlow, R. L.; Ittel, S. D.; Peet, W. G. *Inorg. Chem.* **1983**, *22*, 3944. (e) Bereman, R. D.; Shields, G. D.; Dorfman, J. R.; Bordner, J. *J. Inorg. Biochem.* **1983**, *19*, 75. (f) Baird, D. M.; Maehlmann, W. P.; Bereman, R. D.; Singh, P. *J. Coord. Chem.* **1997**, *42*, 107. (g) Balogh-Hergovich, É.; Kaizer, J.; Speier, G.; Huttner, G.; Jacobi, A. *Inorg. Chem.* **2000**, *39*, 42. (h) Balogh-Hergovich, É.; Speier, G.; Réglier, M.; Giorgi, M.; Kuzmann, E.; Vértes, A. *Inorg. Chem. Commun.* **2005**, *8*, 457. (i) Meder, M. B.; Haller, I.; Gade, L. H. *J. Chem. Soc., Dalton Trans.* **2005**, 1403.
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Figure 1. Alkyl-substituted 1,3-bis(2-pyridylamino)isoindoline, *n′*-RLH, with the numbering scheme for ^{1}H NMR spectra.

Figure 2. Principal resonance forms for 4′-MeLH when coordinated to a metal ion.

plex [Pd(*n′*-RLH)Cl]⁺, formed from the precursor Pd(*n′*-RL)-Cl catalyst, serves as a reactive intermediate in the catalytic hydrogenation of alkenes.

Perhaps the most interesting feature of these pyridine-arm isoindolines is that the ligand (nondeprotonated) can coordinate to metal ions as a charge-neutral, zwitterionic, tridentate pincer ligand and form stable, isolable complexes. This is a consequence of the internal transfer of its pyrrole proton to an imine N atom. Robinson and co-workers[6] in 1967 reported the first examples of transition-metal complexes containing nondeprotonated, pyridine-arm isoindoline ligands, *n′*-RLH, but did not recognize the fact that the pyrrole proton had shifted to an imine N atom. Further examples of *n′*-RLH complexes containing Co(II), Fe(II), and Ru(II) were reported by Gagne and co-workers;[3,7] however, structural validation by X-ray crystallography was not obtained.

A principal objective of this study is to validate the existence of charge-neutral, zwitterionic, *n′*-RLH isoindoline complexes and demonstrate that such complexes can be readily obtained with a variety of metal ions. In a recent Communication, we reported the synthesis and X-ray crystal structure of the seven-coordinate complex Cd(4′-MeLH)-(NO₃)₂ (**6**),[8] where 4′-MeLH = 1,3-bis[2-(4-methylpyridyl)-imino]isoindoline, the first structurally characterized complex containing a charge-neutral, zwitterionic isoindoline ligand. Metric details for the complex suggest that the two principal resonance forms of coordinated 4′-MeLH, shown in Figure 2, contribute equally to the structure of the tridentate isoindoline ligand in **6**. As evidenced by ^{1}H NMR spectroscopy, this complex exhibits prototropic tautomerism in solution, with tautomerism being a consequence of proton transfer between the two imine N atoms of 4′-MeLH. In this
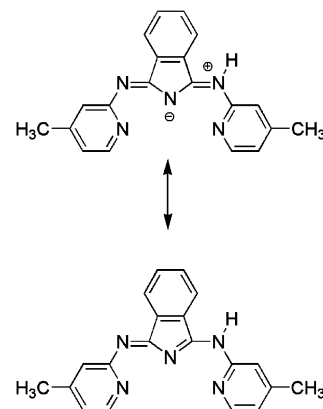
report, our study focuses on newly synthesized 4′-MeLH complexes of Cd(II) and Zn(II) and how the difference in size of these two metal ions affects the reaction chemistry of their respective complexes.

A second objective of this study is to gain a better understanding of the proton-transfer mechanism in solution for complexes containing tautomeric *n′*-RLH isoindoline ligands. Proton-transfer processes are of significant importance in many chemical and biological systems,[9] and these isoindoline complexes provide simple models for examining proton transport in solution. In such complexes, proton transfer and tautomerism are connected because there are two symmetry-equivalent imine N atoms that can serve as proton acceptors.

Tautomerism is a well-known phenomenon in chemistry and especially in N heterocyclic chemistry.[10] Prototropic tautomerism, a special case in which the tautomerism involves movement of a proton from one site to another and not necessarily an equivalent site, occurs in N bases such as imidazoles,[11] pyrazoles,[12] porphyrins,[13] monoprotic porphyrin anions,[13] and N-confused porphyrins.[14] In the case of free acid porphyrins and monoprotic porphyrin anions, for example, proton transfer is very rapid because the N acceptor atoms are spatially close, and proton transfer occurs without the need for a solvent molecule or Lewis base to transport protons in solution. In other molecules, triazines for example,[15] the opposite is true: the two proton acceptor sites in the molecule are distant, and Lewis base mediation is needed to effectuate proton transfer. Pyridine-arm isoindolines are similar to triazines in that both have two N proton acceptor sites sufficiently distant from each other such that direct proton transfer is impossible. In contrast to triazines,

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pyridine-arm isoindolines introduce a further level of complexity with regard to proton transfer because two of these tridentate ligands can coordinate to a metal ion. We demonstrate here how the rate of proton transfer is remarkably different in the complex ions $[M(4'-MeLH)_2]^{2+}$ and $[M(4'-MeLH)(4'-MeL)]^+$, M = Cd and Zn, and discuss the role of entropy in the prototropic tautomerism of these isoindoline complexes.

Experimental Section

The ligand 4'-MeLH was prepared following published procedures.[16] All other chemicals were reagent-grade and commercially available. ^{1}H NMR spectra in CD_2Cl_2 were obtained on Varian Inova 500-MHz and Bruker AMX 750-MHz spectrometers and referenced to the residual proton peak of the solvent. NMR samples were dried under vacuum for a few hours in order to remove traces of water and solvated methanol. CD_2Cl_2 was dried over CaH_2 and transferred on a Schlenk line to samples in J. Young NMR tubes. NMR line-shape analysis was carried out with gNMR software. IR spectra were obtained on a Mattson Gemini spectrometer. Elemental analyses were provided by Desert Analytics and Atlantic Microlab.

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

Synthesis of Cd(4'-MeL)₂ (1). A methanolic tetra-*n*-butylammonium hydroxide solution (1.0 mL, 1.0 M) was added to 30 mL of a solution of 4'-MeLH (0.327 g, 1.0 mmol) in warm methanol. Solid $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol) was then added to the stirred solution. After filtration to remove traces of undissolved solids, slow cooling of the filtrate produced orange rods that proved suitable for X-ray diffraction studies. Yield: 0.109 g, 14%. IR (KBr): $\nu_{C=N/C=C}$ 1630, 1608, 1570, 1520, 1469 cm^{-1}. Anal. Calcd for $C_{40}H_{32}N_{10}Cd$: C, 62.80; H, 4.17; N, 18.31. Found: C, 62.78; H, 4.22; N, 18.31.

Synthesis of Zn(4'-MeL)₂ (2). This complex was prepared from a methanol solution as a microcrystalline solid by a slight modification of the method previously described by Gagné et al.,[1b] with methanolic tetra-*n*-butylammonium hydroxide rather than triethylamine being used to deprotonate 4'-MeLH. The complex was analytically pure as shown by its ^{1}H NMR spectrum. Layering of a CH_2Cl_2 solution of **2** with ether produced yellow rods of a monohydrate that proved suitable for X-ray diffraction studies. ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K): δ 8.05 (m, 7H), 7.95 (d, 5H), 7.67 (m, 8H), 7.14 (s, 3H), 6.51 (d, 6H), 2.19 (s, CH₃).

Synthesis of [Cd(4'-MeLH)₂](ClO₄)₂·CH₃OH·2H₂O (3). Solid $Cd(ClO_4)_2 \cdot 6H_2O$ (0.928 g, 2.21 mmol) was added to a stirred solution of 4'-MeLH (0.327 g, 1.00 mmol) in 20 mL of warm methanol. After filtration to remove traces of undissolved solids, the solution was cooled at 0 °C for a few days. The microcrystalline product that formed was washed with ice-cold methanol and air-dried. Yield: 0.365 g, 73%. IR (KBr): $\nu_{C=N/C=C}$ 1637, 1602, 1550, 1519, 1490, 1471 cm^{-1}; $\nu_{ClO_4^-}$ 1098 cm^{-1}. Anal. Calcd for $C_{41}H_{42}N_{10}CdCl_2O_{11}$: C, 47.62; H, 4.09; N, 13.55. Found: C, 47.62; H, 3.99; N, 13.43.

Synthesis of [Zn(4'-MeLH)₂](ClO₄)₂·1.5H₂O (4). Solid $Zn(ClO_4)_2 \cdot 6H_2O$ (0.0933 g, 0.251 mmol) was added to a stirred solution of 4'-MeLH (0.1614 g, 0.494 mmol) in 10 mL of warm methanol. After filtration to remove traces of undissolved solids,

Table 1. Crystallographic Data for Compounds **1**, **2**, and **5**[a]

compound	1	2	5
chemical formula	$C_{40}H_{32}CdN_{10}$	$C_{40}H_{34}N_{10}OZn$	$C_{42}H_{33}CdClN_{10}O_{9.75}$
fw	765.2	736.1	981.6
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	12.033(3)	11.765(3)	17.625(3)
b, Å	15.946(3)	15.937(4)	10.768(2)
c, Å	18.515(6)	18.606(4)	23.098(4)
β, deg	93.773(6)	93.579(4)	90.989(8)
V, Å^3	3545.0(15)	3481.7(13)	4383.1(14)
Z	4	4	4
T, K	173(2)	155(2)	165(2)
λ, Å	0.7107	0.7107	0.7107
D_{calcd}, g cm^{-3}	1.43	1.40	1.49
μ, mm^{-1}	0.661	.755	0.627
$R(F_o)^a$	0.0370	0.0432	0.0625
$R_w(F_o^2)^a$	0.0952	0.100	0.182

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

the solution was cooled at ambient temperature. The microcrystalline product that formed quickly was washed with ice-cold methanol and air-dried. Yield: 0.0715 g (31%). IR (KBr): $\nu_{C=N/C=C}$ 1638, 1605, 1551, 1523, 1490, 1469 cm^{-1}; $\nu_{ClO_4^-}$ 1100 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K): δ 2.34 (s, 6H), 2.36 (s, 6H), 6.93 (t, 4H), 7.50 (s, 2H), 7.87–7.98 (m, 10H), 8.25 (d, 2H), 8.80 (d, 2H), 10.93 (s, N*H*, 2H). Anal. Calcd for $C_{40}H_{37}N_{10}ZnCl_2O_{9.5}$: C, 50.78; H, 3.95; N, 14.81. Found: C, 50.88; H, 3.94; N, 14.82.

X-ray Diffraction Studies. X-ray diffraction data from single crystals were recorded on a Bruker-Nonius SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Standard Bruker control (*SMART*) and integration (*SAINT*) software was employed, and Bruker *SHELXTL*[17] software was used for structure solution, refinement, and graphics. Selected details related to the crystallographic experiment are listed in Table 1. Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. Intensities were integrated from series of frames (ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using *SADABS*.[18] The structures were solved by direct methods and refined (on F^2 using all data) by a full-matrix, weighted least-squares process. Residual electron density representing disordered solvent molecules of methanol or water was included in the model as O atoms with fractional occupancy.

Results and Discussion

Whereas octahedral coordination is most common for Cd(II) and tetrahedral coordination is most common for Zn(II),[19] both metal ions form octahedral complexes of formula $M(4'-MeL)_2$ when the respective metal nitrate or perchlorate salts are reacted with the deprotonated anion 4'-MeL$^-$ in a 1:2 molar ratio in methanol. In both complexes, the isoindolinate anion coordinates meridionally as a tridentate ligand, albeit with significant distortion from planar geometry.

The structure of **1**, as determined by single-crystal X-ray diffraction, is shown in Figure 3; selected Cd−N bond lengths and angles are listed in Table 2. The isoindoline anion

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Figure 3. Thermal ellipsoid plot (50% probability) showing the structure of **1**.

Table 2. Selected M−N Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, and **5**

	1	2	5
M−N3	2.258(2)	2.038(2)	2.264(5)
M−N5	2.370(2)	2.248(2)	2.363(6)
M−N1	2.392(2)	2.252(2)	2.382(6)
M−N3A	2.233(2)	2.053(2)	2.251(6)
M−N5A	2.379(2)	2.239(2)	2.360(6)
M−N1A	2.354(2)	2.233(2)	2.348(6)
N3−M−N3A	177.91(8)	178.91(8)	176.3(2)
N1A−M−N5A	161.65(8)	167.05(7)	157.0(2)
N1−M−N5	159.27(8)	169.90(7)	160.3(2)

functions as a tridentate ligand using pyrrole and pyridine N atoms to coordinate to Cd. Although the basic coordination geometry about Cd is octahedral, there is considerable ligand distortion. The isoindolinate ligands in **1** are distinctly nonplanar, seemingly in order to minimize *inter*ligand N(pyrrole)−H6 repulsions (H6 refers to the notation introduced in Figure 1). The extent of distortion from planarity in each 4′-MeL⁻ ligand is indicated by the twist angle of the two pyridine arms relative to the central pyrrole ring. The isoindoline ligand defined by N1, N3, and N5 is ruffled. Its two pyridyl rings are twisted by 24.6° and 29.5° in the same direction relative to its pyrrole ring, while the isoindoline defined by N1A, N3A, and N5A is significantly less distorted and has its two pyridyl rings twisted by 12.1° and 12.3° in opposite directions relative to its pyrrole ring. In [Cu(4′-MeL)(H₂O)₂]ClO₄,[20] a distorted trigonal-bipyramidal complex in which the water ligands bind *equatorially* and there is no donor atom situated trans to the pyrrole N atom, the pyridine arms are nearly coplanar and the ring twist angles are only 5.8° and 3.0°. The H6/H6 separation in each of the 4′-MeL⁻ ligands in **1** is another significant marker. These distances are approximately 5.25 and 5.28 Å for the two isoindoline ligands in **1**, whereas this separation is only 3.93 Å in [Cu(4′-MeL)(H₂O)₂]ClO₄.[8] It seems clear that the H6 protons of the pyridine arms in 4′-MeL⁻ restrict unhindered access of a fourth in-plane donor atom and that

(20) Anderson, O. P.; la Cour; Dodd, A.; Garrett, A. D.; Wicholas, M. *Inorg. Chem.* **2003**, *42*, 122.

significant ruffling of at least one isoindoline ligand is necessary for octahedral coordination to occur in **1**. Similar ruffling is present in **2**·H₂O (vide infra).

The pattern of Cd−N bond lengths in **1** [long Cd−N(pyridine) bonds and shorter Cd−N(pyrrole) bonds] is consistent with that observed in other structurally characterized tridentate 4′-MeL⁻ complexes.[1,4,8,20] Although the Cd−N(pyrrole) distances in **1** differ by more than 10σ, the average Cd−N(pyrrole) distance of 2.23 Å in **1** is found, as expected, to be approximately 0.14 Å shorter than the average Cd−N(pyridine) distance of 2.37 Å.

Despite the presence of a water molecule in **2**, the structures of **1** and **2** appear isomorphous.[21] Selected Zn−N bond lengths and angles are listed in Table 2 (the numbering system for atoms in **2** is identical with that in **1**). The Zn−N bonds are approximately 0.2 Å shorter than the comparable Cd−N bonds in **1**, and a similar pattern of M−N bond lengths is observed, with the Zn−N(pyrrole) bond being approximately 0.2 Å shorter than the Zn−N(pyridine) bonds. The smaller size of Zn^{2+} makes this cation a better fit for the isoindoline cavity than Cd^{2+}. This is evident from the *trans*-N(pyridine)−M−N(pyridine) bond angles: 169.9° and 167.0° in **2** in contrast to the more acute angles of 161.6° and 159.3° in **1**. As noted for the structure of **1**, the pyridine rings of each ligand in **2** are similarly twisted with respect to the center fused-ring isoindoline. The isoindoline ligand containing N3 has pyridine twist angles of approximately 25° and 18°, while the isoindoline ligand containing N3A has pyridine twist angles of approximately 15° and 8°.

In the absence of added base, Cd(ClO₄)₂·6H₂O and Zn(ClO₄)₂·6H₂O will react with 4′-MeLH in a 2:1 metal-to-ligand molar ratio to form [Cd(4′-MeLH)₂](ClO₄)₂ (**3**) and [Zn(4′-MeLH)₂](ClO₄)₂ (**4**), respectively. Previous experience with the reaction of Cd(NO₃)₂ and 4′-MeLH to form **6**·CH₃OH showed that a 2−3-fold molar excess of Cd(NO₃)₂ was necessary to deter coformation of **1**, hence, the choice of the unusual stoichiometry for the preparation of **3** and **4**. When reactions of Cd(ClO₄)₂ or Zn(ClO₄)₂ and 4′-MeLH are carried out in a stoichiometric 1:2 metal-to-ligand molar ratio in small volumes of methanol, immediate precipitation of mixed products occurs. On the other hand, when the volume was large and the solution was allowed to evaporate slowly in air, M(4′-MeL)₂ crystals were the sole product. The apparent propensity of 4′-MeLH to relinquish its pyrrole proton in solution without the addition of a base makes the synthesis of charge-neutral, zwitterionic isoindoline complexes less than straightforward.

All of our attempts to prepare single crystals of **3** and **4** suitable for X-ray diffraction studies were unsuccessful. In one preparation of **3**, however, a single crystal of the mixed-ligand complex [Cd(4′-MeLH)(4′-MeL)]ClO₄ (**5**) was picked out of the bulk product. The structure of **5**, as determined by single-crystal X-ray diffraction, is shown in Figure 4. Only one isoindoline ligand appears to be protonated. Its proton, coordinated to imine N atom N2, was located in the difference electron density map and was included in the

(21) The water molecule present in **2** is interstitial and is not H-bonded.
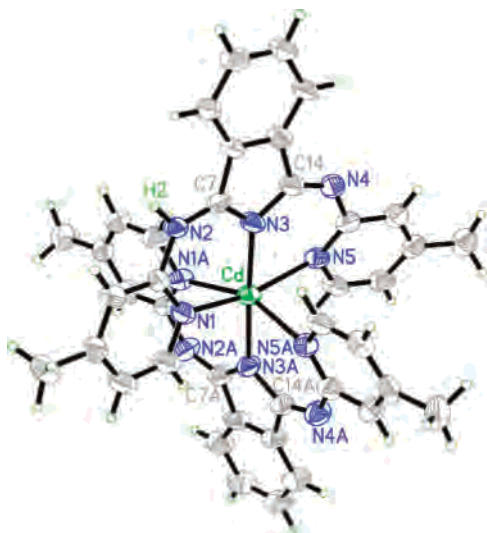
**Figure 4.** Thermal ellipsoid plot (50% probability) showing the structure of **5**.

Table 3. Select C−N Bond Lengths (Å)[a] for Compounds **1**, **5**, and **6**

bond	**1**	**5**	**6**
4-MeL⁻ C−N(pyrrole)	1.39 ± 0.01 C7−N3, C14−N3 C7A−N3A, C14A−N3A	1.376 C7A−N3A 1.390 C14A−N3A	
4-MeL⁻ C−N(imine)	1.29 ± 0.02 C7−N2, C14−N4 C7A−N2A, C14A−N4A	1.302 C7A−N2A 1.297 C14A−N4A	
4-MeLH C−N(pyrrole)		*1.324* C7−N3 1.423 C14−N3	*1.331* C7−N3 1.410 C14−N3
4-MeLH C−N(imine)		*1.311* C7−N2 1.275 C14−N4	*1.344* C7−N2 1.280 C14−N4

[a] Italicized numbers refer to bonds on the protonated side of the isoindoline ligand.

model in an idealized position. This iminium proton is involved in a weak hydrogen bond to O3 of the perchlorate counterion (N2···O3 = 2.725 Å). Selected bond distances and angles are listed in Tables 2 and 3, with the latter table including pertinent comparisons to selected C−N distances in the Cd(II) complexes **1** and **6**. As in both **1** and **2**, steric crowding of the isoindoline ligands in **5** has significant structural consequences. The protonated isoindoline ligand in **5** defined by N1, N3, and N5 has its two pyridyl rings twisted by 12.0° and 19.8° relative to its central pyrrole ring, whereas the isoindolinate anion defined by N1A, N3A, and N5A has its two pyridyl rings canted by 4.2° and 7.6° relative to its central pyrrole ring.

When the crystal structures of **1**, **5**, and **6** are compared, it is found that it is the pattern of C−N bond lengths that serves to distinguish 4′-MeLH from 4′-MeL⁻ coordination. The significant C−N bond lengths in these complexes are C(pyrrole)−N(pyrrole) and C(pyrrole)−N(imine), and these are listed in Table 3. Although the two 4′-MeL⁻ ligands in **1** have distinctly different degrees of ruffling, comparable isoindoline C−N bond lengths in the two ligands vary insignificantly from one another. The average C−N (imine) bond length of 1.29 ± 0.02 Å in **1** is characteristic of a double bond, while the average C−N (pyrrole) bond length of 1.39 ± 0.01 Å is characteristic of a bond order intermedi-
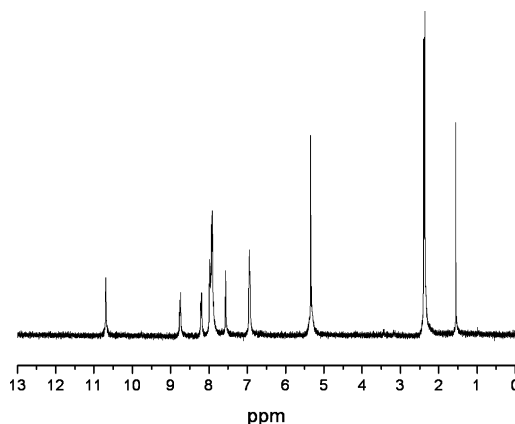
Figure 5. ¹H NMR spectrum of **3** in CD₂Cl₂, 293 K.

ate between single and double.[22] Both are consistent with bond lengths found in **2** and previously characterized 4′-MeL⁻ complexes.[1,4,8,20] Only one iminium isoindoline complex, **6**, has been characterized structurally,[8] and its relevant C−N bond lengths are also listed in Table 3. This complex serves as a useful structural reference for **5**. The variation of C−N bond lengths in **6** can be explained by reference to the two principal resonance forms of the coordinated 4′-MeLH ligand (Figure 4) and, as previously proposed,[8] is consistent with an approximate 50% contribution of each resonance structure. The protonated isoindoline ligand in **5**, defined by N1, N3, and N5, has a C−N bond length pattern strikingly similar to that of **6**, while the isoindoline ligand defined by N1A, N3A, and N5A in **5** has a C−N bond length pattern strikingly similar to that found in **1**.

The ¹H NMR spectra of **1** and **2** in CD₂Cl₂ each have five distinct signals in the aromatic region and one methyl resonance at approximately 2.4 ppm. The spectra are consistent with that reported previously for **2**[1b] and are representative of complexes with two *equivalent*, meridionally coordinated, tridentate isoindoline ligands. Although the isoindoline conformations of each of the ligands in **1** and **2** are somewhat different in the solid state, no evidence of ligand inequivalence is apparent in NMR spectra of CD₂Cl₂ solutions of these complexes at temperatures as low as 193 K.

The ¹H NMR spectrum of **3** at ambient temperature in CD₂Cl₂, shown in Figure 5, is more complex than that of **1**. There are seven distinct resonances in the aromatic region of the spectrum between 8.8 and 6.9 ppm. The presence of two distinct methyl proton resonances at 2.39 and 2.37 ppm and an imine proton resonance at 10.72 ppm confirms that 4′-MeLH is coordinated, as shown in Figure 2. The imine proton resonance is shifted upfield by 3.2 ppm from that of the pyrrole proton resonance in 4′-MeLH. NMR assignments and chemical shifts for **1** and **3** are listed in Table 4. The presence of an iminium proton in **3** causes for the most part only a minor perturbation of the ¹H NMR chemical shifts when compared to those in **1**; however, the 7H and 3H protons in **3**, with chemical shifts of 8.77 and 7.93 ppm,
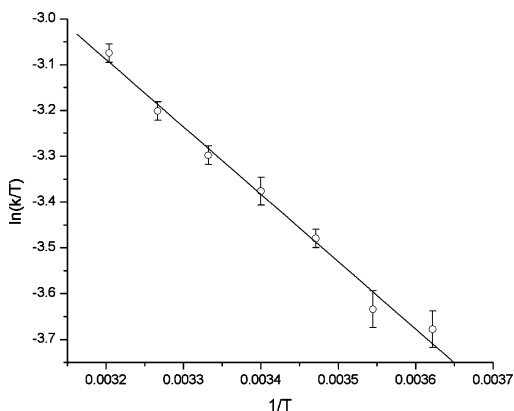
(22) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, L. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, S1.

Table 4. ^{1}H NMR Chemical Shifts for Compounds **1**, **3**, and **5** in CD$_2$Cl$_2$$^{a-c}$

proton	1	3	5
H8	7.65	7.98, 7.97	7.70
H7	8.02	8.22, *8.77*	8.12
H6	7.95	8.00, 7.99	7.95
H5	6.53	6.95, 6.94	6.61
H3	7.21	7.57, *7.93*	7.33
CH$_3$	2.22	2.39, 2.37	2.25
N—H		10.72	

^{a} Chemical shifts in ppm relative to tetramethylsilane at 293 K. ^{b} Resonances listed in italics are those that conclusively could be identified from a one-dimensional NOESY experiment as belonging to protons proximal to the iminium H atom in **3**. ^{c} The iminium proton resonance in **5** was not detected.

Figure 6. Eyring plot for **3** in CD$_2$Cl$_2$.

Figure 7. ^{1}H NMR spectra of **1** + **3** in CD$_2$Cl$_2$: (a) 293 K; (b) 171 K.

respectively, have resonances shifted by approximately 0.7 ppm as a consequence of being spatially close to the iminium H atom.

Line broadening in the NMR spectrum of **3** at 293 K suggests that a fluxional process in the slow-exchange time domain is occurring in solution. A saturation transfer experiment done by irradiating the N—H resonance shows that the iminium protons are mobile and exchanging with protons of adventitious water and methanol of solvation, the two molecules that most likely are carriers of the N—H proton between imine N atoms. In contrast with **6**, however, the rate of fluxionality of **3** in CD$_2$Cl$_2$ appears significantly slower, and signal coalescence of the methyl resonances, although separated by only 10 Hz at 500 MHz, is not achieved at 313 K, the boiling point of CD$_2$Cl$_2$.

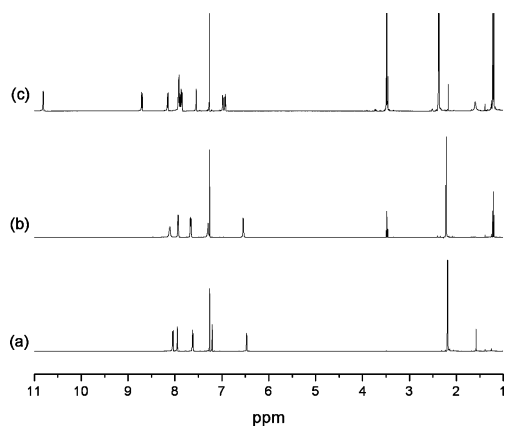The proton-transfer process in **3** was followed in CD$_2$Cl$_2$ over the temperature range 243−312 K by line-shape analysis of the two methyl proton resonances. In the narrow temperature range 276−312 K, a linear Eyring plot was obtained (Figure 6) with the following activation parameters: $\Delta G^{\ddagger}$ = 16.0 ± 0.1 kcal/mol (298 K), $\Delta H^{\ddagger}$ = 2.9 ± 0.1 kcal/mol, and $\Delta S^{\ddagger}$ = −44.0 ± 0.3 cal/mol·K. Upon extension of the plot to lower temperatures, noticeable deviation from linearity was observed, suggesting that two or more proton-transfer mechanisms are operative. The most unusual feature of the kinetic data is the very small change in k, the pseudo-first-order rate constant, with temperature. Over the 30° interval from 276 to 306 K, for example, k increases from 6.98 to 12.46 s^{-1}. The large negative value of $\Delta S^{\ddagger}$ suggests that exchange occurs via a bimolecular
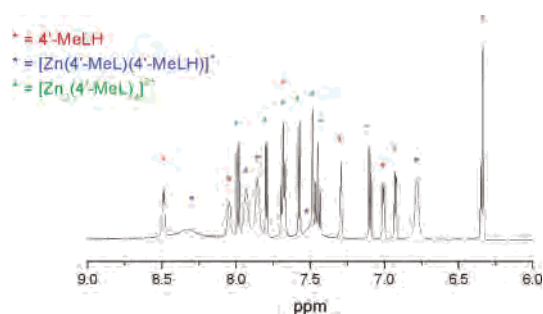
mechanism. A number of exchange mechanisms are possible. These include proton abstraction by adventitious water and/or residual methanol followed by subsequent protonation of the same isoindoline ligand or protonation by acid impurity followed by loss of the iminium proton on the same isoindoline ligand. A third alternative, direct bimolecular proton transfer between two positively charged [Cd(4′-MeLH)$_2$]$^{2+}$ ions, seems highly unlikely. Whatever the prevailing mechanism may be, the rate of tautomerism in **3** is significantly slower than that observed for **6**, and a sharp, well-defined ^{1}H NMR spectrum is observed. Clearly, the small values of k and the very small change in k with temperature are entropy-related, a consequence of the statistical unlikelihood of proton transfer occurring rapidly and simultaneously at *each* of the two isoindoline ligands in **3**.

As further evidence of the slowness of the fluxional process, the addition of 0.5 μL of D$_2$O to a NMR tube containing a solution of **3** in CD$_2$Cl$_2$ caused only a slight perturbation to the ^{1}H NMR spectrum and an insignificant amount of signal broadening. In contrast, the addition of D$_2$O to a solution of **6** in CD$_2$Cl$_2$ caused rapid iminium proton exchange and the emergence of **5** sharp signals in the aromatic region of the NMR spectrum.

Although proton transfer in CD$_2$Cl$_2$ solutions of **3** is slow at ambient temperature, this is remarkably not the case for solutions containing equimolar amounts of **1** and **3**. The NMR spectra of this equimolar mixture at 293 and 171 K are shown in Figure 7. At ambient temperature, only five signals, each somewhat broadened, are observed in the aromatic region of the spectrum. This is a postcoalescence spectrum and signifies that proton transfer is fast. The driving force for this rapid fluxional behavior is most likely entropic. It is a consequence of the distribution of two N—H protons between *eight* iminium N atoms in this equimolar mixture rather than four, as would be the case in **3**. On time average in this equimolar mixture, the species in solution appears to be **5**, with chemical shifts in CD$_2$Cl$_2$ at ambient temperature only slightly different from that of **1** (see Table 4). At 171 K, the NMR spectrum of this mixture assumes a complexity indicative of slow exchange with the appearance of peaks that can be attributed to each of the isoindoline ligands in [Cd(4′-MeLH)(4′-MeL)]$^+$.

Figure 8. ^{1}H NMR spectral changes of **1** in CDCl$_3$ with the addition of HBF$_4$ in ether: (a) no HBF$_4$ added; (b) 1 equiv added; (c) 2 equiv added.

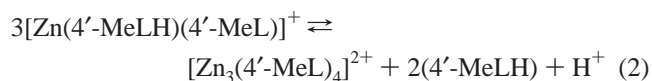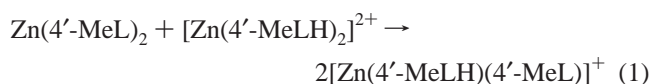**Figure 9.** Partial ^{1}H NMR spectrum with peak assignments for an equimolar mixture of **2** + **4** in CD$_2$Cl$_2$.

Conversion of **1** first to **3** and then to **5** has been accomplished in an NMR tube reaction by the addition of 1 and 2 equiv, respectively, of 1.0 M ethereal HBF$_4$ to a solution of **1** in CDCl$_3$. The changes in the NMR spectrum of **1** are illustrated in Figure 8. While a single crystal of **5** was isolated by accident (see above), attempts to prepare and isolate **5** by the reaction of Cd(ClO$_4$)$_2$·6H$_2$O, 4′-MeLH, and *n*-Bu$_4$NOH in 1:2:1 molar ratios were unsuccessful; mixed products were always obtained.

Whereas the reaction of equimolar quantities of the Cd(II) complexes **1** and **3** produces the mixed-ligand complex **5**, the equivalent NMR tube reaction between Zn(II) complexes **2** and **4** produces entirely different results. The 6−9 ppm segment of the ^{1}H NMR spectrum of an equimolar mixture of **2** and **4** in CD$_2$Cl$_2$ at 293 K is shown in Figure 9 along with the signal assignments. A pyrrole proton resonance at 10.7 ppm, an iminium proton resonance at 13.9 ppm, and four methyl proton resonances are also present.[23] There are no signals present that can be attributed to the two reactants.[24] The peak positions for [Zn$_3$(4′-MeL)$_4$]$^{2+}$ and 4′-MeLH match those reported previously for these two species.[1b,20] The assignments for the five peaks in Figure 9 attributed to [Zn(4′-MeLH)(4′-MeL)]$^+$ were made by reference to the corresponding peaks in the spectrum of

(23) A complete NMR spectrum of the equimolar **2** + **4** mixture is included with the Supporting Information.
(24) Were excess **2** or **4** present in the 1:1 mixture, they would not be detected separately in the NMR spectrum because of the rapid rate of proton exchange with the mixed-ligand complex.

[Cd(4′-MeLH)(4′-MeL)]$^+$. In separate macroscale reactions, we have not been able to prepare the mixed-ligand complex [Zn(4′-MeLH)(4′-MeL)]ClO$_4$ and doubt whether this can be isolated.

The stoichiometry for the reaction of **2** and **4** in CD$_2$Cl$_2$ is shown in eqs 1 and 2.

$$Zn(4'\text{-MeL})_2 + [Zn(4'\text{-MeLH})_2]^{2+} \rightarrow$$
$$2[Zn(4'\text{-MeLH})(4'\text{-MeL})]^+ \quad (1)$$

$$3[Zn(4'\text{-MeLH})(4'\text{-MeL})]^+ \rightleftharpoons$$
$$[Zn_3(4'\text{-MeL})_4]^{2+} + 2(4'\text{-MeLH}) + H^+ \quad (2)$$

The NMR spectrum of an equimolar mixture of **2** + **4** in CD$_2$Cl$_2$ is essentially temperature invariant over the range 263−303 K. On the basis of the stoichiometry of eq 2 and the observed relative integrals for the methyl peaks between 2.8 and 1.8 ppm in the ^{1}H NMR spectrum, we calculate that approximately 60% of a solution of the mixed-ligand complex has been converted to [Zn$_3$(4′-MeL)$_4$]$^{2+}$ plus 4′-MeLH. The temperature invariance of K_{eq} implies that $\Delta H \approx 0$ and that this reaction is entropy-driven.

If eq 2 is an equilibrium reaction, then the reaction of [Zn$_3$-(4′-MeL)$_4$](ClO$_4$)$_2$ with 4′-MeLH should generate a mixed-ligand complex. This occurs over a period of a few hours in CDCl$_3$ and more slowly in CD$_2$Cl$_2$. We believe that a trace acid impurity in both solvents provides the H$^+$ ion necessary for the reverse reaction in eq 2.
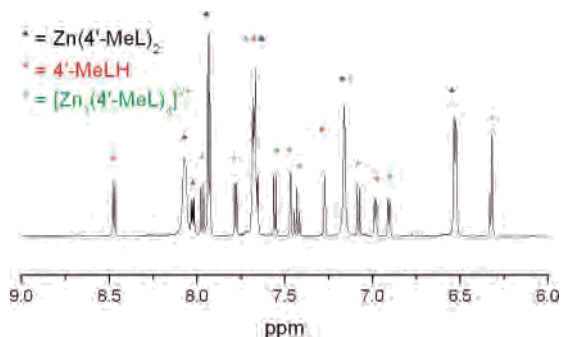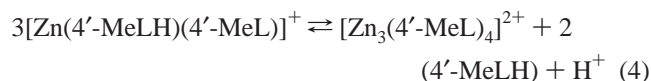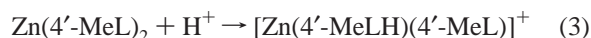
We had previously reported the synthesis and ^{1}H NMR spectrum of [Zn$_3$(4′-MeL)$_4$](ClO$_4$)$_2$.[20] This tetrahedrally coordinated trinuclear complex is formed when Zn(ClO$_4$)$_2$·6H$_2$O reacts with 4′-MeL$^-$ in a 1:1 molar ratio in methanol. That the anticipated six-coordinate complex **2** is not formed with this 1:1 reaction stoichiometry speaks to the special stability of tetrahedrally coordinated Zn^{2+}. It is an instance where the size of the metal ion matters. The Cd^{2+} ion, approximately 0.2 Å larger in radius than Zn^{2+},[25] does not form the analogous trinuclear complex. In all of our attempts to prepare [Cd$_3$(4′-MeL)$_4$](ClO$_4$)$_2$, the only product has been **1**. The larger size of Cd^{2+} makes octahedral coordination more favorable and provides a plausible explanation for the apparent nonexistence of [Cd$_3$(4′-MeL)$_4$]-(ClO$_4$)$_2$.

The respective reactions of **2** and **1** with acid are very different. When a small aliquot of an etherial HBF$_4$ solution, less than 1 equiv, is added to a CD$_2$Cl$_2$ solution of **2** at 293 K, the trinuclear complex [Zn$_3$(4′-MeL)$_4$]$^{2+}$ and 4′-MeLH are immediately formed. The 6−9 ppm region of the ^{1}H NMR spectrum is shown in Figure 10 with peak assignments for [Zn$_3$(4′-MeL)$_4$]$^{2+}$ and 4′-MeLH. The proposed reaction stoichiometry is given below. The peaks labeled "Zn(4′-MeL)$_2$" are somewhat shifted from the resonance positions of pure **2** and represent a time-averaged spectrum due to rapid exchange with [Zn(4′-MeLH)(4′-MeL)]$^+$ present in solution. The further addition of acid shifts the equilibrium in favor of products as evidenced by the

(25) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Figure 10. Partial ^{1}H NMR spectrum with peak assignments for **2** + ethereal HBF_4 in CD_2Cl_2.

growth in the relative intensities of the trinuclear complex and 4′-MeLH peaks.

$$Zn(4′\text{-MeL})_2 + H^+ \rightarrow [Zn(4′\text{-MeLH})(4′\text{-MeL})]^+ \quad (3)$$

$$3[Zn(4′\text{-MeLH})(4′\text{-MeL})]^+ \rightleftharpoons [Zn_3(4′\text{-MeL})_4]^{2+} + 2$$
$$(4′\text{-MeLH}) + H^+ \quad (4)$$

Conclusion. We have demonstrated that the pyridine-arm isoindoline 4′-MeLH reacts with Cd^{2+} and Zn^{2+} to form three distinct octahedral, bis-tridentate complexes with each metal ion, namely, $M(4′\text{-MeL})_2$, $[M(4′\text{-MeLH})_2]^{2+}$, and $[M(4′\text{-MeL})(4′\text{-MeLH})]^+$. Differences in the reaction chemistry of these Cd(II) and Zn(II) complexes are significant and are attributed to the difference in size of the two metal ions.

Thus, while the equimolar mixture of **1** and **3** in CD_2Cl_2 solution forms the stable mixed-ligand complex [Cd(4′-MeL)(4′-MeLH)]$^+$, the more sterically strained [Zn(4′-MeL)-(4′-MeLH)]$^+$, initially formed from the equimolar mixture of **2** and **4**, partially converts in solution to the seemingly more stable tetrahedrally coordinated, trinuclear [Zn$_3$(4′-MeL)$_4$]$^{2+}$ ion. The driving force for the formation of these mixed-ligand complexes appears to be entropic, and it is responsible for the substantially enhanced rate of prototropic tautomerism in solution for [M(4′-MeL)(4′-MeLH)]$^+$ when compared to that for [M(4′-MeLH)$_2$]$^{2+}$. The crystal structure of the complex **5** confirms that the protonation site in coordinated 4′-MeLH is an imine N atom.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**, **2**, and **5** and the ^{1}H NMR spectrum of an equimolar mixture of **2** + **4** in CD_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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