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Fluxional Behavior of a Cadmium Zwitterion Complex: Proton Transport and Tautomerism in Methylene Chloride Solution

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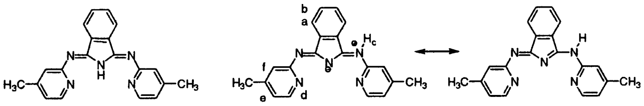
The synthesis and structure of the tautomeric Cd(II) isoindoline zwitterion coordination compound [Cd(4′-MeLH)(NO$_3$)$_2$]·CH$_3$OH (4′-MeLH = 1,3-bis{2-(4-methylpyridyl)imino}isoindoline) are reported. In methylene chloride solution, tautomer interconversion occurs as the N–H proton moves between the identical imine nitrogen atoms. We report the kinetics of proton transfer as followed by variable temperature ^{1}H NMR spectroscopy and demonstrate that methanol of solvation and adventitious water facilitate rapid proton transfer.

The mobility of protons in solution and the mechanism of proton transport are topics of interest in diverse systems such as those related to proton transfer reactions and biological proton transport.[1] Perhaps the simplest example of proton transfer is the case where a proton moves between identical sites in a tautomeric molecule such as a porphyrin.[2,3] Here, rapid proton transfer results from an intramolecular process occurring without solvent mediation. Rapid intramolecular proton transport may also occur in molecules where the proton sites are distant and mediation is involved. Such an example was reported recently for the base-mediated tautomerism of 1,3-bis(fluorophenyl)triazene[4] in ethyl methyl ether-d_8 solution for which added triethylamine transports a proton between two symmetry equivalent nitrogen sites.

Chart 1



I **II**

We present here an example of intramolecular proton transfer that occurs in the tautomeric Cd(II) zwitterion coordination compound [Cd(4′-MeLH)(NO$_3$)$_2$]·CH$_3$OH (**1**) (4′-MeLH = 1,3-bis{2-(4-methylpyridyl)imino}isoindoline) and is related conceptually to the aforementioned triazene. Whereas 4′-MeLH exists in the structure shown here (Chart 1, **I**),[5] it coordinates to Cd(II) as the tridentate iminium zwitterion shown in its two resonance structures (Chart 1, **II**). In CH$_2$Cl$_2$ solution, tautomer interconversion in **1** occurs rapidly as the N−H proton moves between the imine nitrogens. We report herein the kinetics of proton transfer as followed by variable temperature ^{1}H NMR spectroscopy and demonstrate that methanol of solvation and adventitious water catalyze the rapid proton transfer.

Although a number of transition metal isoindoline complexes have been prepared and structurally characterized, all but one are complexes containing the deprotonated 4′-MeL$^-$ ligand.[6] In the one instance where a zwitterion Cu(I) complex has been reported,[7] we believe the crystal structure is actually that of a Cu(II) complex containing deprotonated isoindolinate ion (see below). Thus, we believe that **1** is the first structurally characterized compound in which a charge-neutral isoindoline coordinates as the zwitterion. It is prepared by reaction of cadmium nitrate and 4′-MeLH in methanol in a 3:1 metal to ligand molar ratio,[8] the large excess of Cd(II) being chosen in order to suppress ligand deprotonation and formation of the *mer*-octahedral complex Cd(4′-MeL)$_2$.[9]

The ^{1}H NMR spectrum of **1** in CD$_2$Cl$_2$ at 300 MHz, Figure 1b, lacks definition and suggests that the complex is fluxional. Also present in the spectrum are the CH$_3$ and OH

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(5) The ^{1}H NMR spectrum of 4′-MeLH in CDCl$_3$ shows no evidence of tautomerism.

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(8) [Cd(4′-MeLH)(NO$_3$)$_2$]·CH$_3$OH, **1**. To a solution of 4′-MeLH (0.327 g, 0.10 mmol) dissolved in 30 mL of methanol was added solid Cd(NO$_3$)$_2$·4H$_2$O (0.924 g, 3.0 mmol) with stirring. The solution was filtered warm and allowed to evaporate slowly in air to approximately 20 mL. Yellow crystals (0.215 g, 36%) were isolated. Anal. Calcd for C$_{21}$H$_{21}$CdN$_7$O$_7$: C, 42.36; H, 3.56; N, 16.47. Found: C, 42.29; H, 3.59; N, 16.44.

(9) When reactions were carried out in 1:1 molar stoichiometry, Cd(4′-MeL)$_2$ was formed as one of the products.

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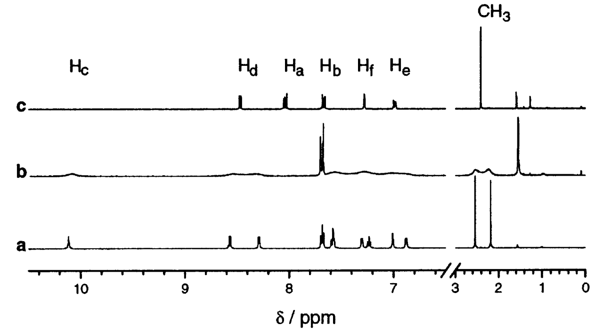

Figure 1. ^{1}H NMR spectra of **1** in CD_2Cl_2 at ambient temperature: (a) 500 MHz; (b) 300 MHz; (c) 300 MHz, D_2O added, with assignments.

methanol proton resonances at 3.41 and 0.98 ppm, respectively (not shown), and a peak for adventitious water at 1.56 ppm. Addition of a small drop of D_2O (Figure 1c) confirms that water catalyzes the exchange process. The N−H resonance at 10.2 ppm has disappeared, the methyl resonances at 2.2 and 2.4 ppm have merged, and five sharp signals are clearly resolved in the aromatic region between 7 and 9 ppm. This simplified spectrum is consistent with that expected for a complex with time-averaged C_{2v} symmetry and rapid proton transfer relative to the NMR time scale. The spectrum is also consistent in pattern with that observed for Zn(4′-MeL)$_2$.[10] Addition of a small drop of methanol-d_4 to **1** in CD_2Cl_2 also causes a sharpening of the spectrum, but the effect is not as dramatic as that observed with the addition of D_2O. A saturation transfer experiment on the original sample (no D_2O added) done by irradiation of the N−H resonance shows enhancement of the OH resonance of methanol of solvation and the proton resonance of adventitious water.

The fluxional behavior of **1** is the result of proton shuttling between the imine nitrogens of the ligand and is mediated by methanol and water. The tautomerism process appears to be in the intermediate-exchange regime ($k \approx \Delta\delta$) on the NMR time scale of a 300 MHz spectrometer for all but the H_a protons.[11] On the other hand, the spectrum at 500 MHz (Figure 1a) is well resolved, a consequence of the higher spectrometer frequency and larger values of $\Delta\delta$, and 10 distinct resonances are discernible in the aromatic region. Assignments for the 300 MHz spectrum (D_2O added) are listed above Figure 1c. Discussion of the chemical shift assignments for the 500 MHz spectrum of **1** along with those for related Cd complexes will be presented in a future publication.

The proton transfer process in **1**, with adventitious water present, was followed in CD_2Cl_2 solution over the temperature range 248−308 K at 300 MHz (Figure 2) by total line shape analysis of the methyl proton resonances. Linear regression analysis of the Eyring plot gave the following activation parameters: $\Delta G^\ddagger = 14.1 \pm 0.1$ kcal/mol (298 K), $\Delta H^\ddagger = 5.9 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -27.5 \pm 0.5$ cal/mol·K. Since added D_2O or methanol accelerates the fluxional process, proton transfer appears to be occurring by an intermolecular process.[12] For the tautomeric molecule *meso*-tetraphenylporphyrin, where proton transfer is intramolecular and unassisted by solvent or base,[3] the activation parameters are $\Delta G^\ddagger = 13$ kcal/mol (265 K), $\Delta H^\ddagger = 9$ kcal/mol, and $\Delta S^\ddagger = -10$ cal/mol·K.[13] The much more negative entropy of activation for **1** is consistent with an intermolecular proton transfer process. Also consistent with this interpretation, we find that the rate of proton transfer is dependent on the concentration of **1** and increases with increasing concentration.

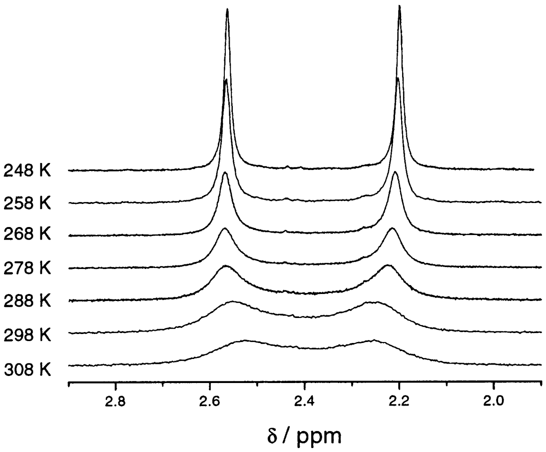

Figure 2. Variable temperature ^{1}H NMR spectra of the methyl proton resonances of **1** in CD_2Cl_2.

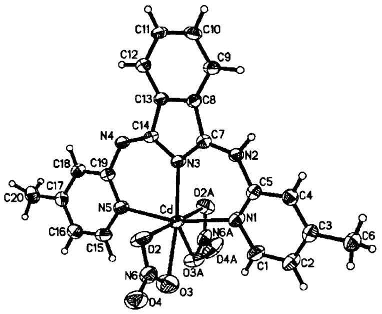

Figure 3. Thermal ellipsoid plot (50% probability) for **1**. Important bond distances (Å) and angles (deg): Cd−N1 2.323 (2), Cd−N3 2.234 (2), Cd−N5 2.282 (2), Cd−O2 2.502 (3), Cd−O2A 2.583 (2), Cd−O3 2.430 (3), Cd−O3A 2.301 (2), N2−C7 1.344 (4), N3−C7 1.331 (3), N3−C14 1.410 (3), N4−C14 1.280 (3), N1−Cd−N5 164.35 (9), N3−Cd−O3 141.69 (8), N3−Cd−O3A 140.55 (8).

The structure of **1** is shown in Figure 3.[14] The proton on the imine nitrogen N2 was located in the difference electron

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(11) The ^{1}H resonances for the two H_a protons are essentially isochronous at 300 MHz (Figure 1b) and appear as a sharp doublet with $^3J = 8.1$ Hz as a result of coupling with H_b.

(12) The mechanism for proton exchange could include direct transfer by water, methanol, or detached nitrate. It could also occur by initial protonation at the nonprotonated imine nitrogen followed by deprotonation at the other nitrogen. What is clear, however, is that added D_2O produces a significantly more causative effect than added methanol.

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(14) Crystallographic data for **1**: $C_{21}H_{21}CdN_7O_7$, MW = 595.85, T = 173-(2) K, triclinic, $P\bar{1}$, a = 10.517(2) Å, b = 10.704(2) Å, c = 11.349(3) Å, α = 69.288(4)°, β = 82.681(5)°, γ = 79.189(5)°, V = 1171.2(4) Å^3, Z = 2, R1 = 0.0342 [$I > 2\sigma(I)$], wR2 (all data) = 0.0947, GOF = 1.066.

density map and refined independently with satisfactory results. The fact that the C7−N3 bond length is 0.08 Å less than that of C14−N3 and the C14−N4 bond length is 0.06 Å less than that of C7−N2 is consistent with the zwitterion resonance formulation and suggests an approximate 50% contribution of each resonance structure. The trans N1−Cd−N5 bond angle of 164.35(9)° is nonlinear due to the large size of Cd(II). In [Zn(4′-MeL)(CH_3OH)(NO_3)], the comparable bond angle is 176.8(2)°.[15]

The coordination geometry about Cd is best described as seven-coordinate pseudo-octahedral with O3 and O3A straddling the sixth position of the octahedron. While seven-coordination is rare, it is not unprecedented for nitrate complexes. Both [Cu(NO_3)$_2$(py)$_2$]$_2$·py[16] (py = pyridine) and polymeric [Cu(phen)(NO_3)$_2$][17] (phen = 1,10-phenanthroline), for example, contain two bidentate nitrate ions and also exhibit seven-coordinate pseudo-octahedral coordination.

There has been one previous structural report of a zwitterion isoindoline complex[7] which purportedly contains a charge-neutral, isoindoline zwitterion coordinated to square planar Cu(I). However, the equal C−N (pyrrole) bond lengths, the low Cu−N bond lengths of 1.90−2.03 Å, and the fact that the color of the chosen crystal was green all point to the conclusion that the crystal contained Cu(II) coordinated to isoindolinate.

The 4′-MeLH zwitterion is a nitrogen donor pincer ligand quite similar to the quinolinylamido ligand recently reported by Peters et al.,[18] but with the significant difference that it is charge-neutral and contains a strongly acidic iminium proton. As a template for metal alkyl complexes, it could very well be a proton donor suitable for the kinetic study of alkane formation as related to C−H activation.[19,20] We are currently investigating the reactions of 4′-MeLH with other metal ion systems, including those containing monomethyl and dimethyl platinum(II).

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

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