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4-Cyanoimidazolate: A New Pseudo-Cyanide?

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Because of its exobidentate nature, pK_a, and electronic properties, 4-cyanoimidazole has been examined as a ligand and as a pseudo-cyanide. The ligand reacts readily as an anion with both cobalt and nickel ions in solution to form coordination polymers. The magnetic susceptibility and thermal stability of these materials are reported. 4-Cyanoimidazolate forms a hexakis complex with nickel, to form the first observed hexakis imidazolate nickelate complex.

Introduction

Imidazole has long been studied by inorganic chemists.[1] In addition to being a good ligand for a variety of metals, imidazole is of particular interest to bioinorganic chemists as a model for the active site in the histidine residue. As an example, superoxide dismutase has received much attention in the literature as an enzyme easily modeled with imidazolate complexes.[2−9] More recently, the possibility of the imidazole anion to act as an exobidentate unit has seen this molecule applied as a "linker" in extended structures.[10−20] Generally, these materials form as amorphous or poorly crystalline products, with only a few examples of diffraction-quality crystals being described in the literature.[16,17] The imidazolate ring has been repeatedly seen to mediate antiferromagnetic coupling between metal centers, thus making the poly(metal imidazolates) candidates for molecular magnets. An imidazolate coordination polymer of silver has proven applicable as an antibacterial coating.[15]

Cyanide is another ligand long studied by chemists. Cyanide is a strong field ligand used in many industrial processes, although its toxicity makes its replacement a desirable goal whenever possible. Much like imidazole, cyanide is currently undergoing a resurgence in research interest because of its ability to bind in a linear bidentate manner for the formation of extended structures.[21] Prussian Blue, first made in 1704 by Diesbach, has seen continual use since that time in a variety of applications. New extended cyanide structures are being explored for gas storage,[22] electrochromic devices,[23,24] molecular magnets,[25,26] and nonlinear optical applications.[27] Cyanide gains its unique properties from its

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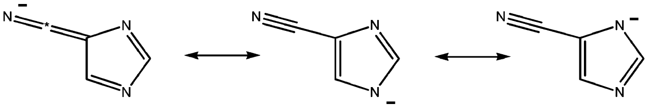

Figure 1. Resonance structures of the MCI anion, showing the inequivalence of the 1 and 3 positions.

ability to both σ donate and π accept when bonding to a metal. Additionally, the fact that the two sides of the ion are inequivalent allows for a certain selectivity in binding, with the carbon atom always being the first bound in all known structures. This leads to predictable three-dimensional structures based on the ability to form preassembled building blocks.

It was our thought that an imidazole modified to allow it to both σ donate and π accept in a nonsymmetric way might be able to mimic cyanide's binding properties. To create a better π-acceptor, a strong electron-withdrawing group needed to be added, and to break the symmetry of imidazole, it should be added at the 4(5) position. 4(5)-Cyanoimidazole had previously been reported in the literature as a pharmaceutical[28] and agricultural product[29] but had never been examined as a ligand. Resonance structures, shown in Figure 1, indicate that the 1 and 3 positions of the MCI anion are inequivalent and, interestingly, the 1 position nitrogen is able to "push" its charge directly to the nitrile, whereas the 3 position must inductively transmit charge to the nitrile via the 1 position. We hypothesized, therefore, that the 1 position would be the preferential binding site to metals in MCI, much as the carbon of cyanide is the preferred binding site. On the basis of these preliminary observations, we began investigating 4-cyanoimidazole as a potential pseudo-cyanide.

Experimental Section

Materials. Unless otherwise noted, all reagents and solvents were used as supplied, without further purification. 4-Cyanoimidazole was prepared by literature methods.[30] All manipulations were carried out under aerobic conditions.

Infrared Spectroscopy. Infrared measurements were made at room temperature under a dry nitrogen purge using a Perkin-Elmer Spectrum BX FT-IR spectrometer. The samples were mounted in KBr pellets and measured in the 400−4000 cm^{-1} range.

Powder X-ray Diffraction (PXRD). PXRD data were recorded at room temperature on a Bruker AXS D_8 Advance powder diffractometer at 40 kV, 40 mA with a Cu Kα source ($\lambda = 1.5406$ Å) between 10 and 50° 2θ with a scan speed of 1.0 s/step and a step size of 0.050°. Samples were measured on a glass plate in an aluminum holder.

Elemental Analysis (EA). Combustion analysis was performed using a Perkin-Elmer 2400 Series II Analyzer.

Magnetic Measurements. Magnetization studies were carried out on powdered samples sealed in gelatin caps using a Quantum Design (MPMS) SQUID magnetometer. The measurements were carried out at an applied filed of 10000 G in the temperature range of 5−300 K.

Electronic Spectroscopy. A standard Shimadzu UV-1601 UV−vis spectrometer was used for transmission spectroscopy in the range from 190 to 1100 nm. Solutions were made using spectroscopy-grade acetonitrile and measured in 1-cm quartz cuvettes. Diffuse reflectance was performed on a neat solid powder in the range 385−815 nm using a microspectrophotometer. The microscope used was a Zeiss 20 epi-illumination system, coupled to a 15-V, 150-W tungsten filament illuminator via fiber optic cables. Signal was output to an Ocean Optics PS2000 spectrometer via an Ocean Optics single-strand 100-μm fiber.

Thermal Analysis. Thermal gravimetric studies were conducted using a Perkin-Elmer TGA-7 thermogravimetric analyzer. Powdered samples were measured under air at a flow rate of 20 mL/min between 50 and 700 °C.

Synthesis of Nickel Cyanoimidazolate Hydrate, Ni(MCI)$_2$·1.5H$_2$O (1). To 5 mL of an aqueous solution of nickel nitrate hexahydrate (76 mg, 0.27 mmol) was added 5 mL of an aqueous solution of the sodium salt of MCI (119 mg, 1.0 mmol). A pale green precipitate formed immediately that was taken up in a 20-mL syringe and collected on a 0.45-μm polypropylene filtration membrane. The product was washed with DI water (3 × 20 mL) and then placed in a ceramic boat and loaded into a tube furnace for drying. The sample was heated to 260 °C under a stream of nitrogen for 3 days. Anal. Calcd for $C_8H_7N_6NiO_{1.5}$: C, 35.60; H, 2.61; N, 31.14. Found: C, 35.61; H, 2.40; N, 31.75. IR (cm^{-1}): 3370, 3136, 2220, 1638, 1584, 1116, 658.

Synthesis of Cobalt Cyanoimidazolate Hydrate, Co(MCI)$_2$·1.5H$_2$O (2). To 5 mL of an aqueous solution of cobalt nitrate hexahydrate (78 mg, 0.26 mmol) was added 5 mL of an aqueous solution of the sodium salt of MCI (117 mg, 1.0 mmol). A deep purple precipitate formed immediately that was taken up in a 20-mL syringe and collected on a 0-45 μm polypropylene filtration membrane. The product was washed with DI water (3 × 20 mL) and then placed in a ceramic boat and loaded into a tube furnace for drying. The sample was heated to 260 °C under a stream of nitrogen for 3 days. Anal. Calcd for $C_8H_7N_6CoO_{1.5}$: C, 35.57; H, 2.61; N, 31.11. Found: C, 35.76; H, 2.36; N, 30.70. IR (cm^{-1}): 3378, 3129, 2224, 1646, 1591, 1114, 665.

Synthesis of Tetrakis Tetrabutylammonium Hexakis Cyanoimidazolate Nickelate Dihydrate, (NBu$_4$)$_4$ Ni(MCI)$_6$·2H$_2$O (3). Nickel cyanide, Ni(CN)$_2$ (115 mg, 0.97 mmol), and HMCI (928 mg, 10 mmol) were suspended in 100 mL of methanol. To the suspension was added 10 mL of 1 M tetrabutylammonium hydroxide in methanol (10 mmol). The solution was gently heated with stirring until a yellow solution formed. Upon standing for 24 h, the solution turned green. Complete removal of solvent in vacuo afforded a yellow brown powder. This powder was dissolved in a minimum of hot ethyl acetate to give an intensely yellow solution. Upon slow evaporation, pale purple crystals of diffraction quality formed. The crystals proved to be stable in air indefinitely. IR (cm^{-1}): 3575, 2962, 2875, 2202 (shoulder at 2191), 1482, 1113, 661. Single-crystal diffuse reflectance vis: 562.18 nm.

Crystallography of (NBu$_4$)$_4$Ni(MCI)$_6$·2H$_2$O (3, Figure 2). A purple plate of dimensions 0.48 × 0.48 × 0.40 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal-focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000-W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance 4.954 cm from the crystal. A total of 2168 frames were collected with a scan width of 0.3° in

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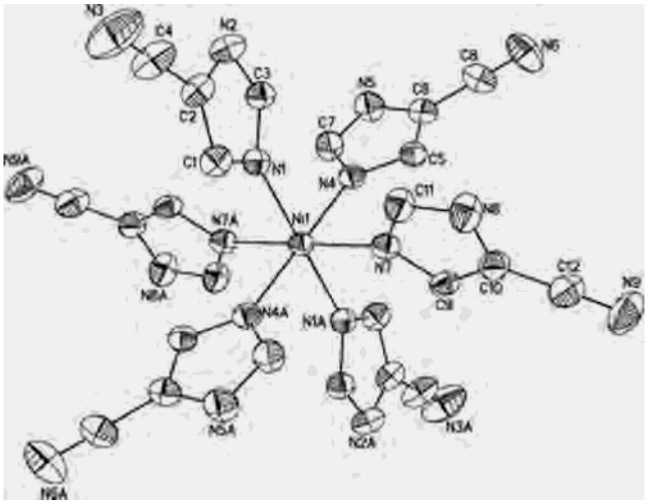

Figure 2. Anion of **3** shown with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

ω and φ and an exposure time of 30 s/frame. The integration of the data yielded a total of 50897 reflections to a maximum 2θ value of 56.67° of which 9911 were independent and 7697 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the *xyz* centroids of 7826 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[31] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package,[32] in the space group $P2_1/c$ with $Z = 2$ for the formula $C_{88}H_{160}N_{22}O_2Ni$, which includes the contribution of two lattice water solvate molecules per nickel complex. The unit cell dimensions were found to be $a = 14.9380(18)$, $b = 21.368(3)$, and $c = 16.926(2)$ Å, with $\beta = 115.863(2)°$. All non-hydrogen atoms were refined anisotropically, with the hydrogen atoms placed in idealized positions. Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0707 and wR2 = 0.1917 [based on $I > 2\sigma(I)$], R1 = 0.0909 and wR2 = 0.2058 for all data.

Results and Discussion

Analysis of HMCI. Although HMCI was known, the pK_a of the molecule had never been reported. Interestingly, the pK_a of HMCI turns out to be 9.2, strikingly similar to that of HCN. To estimate the degree to which the two nitrogens of the heterocycle are inequivalent, ab initio calculations[33] were used to determine the energy difference between 4-cyanoimidazole and 5-cyanoimidazole. It was found that 4-cyanoimidazole was the energetically favored isomer by 3.98 kJ/mol. Similar results were found independently in the works of Mazurek and co-workers.[34] Our high-resolution X-ray structure that was obtained from a single crystal grown via sublimation confirmed the ab initio prediction that the proton was indeed located so as to give a 4-cyanoimidazole in the solid state.[30]

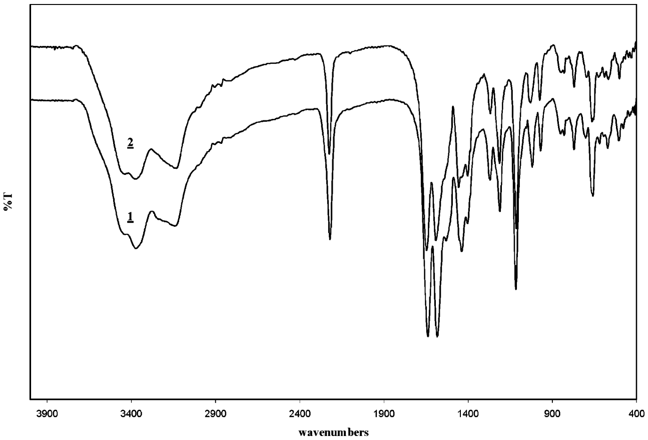

Figure 3. FTIR spectra of **1** and **2** from 4000 to 400 cm^{-1} in KBr.

$M(MCI)_2$ Polymers. The first experiments were carried out on simple salts of nickel to explore the ligand's ability to stabilize low-spin, square-planar complexes of d^8 metals, which would indicate a ligand of similar field strength to cyanide. No reaction occurred between HMCI and metal ions, indicating a significantly lower coordinating tendency than imidazole. Solutions of the MCI anion made from the sodium or triethylamine salts reacted instantly with Ni^{2+} ions to give the insoluble, voluminous green coordination polymer **1**. Various reaction conditions were tried, including those of Masciocchi and co-workers[11,12,14] and those of Storr et al.,[17−20,35,36] and all afforded the same structurally amorphous materials. Infrared spectroscopy of the product shows binding of the ligand, and combustion analyses determined the formula to be $Ni(MCI)_2 \cdot 1.5H_2O$. Insolubility in both water and common organic solvents prevented any form of recrystallization. The material can be dissolved in acids, although this is accompanied by decomposition of the complex. These experiments were repeated with cobalt salts to give **2**. In addition to having the same stoichiometry by EA, infrared spectroscopy shows the two compounds to be isostructural (Figure 3). Despite the results of the combustion analysis, it might be more realistic, judging from magnetic evidence (see below), to assume that there are two ligated waters for each metal, thus allowing for undistorted octahedral coordination.

Magnetic Susceptibility of the Metallopolymers. Weak antiferromagnetic coupling is shown for both **1** and **2** in the χT versus temperature plot (Figure 4), although when χ is plotted versus temperature (Figure 5), neither product shows a Néel temperature. This would indicate that the coupling constant, J, is very small, and indeed, the Weiss constants for **1** and **2**, −23.81 and −24.68 K, respectively, support this conclusion. Using the Curie law, compound **1** was found to have $\mu_{eff} = 2.84\ \beta$, corresponding to the value expected for a spin-only octahedral system. Compound **2** was found to have a μ_{eff} value of 4.12 β, consistent with an octahedral complex with orbital contribution.

The χT data were fit using an isotropic Heisenberg chain model developed by Hiller et al.[37] to describe antiferromag-

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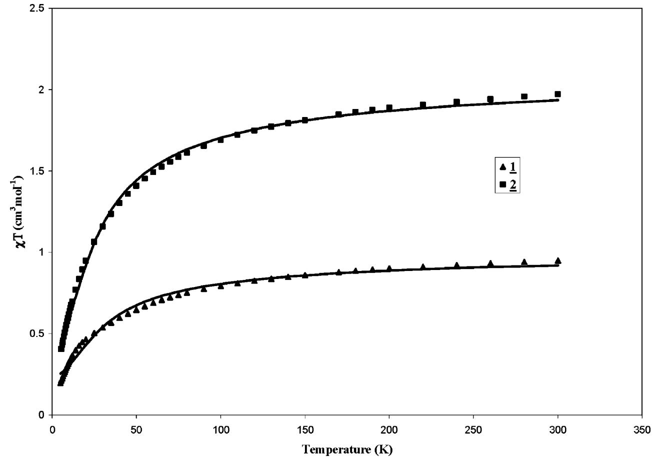

Figure 4. Magnetic moment versus temperature at 10000 G. Theoretical values are shown as solid lines.

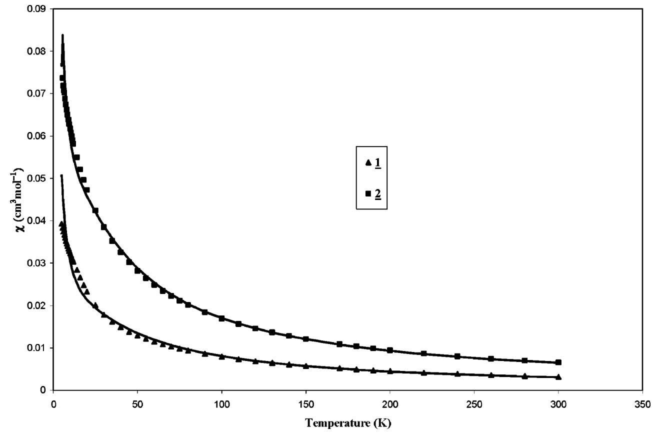

Figure 5. Magnetic susceptibility vs temperature at 10000 G. Theoretical values are shown as solid lines.

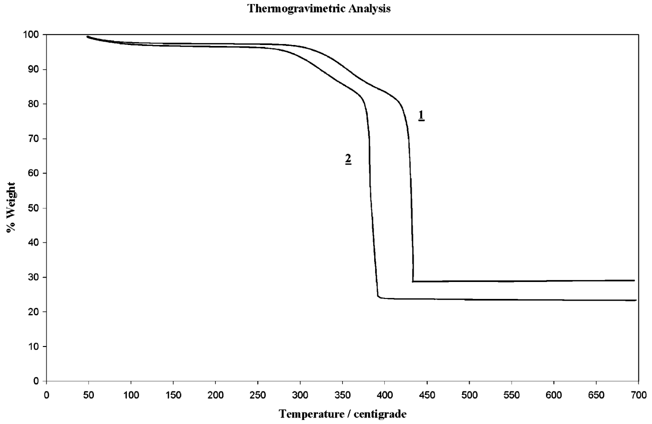

Figure 6. Thermogravimetric data for Ni(MCI)$_2$·1.5H$_2$O (**1**) and Co(MCI)$_2$·1.5H$_2$O (**2**). Experiments were conducted from 50 to 700 °C at 5 °C/min under air.

netically coupled linear chains. Attempts to fit the data using other models were unsuccessful. To obtain a satisfactory fitting, it was necessary to allow for a percentage of paramagnetic impurities (P) in the sample as proposed by Patrick et al.[16] Thus, the final expression used was

$$\chi T = T(1 - P)\left(\frac{Ng^2\beta^2}{kT}\right)\left[\frac{A + Bx^2}{1 + Cx + Dx^3}\right] + PT\left(\frac{2Ng^2\beta^2}{kT}\right)$$

where $x = |J|/kT$; g is the Lande factor; and the coefficients $A-D$ are dependent on S, the total spin of the system. Thus, in **1** where $S = 1$, $A-D$ were set to 0.6667, 2.5823, 3.6035, and 39.558, respectively. The cobalt complex, **2**, has $S = {}^3/_2$, and $A-D$ were set to 1.2500, 17.041, 6.7360, and 238.47, respectively. Allowing g, J, and P to vary freely in a least-squares fitting method, the best fit of theory to experimental data gave $-J_1 = 6.434$ cm^{-1}, $g_1 = 1.85$, and $P_1 = 0.082$ with $R^2 = 0.9897$. For **2**, the values were found to be $-J_2 = 3.013$ cm^{-1}, $g_2 = 2.047$, and $P_2 = 0.099$ with $R^2 = 0.9899$. The solid lines in Figures 4 and 5 are calculated using these parameters and are of comparable R^2 values. The cobalt system, at least by visual inspection of goodness of fit, is better described by this fitting model than the nickel system.

These results stand in contrast to those found for other nickel and cobalt imidazolate systems. All of the magnetically characterized Ni(imid)$_2$ systems reported in the literature to date have been diamagnetic square-planar complexes.[13,38] Co(imid)$_2$ has been magnetically characterized as being an antiferromagnetic system with a sharp Néel temperature.[20] In fact, imidazolate and alkyl-substituted imidazolates appear to almost always mediate an antiferromagnetic superexchange. It is generally accepted that this superexchange occurs through the σ system of the ring, as the π orbitals do not form adequate dihedral angles with the d orbitals of the paramagnetic center.[3] Additionally, in the copper systems studied by Strothkamp and Lippard,[3] it was seen that maximum values of J were obtained in systems where the M−N bond was closest to parallel with the C−C double bond of the imidazole ring. Furthermore, Strothkamp and Lippard reported that, although the steric effects of substituents influence the ring's ability to promote antiferromagnetic coupling, electronic effects of substituents are an equal or even greater factor, and they draw a parallel between pK_a and coupling constants.[3] We therefore postulate that M(MCI)$_2$ systems show only weak antiferromagnetic coupling due to the steric and inductive effects of the nitrile substituent. As previously observed, HMCI has a pK_a a striking 5 orders of magnitude lower than that of imidazole. Given the clear trend of decreasing $|J|$ with decreasing pK_a, it is understandable that neither **1** nor **2** shows strong antiferromagnetic coupling.

Thermal Experiments on the Metallopolymers. Initial thermal experiments were carried out on the wet gels to determine a suitable temperature at which they could be dried for elemental analysis and magnetic susceptibility studies. It was seen that there was a stable plateau from about 200−300 °C (see Figure 6). Using the midpoint of the plateau, samples of **1** and **2** were dried at 260 °C for 3 days in a tube furnace under a constant N$_2$ flow. Thermogravimetric analysis was then performed on the samples, revealing

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remarkably stable materials. In the nickel polymer, we observe a weight loss of 68% from complex to nickel oxide at 294 °C under air. Compound **2** shows a similar result with a loss of 72% beginning at 264 °C, again in air. In the cobalt polymer, this corresponds exactly to the decomposition of $Co(MCI)_2{\cdot}1.5H_2O$ to CoO. Although the numbers are not as exact in the nickel polymer, they are similar. In both experiments, a change in slope is observed approximately 100 °C after the onset of the decomposition. This mass corresponds approximately to the fully dehydrated polymer. Decomposition to the metal oxide follows.

Molecular Species $[(NBu_4)_4Ni(MCI)_6{\cdot}2H_2O]$. Attempts were made to modify a nickel center in such a way as to afford a crystalline compound containing MCI. It was found that, when using the substitution-inert $Ni(CN)_2$ starting material in the presence of excess MCI, diffraction-quality crystals of the formula $(NBu_4)_4Ni(MCI)_6{\cdot}2H_2O$ (**3**) are readily formed. The nearly perfect octahedral anion shown in Figure 4 is in the S_6 point group. There are 15 examples of hexakis imidazole nickel complexes in the Cambridge Crystallographic Database.[39−53] Each of these is a complex cation, making **3** the first known hexakis imidazolate complex anion. As is expected, at an average bond length of 2.114 Å, **3** has slightly shorter bonds than what is seen in the hexakis 1-H imidazole complexes, where the average bond length is 2.128 Å. The Ni−N bond lengths in the *N*-alkylimidazole complexes closely match those observed in our system.

Electronic Spectra of 3. Single-crystal diffuse reflectance spectroscopy was performed on **3** in the range of 700−420 nm. Maximum absorbance was observed at 562.18 nm, corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition. Comparing this value with that of the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition in known octahedral nickel complexes, it is seen MCI falls between ammonia and ethylenediamine in the spectrochemical series. The same transition in $Ni(NH_3)_6^{2+}$ occurs at 571 and 545 nm in $Ni(en)_3^{2+}$.[54] This would give MCI a Δ_o value of between 10.8 and 11.5 kK.[54]

Although no crystallographic evidence has been found for the ability of MCI to support low-spin d^8 complexes, evidence that $(NBu_4)_4Ni(MCI)_6{\cdot}2H_2O$ can dissociate in solution to a kinetic product of the square-planar complex was observed in the solution UV−vis spectrum. When the purple solid is placed in acetonitrile, a yellow solution forms. Previous electronic spectroscopy studies conducted on $Ni(imid)_2$ had concluded that it is most likely a square-planar structure.[38,55] Recently, Masciocchi and co-workers were able to solve the solid-state structure of $Ni(imid)_2$ and confirm that the metal is indeed in a square-planar coordination geometry.[13] Comparison of our spectra with those previously reported is difficult, as we have used a solution, whereas the $Ni(imid)_2$ spectra were collected via diffuse reflectance on solid samples; however, as discussed below, there are some similarities between the spectra that indicate that square-planar $Ni(MCI)_4^{2-}$ might be present in solution. Further complicating a comparison of the data is the fact that $Ni(imid)_2$ is a coordination polymer, whereas our samples are molecular in nature.

The previous investigators found that $Ni(imid)_2$ has a peak at 450 nm, attributed to the $A_{1g} \rightarrow B_{1g}$ transition.[38,55] The solution of $Ni(MCI)_4^{2-}$ exhibits a peak at 445 nm, with $\epsilon = 92.63\ M^{-1}\ cm^{-1}$, an intensity appropriate to a d−d transition. Eilbeck and co-workers observed a peak at 673 nm,[55] possibly corresponding to the $Ni(MCI)_4^{2-}$ observed peak at 647 nm. The lower energy of the transition in $Ni(imid)_2$ might be due to the reduced crystal field strength of imidazolate when acting as a bidentate ligand.

After 1 week's time, the solution of $(NBu_4)_4Ni(MCI)_6{\cdot}2H_2O$ had a greenish hue. The number of peaks in the spectrum increased from two to six. After 2 weeks, the solution had changed color to lime green. A third electronic spectrum was collected, showing only three relatively intense peaks in the visible range. Two of the three absorption bands, occurring at 657 and 701 nm, correspond almost exactly to those observed in the tetrahedral $NiCl_4^{2-}$.[54] The complication of the second spectrum is presumably due to the mixture of coordination geometries present. It can be postulated that the square-planar complex is the kinetic dissociation product but that, thermodynamically, the tetrahedral geometry is favored.

Conclusions. 4-Cyanoimidazole has been synthesized in a novel manner from a combination of partial literature procedures. Its pK_a of 9.2 lends it to use as an exo-bidentate ligand in systems where the harsher conditions required for binding imidazolate in the same manner are unacceptable. Resonance structures, acidity, and ab initio calculations indicate that the molecule is a potential mimic for cyanide in metal complexes. Despite these indicators, it appears that the two nitrogens are more equivalent than might have been expected, leading to less-selective coordination than exhibited by cyanide. The ligand reacts rapidly and causes immediate precipitation of product before a complex anion is formed,

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in contrast to the behavior of cyanide. Judging from electronic spectroscopy, MCI is not a strong field ligand, supporting a square-planar nickel complex as only an intermediate between the octahedral and tetrahedral states. Thus, although not a pseudo-cyanide, 4-cyanoimidazolate is a remarkably effective ligand to divalent transition metals. As could be predicted from the pK_a and the steric hindrance introduced by the nitrile functionality, MCI mediates only a very weak antiferromagnetic coupling. This could perhaps be increased if a means were found to introduce greater long-range order to the sample. In reactions where a gross excess of ligand is present, MCI has proven capable of binding monodentate.

4-Cyanoimidazole is a strong candidate for use in model compounds of biological systems for which metal coordination and pK_a are important factors. This is particularly true of the superoxide dismutase enzymes, where an imidazolate bridges two metal centers. In addition to the uses already being explored for imidazolate coordination polymers (nonlinear optics, antibacterial coatings, anticorrosive coatings, and magnetic materials) MCI could find use as a metal scavenger in wastewater remediation efforts. Additionally, given the large body of organic transformations that can be carried out on nitrile functionalities, MCI complexes are potential starting materials for much larger systems.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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