between the parameter values themselves are regarded to be of no consequence. We take model A as "best model". Table II is the correlation matrix for model A.

Discussion

Although the structures of O_2F_2 derived from our work and the microwave work are in good agreement (Table I), some small differences do exist. The differences may be attributed partly to the fact that the two methods lead to interatomic distances that are defined in different ways—in this case, a mixed r_0/r_s type from microwave spectroscopy (since they were obtained from atomic coordinates calculated by joint use of isotopic substitution and center-of-mass conditions), and the usual r_a type from electron diffraction.[22] In part the differences may also be due to uncertainty in the fluorine atom coordinates as deduced from the microwave spectrum: these atoms lie rather close (about 0.1 Å) to one of the inertial axes.

Our attempts to obtain data for the molecules O_2F and/or O_4F_2 were unsuccessful. In none of our experiments did we find convincing evidence that we had generated identifiable amounts of these species, nor did we find evidence for the presence of O_2F_2 dimer or of an anti conformer of O_2F_2 itself. We are able, however, to draw some useful conclusions from these experiments. The results of run 6, which led to no discernible reaction, suggest that either (1) O_2F_2 and O_2 react to form O_2F only very slowly compared to the transit time of the material through the gas nozzle (about 1.5 s) or (2) the equilibrium $O_2F_2 + O_2 = 2O_2F$ lies too far to the left to permit detection of O_2F in our experiments.

The bonding in O_2F_2 with its short central and long peripheral bonds is clearly quite different from that in N_2F_4,[23] in which the distances correspond essentially to N–N and N–F single bonds and in which the internal rotation is only slightly restricted. Jackson[5] has discussed the bonding in O_2F_2 in terms of contributions from valence-bond structures of the type $F^-O{=}^+O{-}F$. These structures imply elongation of the F–O bonds and shortening of the O–O bond from the values found in F_2O and in H_2O_2, respectively, in agreement with observation. The structure may also be rationalized from the molecular orbital point of view:[5] the two electrons assumed to occupy individually $\pi_y^*(2p)$ and a $\pi_z^*(2p)$ orbital on O_2 are respectively paired with electrons from fluorine atoms to form three-center bonds. The resulting picture accounts nicely for the bond lengths and torsion angle and for the relatively high barrier to internal rotation that is apparent from the narrowness of the F···F peak in our radial distribution curve. However, detailed theoretical calculations[13-16] indicate that the actual bonding picture is not so simple.

Acknowledgment. We gratefully acknowledge the valuable experimental assistance of L. B. Asprey, S. A. Kinkead, R. A. Kissane, and J. D. Purson of the Los Alamos National Laboratory. The Oregon State part of the work was supported by the National Science Foundation under grant CHE84-11165. The work at Los Alamos was done under the auspices of the U.S. Department of Energy.

Registry No. O_2F_2, 7783-44-0.

Supplementary Material Available: Tables III and IV, giving the internal and symmetrized (C_2) force constants, and Tables V–VII, giving the total scattered intensities from each plate, the calculated backgrounds, and the averaged intensities from each camera distance (13 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of New Transition-Metal Complexes of Dipyridylmethane Dicarboxylic Acids. Crystal Structure of the Copper(II) Complex of 1,1-Bis(6-carboxy-2-pyridyl)-1-methoxypropane

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Received April 22, 1987

The preparation of new complex-forming ligands of tetradental bis(picolinic acids), 1,1-bis(6-carboxy-2-pyridyl)alkanes, is described. These ligands are shown to readily form 1:1 complexes with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Fe^{3+} ions and, provided they are lipophilic enough, to be versatile reagents for the extraction of these metal ions from an aqueous phase into an organic phase. The crystal and molecular structure of the tetrahydrate of the copper(II) complex of 1,1-bis(6-carboxy-2-pyridyl)-1-methoxypropane has been determined. The space group is monoclinic, $P2_1/n$, with $Z = 4$. The unit cell dimensions are $a = 11.5711$ (6) Å, $b = 7.7308$ (3) Å, $c = 21.7034$ (7) Å, and $\beta = 103.92$ (4)°. The final reliability index R is 0.044 for 2785 reflections. The 1,1-bis(6-carboxy-2-pyridyl) moiety is slightly bent. The copper(II) ion is (4+1) coordinated in a nearly square-pyramidal arrangement. The distance from the copper to the "apex" oxygen, a hydrate O atom, is 2.244 (2) Å. The crystal structure is held together by a network of hydrogen bonds. Spectroscopic data indicate that the N_2O_2 atoms in the copper complex of 1,1-bis(6-carboxy-2-pyridyl)octene form a pseudotetrahedral arrangement, probably due to steric interactions between the side chain and a pyridine ring. The dehydration of precipitated metal complexes of 1,1-bis(6-carboxy-2-pyridyl)-1-methoxyalkanes as well as 4-(3-heptyl)pyridine-2-carboxylic acid has been monitored by means of TG and DSC measurements. Structural data combined with spectroscopic, TG, and DSC data are discussed in terms of the coordination around the metal ion.

Introduction

To allow control of properties such as metal ion selectivity, it is of fundamental importance to design and prepare rigid ligands with appropriate donor atoms forced into desired positions. We are currently studying consequences of various substituents on the coordinating properties of pyridine- and quinolinecarboxylic acids and have found that groups influencing the stereochemistry and the electronic distribution of the ligands may have a pronounced effect on these properties.[2-5] To enable an understanding

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of the factors governing these changes, detailed structural knowledge of metal complexes is needed.

Metal ion complexes with picolinic acid, i.e. pyridine-2-carboxylic acid, have been known for the last 50 years,[6] and the structures and properties of many such complexes have been extensively studied.[7-17] Divalent metal ions usually form complexes with a ligand to metal ratio of 2:1 and with planar trans coordination of the ligands,[7,11-14] although complexes with other structures and stoichiometries are known.[15-17] We have recently shown that substituents containing additional coordinating groups may profoundly change the coordinating properties of picolinic acids and thus allow the design of ligands capable of separating a desired metal ion from a mixture of several ions.[18] In this paper we present the preparation of bis(picolinic acids) that are obliged to coordinate to metal ions is a cis fashion and that, depending on the substituents, may prefer planar or nonplanar coordination. The effects of these changes in geometry on the properties of the ligands and their metal complexes are described.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WP 200 spectrometer at 200 MHz and electronic spectra on a Varian Cary 219 spectrophotometer. A Perkin-Elmer 603 atomic absorption spectrophotometer was used for metal determinations. The X-ray intensity data were collected on a computer-controlled Philips PW 1100 diffractometer. The TG and DSC measurements were carried out with a Perkin-Elmer TG 2 unit and a Perkin-Elmer DSC-2C calorimeter. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, FRG. All melting points are uncorrected.

Dipyridyl ketone was purchased from Aldrich. L^2H was prepared as previously described.[4] Tetrahydrofuran (THF), diethyl ether, and dimethoxyethane (DME) were distilled from benzophenone ketyl before use.

1,1-Bis(6-carboxy-2-pyridyl)-1-methoxynonane (L^1H_2). 1,1-Di-2-pyridylnonanol. Di-2-pyridyl ketone (10.0 g, 54.3 mmol) dissolved in 200 mL of diethyl ether was slowly added to a solution of *n*-octylmagnesium bromide (100 mL; ca. 1.09 M) kept at ambient temperature under nitrogen. A deep red solution resulted. After 4 h at reflux temperature the reaction was quenched by the addition of 70 mL of saturated aqueous NH_4Cl. The crude material (obtained after phase separation, drying, and evaporation of solvent) was chromatographed (filtered) on a silica gel column (width 4 cm) with EtOAc/petroleum ether 1:4 as eluent to give 11.6 g of the desired product, contaminated by some hydrocarbon (according to ^{1}H NMR). Distillation of this mixture (160 °C (0.07 mmHg)) gave 7.20 g (44.5%) of 1,1-di-2-pyridylnonanol as a colorless oil. ^{1}H NMR: δ 0.84 (3 H, t, $J \approx 7$ Hz, CH_3), 1.20 (12 H, m, $-CH_2-$), 2.35 (2 H, m, $-CH_2-C_7H_{15}$), 6.47 (1 H, s, OH), 7.13 (2 H, ddd, J = 7.4, 4.8, and 1.2 Hz, 5-pyridyl), 7.64 (2 H, ddd, J = 8.0, 7.4, and 1.8 Hz, 4-pyridyl), 7.84 (2 H, dt, J = 8.0 and 1.1 Hz, 3-pyridyl), 8.51 (2 H, ddd, J = 4.8, 1.8 and 1.0 Hz, 6-pyridyl).

1,1-Di-2-pyridylnonanol *N,N'*-Dioxide. To a solution of 1,1-di-2-pyridylnonanol (6.80 g, 22.8 mmol) in 100 mL CH_2Cl_2 was added 3-chloroperoxybenzoic acid (MCPBA) (8.3 g, 47.9 mmol) in portions. After 3 days at ambient temperature another 100 mL of CH_2Cl_2 was added, and the reaction was terminated by bubbling NH_3(g) through the reaction mixture for a few minutes. The ammonium salt formed was filtered off and the filtrate dried with $MgSO_4$. Evaporation of the solvent and thorough drying gave 6.93 g (92%) of the desired *N*-oxide. ^{1}H NMR: δ 0.86 (3 H, t, $J \approx 7$ Hz, CH_3), 1.23 (12 H, m, $-CH_2-$), 2.63 (2 H, m, $-CH_2-C_7H_{15}$), 7.20 (2 H, ddd, J = 7.5, 6.5, and 1.9 Hz, 5-pyridyl), 7.42 (2 H, dt, $J \approx 7.9$ and 1.2 Hz, 4-pyridyl), 7.98 (4 H, m, 3- and 6-pyridyl), 8.58 (1 H, s, OH).

1,1-Bis(6-cyano-2-pyridyl)nonanol. To a solution of the *N*-oxide (6.82 g, 20.7 mmol) in 25 mL of CH_2Cl_2 were added *N,N*-dimethylcarbamoyl chloride (3.8 mL, 41.3 mmol) and then trimethylsilyl cyanide (6.2 mL, 49.6 mmol). After 30 days of stirring at ambient temperature, the reaction was terminated by the addition of 10 mL of brine. After phase separation, drying, and evaporation of the solvent, a crystalline product consisting mainly of 1,1-bis(6-cyano-2-pyridyl)-1-((trimethylsilyl)oxy)nonane was obtained. This compound was desilylated by dissolving it in methanol containing HCl, which had been introduced by bubbling dry HCl(g) through the methanol for 5–10 s, followed by stirring for 20 min. The methanol was evaporated, and saturated aqueous $NaHCO_3$ was added. Extraction of this aqueous solution with CH_2Cl_2 yielded, after evaporation of the solvent, 6.2 g of crude material. Chromatography (column width 2 cm) with EtOAc/petroleum ether (3:7) gave 5.80 g (81%) of 1,1-bis(6-cyano-2-pyridyl)nonanol as a colorless oil. ^{1}H NMR (resonance enhancement): δ 0.85 (3 H, t, $J \approx 6.5$ Hz, CH_3), 1.21 (12 H, m, $-CH_2-$), 2.28 (2 H, m, $-CH_2-C_7H_{15}$), 5.83 (1 H, s, OH), 7.61 (2 H, dd, J = 7.6 and 1.2 Hz, 5-pyridyl), 7.87 (2 H, dd, J = 8.1 and 7.6 Hz, 4-pyridyl), 8.19 (2 H, dd, J = 8, 2, and 1.2 Hz, 3-pyridyl).

1,1-Bis(6-cyano-2-pyridyl)-1-methoxynonane. To a suspension of sodium hydride (0.37 g, 15.6 mmol) in 15 mL of DME was added 1,1-bis(6-cyano-2-pyridyl)nonanol (5.42 g, 15.6 mmol) in 45 mL of DME under nitrogen at ambient temperature. A few drops of MeI were added in order to initiate formation of the alcoholate. When the evolution of hydrogen gas had ceased, the remaining methyl iodide (0.97 mL, 15.6 mmol) was added. After 3 h the solvent was evaporated and the crude product chromatographed (column width 4 cm) with EtOAc/petroleum ether (3:7) to give 3.95 g (70%) of 1,1-bis(6-cyano-2-pyridyl)-1-methoxynonane. Further purification was achieved by recrystallization from petroleum ether; mp 90.5–91.5 °C. ^{1}H NMR: δ 0.86 (3 H, t (distorted), CH_3), 0.97 (2 H, m, $Ar_2C(OH)CH_2-CH_2-$), 1.22 (10 H, s (broad), $-CH_2-$), 2.61 (2 H, m, $-CH_2-C_7H_{15}$), 3.16 (3 H, s, OCH_3), 7.56 (2 H, m, 5-pyridyl), 7.78 (4 H, m, 3- and 4-pyridyl).

L^1H_2. 1,1-Bis(6-cyano-2-pyridyl)-1-methoxynonane (3.78 g, 10.4 mmol) and potassium hydroxide (5.8 g, 101 mmol) dissolved in 70 mL of an ethanol/water (6:1) mixture were kept at 80 °C for 3 days. After the reaction mixture had cooled, the pH was adjusted to ca. 5–6 by the addition of 2 M HCl. Extraction with CH_2Cl_2 (2 × 30 mL) followed by drying and evaporation of solvent yielded 3.96 g of a yellow oil that slowly crystallized. Further purification by recrystallization from CH_3CN/H_2O gave 3.1 g (74%) of L^1H_2, mp 110–112 °C. ^{1}H NMR: δ 0.86 (3 H, t (distorted), CH_3), 1.05 (2 H, m, $Ar_2C(OMe)CH_2-CH_2-$), 1.22 (10 H, m, CH_2), 2.66 (2 H, m, $-CH_2-C_7H_{15}$), 3.19 (3 H, s, OCH_3), 7.89 (2 H, dd, J = 7.9 and 1.4 Hz, 3-pyridyl), 7.94 (2 H, dd, J = 7.9 and 7.4 Hz, 4-pyridyl), 8.13 (2 H, dd, J = 7.4 and 1.4 Hz, 5-pyridyl).

1,1-Bis(6-carboxy-2-pyridyl)octene (L^3H_2). 1,1-Bis(6-bromo-2-pyridyl)octene. The ylide of heptyl triphenylphosphonium bromide[19] (0.28 g, 0.64 mmol) was prepared by adding *n*-butyllithium (0.40 mL, 1.6 M) to a THF solution (5 mL) of this compound at ambient temperature under N_2. An orange-colored solution resulted. After 10 min the ylide was transferred to a THF solution (5 mL) of bis(6-bromo-2-pyridyl) ketone (0.20 g, 0.59 mmol), resulting in an immediate decolorization of the ylide. (If an excess of ylide was used, a complicated reaction mixture resulted.) After 30 min of reflux, the solvent was evaporated and the crude product chromatographed (column width 2 cm) with EtOAc/petroleum ether (12:88) as eluent to give 0.175 g (70%) of 1,1-bis(6-bromo-2-pyridyl)octene. ^{1}H NMR:[20] δ 0.86 (3 H, t, CH_3), 1.24 (6 H, m, CH_2), 1.49 (2 H, m, $C{=}CHCH_2CH_2-$), 2.13 (2 H, q, J = 7.5 Hz, $C{=}CHCH_2-$), 6.87 (1 H, dd, J = 7.4 and 1.0 Hz, 3-pyridyl), 7.05 (1 H, t, J = 7.8 Hz, $C{=}CH$), 7.21 (1 H, dd, J = 7.4 and 1.0 Hz,

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3-pyridyl), 7.29 (1 H, dd, J = 7.9 and 1.0 Hz, 5-pyridyl), 7.38 (1 H, dd, J = 7.8 and 7.4 Hz, 4-pyridyl), 7.47 (1 H, dd, J = 7.9 and 1.0 Hz, 5′-pyridyl), 7.60 (1 H, dd, J = 7.9 and 7.4 Hz, 4′-pyridyl).

L^3H_2. To a solution of the dibromide (1.88 g, 4.4 mmol) in 60 mL of dry diethyl ether kept at −78 °C under N_2 was added *tert*-butyllithium (11.1 mL, 1.6 M) dropwise during 10 min, resulting in a deep red solution. After 10 min of stirring, dry and precooled CO_2(g) was bubbled through the reaction mixture. A second phase immediately formed. After 20 min, 20 mL of wet ether was added at −78 °C and then 50 mL of water in small portions. The mixture was then allowed to warm to room temperature, resulting in a color change from dark brown to light yellow, and 50 mL of saturated aqueous NH_4Cl was finally added. The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (2 × 25 mL), and the combined organic phase was treated with aqueous acid at pH 2–3. (This pH was necessary in order to obtain a product free from lithium carboxylate). Drying and evaporation of the solvent gave 1.31 g (83%) of L^3H_2. ^1H NMR:[20] δ 0.86 (3 H, t, CH_3), 1.26 (6 H, m, CH_2), 1.52 (2 H, m, $C{=}CHCH_2CH_2{-}$), 6.98 (1 H, t, J = 7.8 Hz, $C{=}CH$), 7.37 (1 H, dd, J = 7.9 and 1.0 Hz, 3-pyridyl), 7.57 (1 H, dd, J = 7.7 and 1.1 Hz, 3′-pyridyl), 7.90 (1 H, t, J = 7.8 Hz, 4-pyridyl), 8.08 (1 H, t, J = 7.7 Hz, 4′-pyridyl), 8.12 (1 H, dd, J = 7.7 and 1.1 Hz, 5-pyridyl), 8.27 (1 H, dd, J = 7.8 and 1.1 Hz, 5′-pyridyl), 10.25 ppm (2 H, s broad), CO_2H).

1,1-Bis(6-carboxy-2-pyridyl)-1-methoxypropane (L^4H_2). This ligand was prepared in a manner analogous to that of L^1H_2. Reaction of di-2-pyridyl ketone with ethylmagnesium bromide afforded 1,1-di-2-pyridylpropanol (64%), which was oxidized to the *N*-oxide (76% from toluene–petroleum ether, mp 189 °C). This compound was transformed into 1,1-bis(6-cyano-2-pyridyl)propanol (83%) by treatment with *N*,*N*-dimethylcarbamoyl chloride and trimethylsilyl cyanide. Methylation (90%) and final hydrolysis afforded L^4H_2 (87%). ^1H NMR: δ 0.72 (3 H, t, J = 7 Hz, CH_3), 2.71 (2 H, q, J = 7 Hz, CH_2), 3.18 (3 H, s, OCH_3), 7.88 (2 H, dd, J = 8.0 and 1.4 Hz, 3-pyridyl), 7.97 (2 H, dd, J = ca. 7 Hz, 4-pyridyl), 8.13 (2 H, dd, J = 7.4 and 1.4 Hz).

Metal Extraction Tests. Aqueous solutions of mixtures of metal sulfates (Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Fe^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}, or Cu^{2+}, Zn^{2+}, Fe^{3+}, and Cd^{2+}), ca. 2 mM in each metal ion, at pH ca. 2 or 4 were agitated with equal volumes of 10 (for 1:1 complexes) or 20 mM (for 2:1 complexes) solutions of the appropriate reagent in chloroform until equilibrium was reached. The pH of the aqueous phase was adjusted when necessary. The two phases were then separated, and the concentrations of metal ions in the aqueous phase were determined by atomic absorption spectrophotometry.

Preparation of Metal Complexes. Method 1 (Used for the Preparation of L^1Cu, L^1Ni, L^1Co, $(L^2)_2Cu$, $(L^2)_2Ni$, and $(L^2)_2Co$). An aqueous solution (0.25 mL) of the appropriate metal acetate (0.125 mmol) was added to the ligand (1 equiv) in EtOH (0.25 mL) at 60 °C. After cooling, an additional 0.25 mL of water was added, and the precipitate formed was filtered off.

Method 2 (Used for the Preparation of L^1Cu, L^1Co, L^3Cu, L^3Co, and L^4Cu). A 0.125 M chloroform solution of L^1H_2, L^3H_2, or L^4H_2 was shaken with an equal volume of a 0.25 M aqueous solution of the appropriate metal acetate for a few minutes. Complexes of L^1H_2 and L^3H_2 were obtained from the organic phase after drying ($MgSO_4$) and evaporation of the solvent, whereas L^4Cu crystallized from the aqueous phase.

L^1Cu. Anal. Calcd for $C_{22}H_{26}N_2O_5Cu$: C, 57.19; H, 5.67; N, 6.07; Cu, 13.75. Found: C, 57.58; H, 5.89; N, 6.03, Cu, 13.95.

Crystallography. Data Collection and Reduction. The Cu(II) complex of L^4H_2 crystallizes as a tetrahydrate from water (fw 449.9). A deep blue single crystal with the approximate dimensions 0.05 × 0.21 × 0.18 mm was selected and sealed in epoxy glue for X-ray diffraction study. A total of 3578 reflection intensities ($\theta < 67°$) were collected at room temperature by using Cu Kα radiation and the ω–2θ scan technique. The net intensities were corrected for Lorentz, polarization, and absorption effects (μ = 20.7 cm^{-1}).

The monoclinic structure with the space group $P2_1/n$ and Z = 4 has the unit cell dimensions a = 11.5711 (6) Å, b = 7.7308 (3) Å, c = 21.7034 (7) Å, β = 103.92 (4)°, and V = 1884.4 (4) Å^3. These dimensions were refined by using the angular settings of 35 well-centered reflections (34.5° < 2θ < 87.5°), accurately measured by the diffractometer.

Solution and Refinement of the Structure. The position of the Cu atom, derived from a Patterson synthesis, served as a starting point for solution of the structure. Difference Fourier syntheses and full-matrix least-squares calculations with the SHELX 76[21] program system were used to complete and refine the structural model. In the final stage, the positions and anisotropic temperature factors of the non-hydrogen atoms were refined. The hydrogen atoms were held fixed at the positions that were derived from difference electron density calculations; only their isotropic temperature factors were refined. Eight very strong low θ reflections (θ < 17°) with considerably lower F_o than F_c (ΔF) > $F_o/6$), probably due to extinction, were excluded from the calculation when the final reliability indeces, R = 0.0436 and R_w = 0.0494[21] were reached for 2785 reflections, all with $F/\sigma(F)$ > 6. The weights of the structure factors were calculated as $w = 1.282/(\sigma^2(F) + 0.0021F^2)$ with $\sigma(F)$ derived from counter statistics.

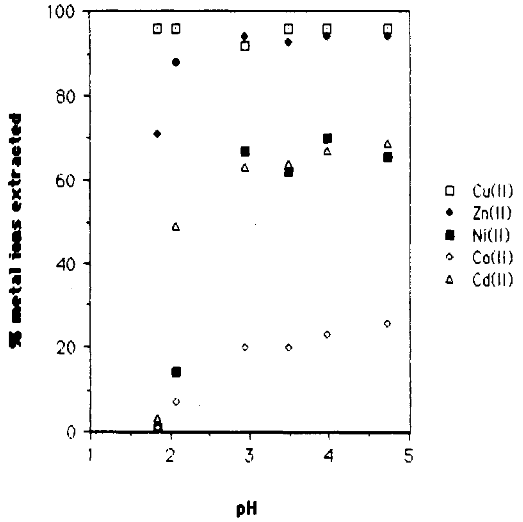
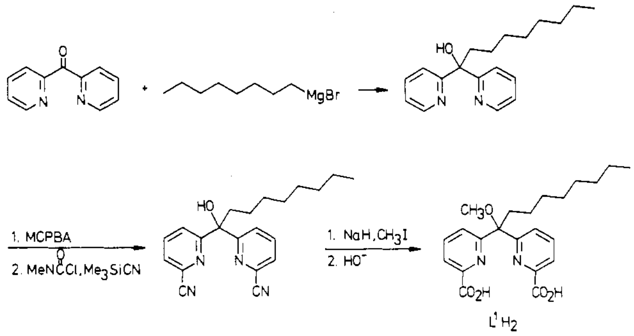


Figure 1. Amounts of metal ions extracted from an aqueous solution into a chloroform solution of L^1H_2.

Scheme I



TG and DSC Measurements. The dehydration processes of L^1Cu, $(L^2)_2Cu$, L^4Cu, L^1Ni, $(L^2)_2Ni$, and $(L^2)_2Co$ were monitored thermogravimetrically and with use of a differential scanning calorimeter. Prior to the TG and DSC measurements, all complexes, except L^4Cu, were dried in an evacuated desiccator containing silica gel. Crystals of the L^4 complex were picked out of the mother liquor and carefully dried before use in the TG and DSC experiments. The measurements were carried out with 1–3 mg samples, at a heating rate of 2.5° min^{-1} in an argon atmosphere.

Results and Discussion

Preparation of Ligands and Metal Extractions. The ligand 1,1-bis(6-carboxy-2-pyridyl)-1-methoxynonane, L^1H_2, was prepared starting from di-2-pyridyl ketone, which was reacted with *n*-octylmagnesium bromide to give a dipyridylcarbinol. Peracid oxidation of this compound and treatment of the resulting bis(*N*-oxide) with *N*,*N*-dimethylcarbamoyl chloride and trimethylsilyl cyanide gave a dinitrile, which after methylation of the alcohol function, was hydrolyzed to give L^1H_2 (Scheme I).

The metal ion selectivity of L^1H_2 was tested by extracting aqueous solutions of metal sulfates with chloroform solutions of the ligands. The amounts of metal ions extracted were determined by atomic absorption measurements of the metal ion concentration in the aqueous phase before and after extraction. The results of the extractions at various pH values are shown in Figure 1. The ligand L^1H_2 is a good extractant for Cu^{2+} and Zn^{2+} in particular, but also for Cd^{2+}, Ni^{2+} and Fe^{3+} (81% extracted at pH 1.82), while Co^{2+} is only poorly extracted.

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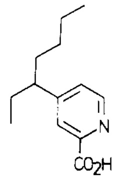
Table I. Extraction of Metal Ions at pH Ca. 4[a]

	% extraction			% extraction	
	L^1H_2	L^2H		L^1H_2	L^2H
Cu	96	100	Zn	94	77
Ni	70	99	Cd	67	51
Co	23	68			

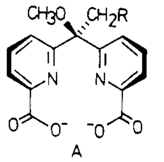
[a] The extractions were performed with equal volumes of an aqueous phase containing initially 2 mM metal sulfates and 10 mM (for L^1H_2) or 20 mM (for L^2H) chloroform solutions of the ligands.

These results differ somewhat from those obtained in extractions with the previously known[4] bidentate picolinic acid 4-(3-heptyl)pyridine-2-carboxylic acid (L^2H). Table I shows the amounts of metal ions extracted by the two ligands at pH 4. More Ni^{2+} and Co^{2+} is extracted with L^2H, while this ligand is somewhat less efficient than L^1H_2 for Zn^{2+} and Cd^{2+}.

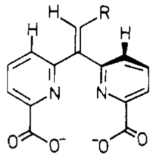


L^2H

The spatial arrangement of the N_2O_2 donor atoms is probably a crucial factor determining the metal ion selectivity. Inspection of space-filling molecular models suggests that the pyridine rings of L^1H_2 are freely rotating and that, upon complexation, a planar cis arrangement of the N_2O_2 atoms should be favored (A). A change of the hybridization of the carbon atom connecting the two pyridine rings would, however, influence the geometry of the ligand. In spite of the extended conjugation, an ethylenic ligand (B) possessing a sp^2 carbon in this position is forced into a nonplanar conformation due to steric repulsion between the alkyl group and one of the pyridine rings.

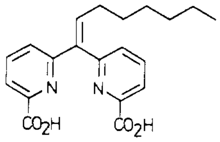


A



B

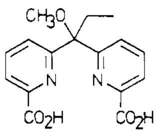
In order to test if this structural change would really influence the geometry of the ligand and, as a consequence, the complexing behavior, the vinylic ligand 1,1-bis(6-carboxy-2-pyridyl)octene (L^3H_2) was prepared by a Wittig reaction of bis(6-bromo-2-pyridyl) ketone with the ylide of heptyl triphenylphosphonium bromide, followed by lithiation and subsequent carbonation.



L^3H_2

Unfortunately, L^3H_2 was not completely suitable for metal extraction tests since some of the metal complexes formed were soluble in the aqueous phase and therefore did not yield reliable test data for these ions. In addition, the ligand readily polymerized under acidic conditions. This ligand extracted 73% Zn^{2+} and 93% Fe^{3+} at pH 1.82 and is thus even more efficient than L^1H for the extraction of Fe(III). It also extracted slightly more Fe(II) than L^1H, but with the data available it is not possible to draw conclusions about the Ni^{2+}/Co^{2+} selectivity.

Crystallographic Description of the Structure of $L^4Cu{\cdot}4H_2O$. A copper complex was prepared from L^1H_2 and copper acetate in ethanol–water. Attempts to crystallize this complex resulted in a partly crystalline solid, possibly due to the long, flexible carbon chain of L^1H_2. Therefore, a ligand with a shorter alkyl chain, L^4H_2, was prepared by a method analogous to that used for the preparation of L^1H_2, and its copper complex, which crystallized from water as a tetrahydrate, was studied by X-ray diffraction.



L^4H_2

A perspective view of the L^4Cu complex, with one crystal water molecule and with the atomic labeling used, is shown in Figure 2. The final fractional atomic coordinates and selected bond distances and angles are listed in Tables II and III, respectively. The packing is illustrated in Figure 3.

As seen in Figures 2 and 3, the 1,1-bis(6-carboxy-2-pyridyl) moiety is not accurately planar but is slightly bent. The dihedral angle between the planes of the two pyridine rings is 23.78 (7)°,

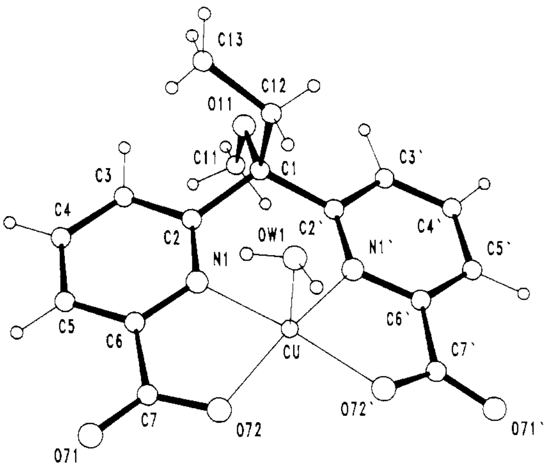


Figure 2. Perspective view of the copper complex of 1,1-bis(6-carboxy-2-pyridyl)-1-methoxypropane with one crystal water, which completes the coordination around the metal ion.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Fractions of the Non-Hydrogen atoms[a]

atom	*x/a*	*y/b*	*z/c*	U_{eq},[b] Å²
Cu	0.80068 (3)	0.15013 (5)	−0.01796 (2)	0.0284 (2)
C(1)	0.8253 (3)	0.0602 (4)	0.1349 (2)	0.032 (1)
O(11)	0.8578 (2)	−0.0285 (3)	0.1936 (1)	0.040 (1)
C(11)	0.9244 (4)	−0.1851 (5)	0.1944 (2)	0.054 (2)
C(12)	0.7523 (3)	0.2200 (4)	0.1469 (2)	0.040 (1)
C(13)	0.8188 (4)	0.3418 (5)	0.1985 (3)	0.066 (2)
N(1)	0.9339 (2)	0.1714 (3)	0.0563 (1)	0.027 (1)
C(2)	0.9383 (3)	0.1233 (4)	0.1167 (2)	0.030 (1)
C(3)	1.0424 (3)	0.1478 (4)	0.1632 (2)	0.038 (1)
C(4)	1.1410 (3)	0.2197 (4)	0.1477 (2)	0.041 (1)
C(5)	1.1343 (3)	0.2697 (4)	0.0857 (2)	0.036 (1)
C(6)	1.0292 (2)	0.2428 (3)	0.0417 (2)	0.028 (1)
C(7)	1.0120 (3)	0.2955 (4)	−0.0277 (2)	0.030 (1)
O(71)	1.0922 (2)	0.3706 (3)	−0.0447 (1)	0.042 (1)
O(72)	0.9109 (2)	0.2525 (3)	−0.0636 (1)	0.036 (1)
N(1′)	0.7176 (2)	−0.0156 (3)	0.0240 (1)	0.028 (1)
C(2′)	0.7374 (3)	−0.0498 (4)	0.0863 (2)	0.031 (1)
C(3′)	0.6672 (3)	−0.1728 (4)	0.1075 (2)	0.043 (1)
C(4′)	0.5806 (3)	−0.2616 (4)	0.0647 (2)	0.044 (1)
C(5′)	0.5634 (3)	−0.2283 (4)	−0.0001 (2)	0.038 (1)
C(6′)	0.6336 (2)	−0.1032 (4)	−0.0181 (2)	0.030 (1)
C(7′)	0.6220 (3)	−0.0497 (4)	−0.0861 (2)	0.033 (1)
O(71′)	0.5559 (2)	−0.1313 (3)	−0.1301 (1)	0.045 (1)
O(72′)	0.6845 (2)	0.0811 (3)	−0.0939 (1)	0.037 (1)
O(1W)	0.7141 (2)	0.4029 (4)	−0.0050 (1)	0.040 (1)
O(2W)	0.5958 (2)	0.5030 (3)	−0.1270 (1)	0.053 (1)
O(3W)	0.7624 (3)	0.3468 (3)	−0.1871 (1)	0.054 (1)
O(4W)	0.8722 (3)	0.5328 (4)	−0.2642 (1)	0.059 (1)

[a] The esd's are in parentheses. The atoms are numbered according to Figure 1. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}{\cdot}\mathbf{a}_i^*{\cdot}\mathbf{a}_j^*{\cdot}\mathbf{a}_i{\cdot}\mathbf{a}_j$.

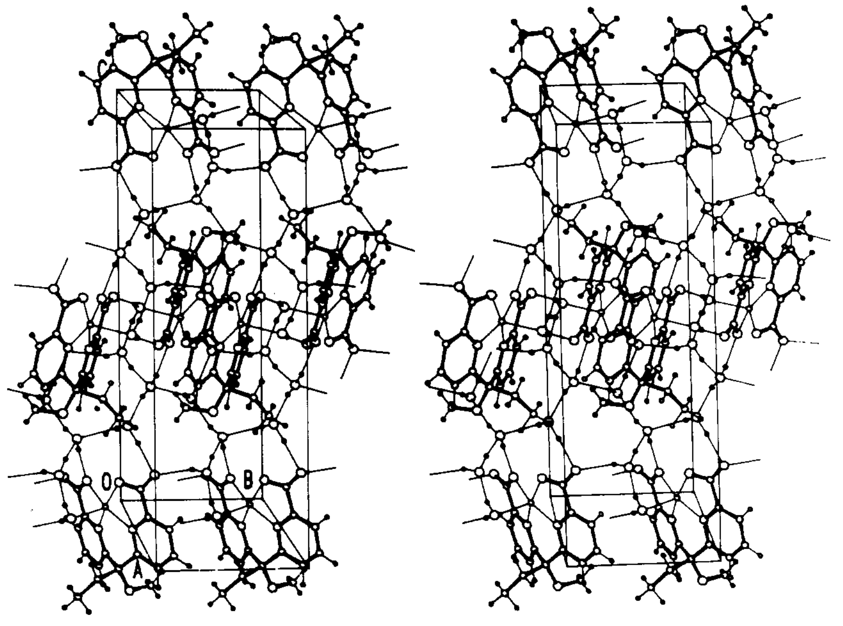


Figure 3. Stereodiagram of the packing of the crystal structure.

Table III. Selected Intramolecular Bond Distances and Bond Angles Involving the Non-Hydrogen Atoms[a]

	Bond Distances (Å)		
Cu–N(1)	1.951 (2)	C(7)–O(71)	1.224 (4)
Cu–N(1′)	1.953 (3)	C(7′)–O(71′)	1.242 (3)
Cu–O(72)	1.960 (2)	C(7)–O(72)	1.284 (3)
Cu–O(72′)	1.935 (2)	C(7′)–O(72′)	1.278 (4)
Cu–O(1W)	2.244 (2)		
	Bond Angles (deg)		
O(72′)–Cu–O(1W)	96.2 (1)	Cu–N(1)–C(6)	111.8 (2)
N(1′)–Cu–O(1W)	103.2 (1)	Cu–N(1)–C(2)	128.0 (3)
N(1′)–Cu–O(72′)	84.1 (1)	C(1)–C(2)–N(1)	120.1 (3)
O(72)–Cu–O(1W)	94.4 (1)	O(71)–C(7)–O(72)	125.8 (3)
O(72)–Cu–O(72′)	94.8 (1)	Cu–O(72)–C(7)	113.9 (2)
O(72)–Cu–N(1′)	162.4 (1)	Cu–N(1′)–C(6′)	111.7 (2)
N(1)–Cu–O(1W)	96.4 (1)	Cu–N(1′)–C(2′)	127.9 (2)
N(1)–Cu–O(72′)	167.5 (1)	C(1)–C(2′)–N(1′)	120.5 (3)
N(1)–Cu–N(1′)	92.9 (1)	O(71′)–C(7′)–O(72′)	124.2 (3)
N(1)–Cu–O(72)	84.4 (1)	Cu–O(72′)–C(7′)	113.8 (2)
C(2)–C(1)–C(2′)	117.7 (3)		

[a] The esd's are given in parentheses.

and the carboxy groups are inclined to the LS planes of the respective pyridine rings at angles of 4.2 (1)° (at C(6)] and 7.5 (2)° [at C(6′)].

The copper(II) ion is (4+1) coordinated. The four nearest neighbors, which are cis-positioned pairs of N and O atoms of the bis(picolinic acid) moiety, form a square-planar arrangement. An oxygen atom of one of the four crystal water molecules completes the coordination above the copper ion, in a direction approximately perpendicular to the square. Thus the coordination figure is a "nearly square pyramid" with the following dimensions: the base edges are 2.628 (3) [N(1)···O(72)], 2.829 (3) [N(1)···N(1′)], 2.604 (3) Å [N(1′)···O(72′)], and 2.867 (3) Å [O(72)···O(72′)] and the height is 2.492 (3) Å. The copper ion is displaced 0.254 (1) Å from the basal plane toward the hydrate O(1W) atom.

The N(1)–C(2)–C(1)–C(2′)–N(1′)–Cu ring between the two aromatic rings has a flattened boat conformation with the ethyl group in an axial and the methoxy substituent in an equatorial position. The ring-puckering parameters, calculated according to Cremer and Pople,[22] are $\varphi = 119.8$ (3)°, $\theta = 84.5$ (4)°, and $Q = 0.423$ (3) Å.

The four hydrate molecules stabilize the crystal structure by forming a hydrogen-bond network that links the L^4Cu complexes together (Figure 3). Each water molecule takes part in hydrogen bonds both as a donor and as an acceptor except the $O(W1)H_2$ molecule, which functions only as a proton donor in two H bonds but coordinates also to the copper ion.

Thermal Analysis. Metal complexes of L^1H_2 and L^2H were prepared either by the addition of aqueous solutions of metal acetates to the ligand in ethanol or by the extraction of metal ions from an aqueous phase into a chloroform solution of the ligand. Metal complexes of L^3H_2 were more conveniently prepared by the latter method, due to the lability of this ligand in acidic media.

The thermogravimetric measurements of L^1Cu, $(L^2)_2Cu$, and L^4Cu showed that these complexes contained 1, 0.5, and 4 molecules of H_2O, respectively, as seen in Table IV. The dehydration of these complexes takes place in one step. With either the DSC peak temperature, T_{max}, or the completion temperature used as a measure of the thermal stability of the hydrated complexes, the stability sequence proved to be $(L^2)_2Cu > L^1Cu > L^4Cu$. The ΔH values per formula unit ($L^xCu{\cdot}nH_2O$) for the dehydration process were found to decrease with decreasing water content. If these ΔH values are divided by the respective n values in $L^xCu{\cdot}nH_2O$ ($\Delta H'$ in Table IV), a value around 40 kJ/mol is obtained for all three complexes. Thus it seems that the energy associated with the removal of one H_2O molecule per formula unit is roughly the same in all Cu complexes in spite of the different ligands. The observation that the dehydration of the L^4 complex takes place in one step and not in two or more steps also indicates that the four H_2O molecules have almost equal bonding energies.

The TG and DSC curves of the $(L^2)_2Ni$ and $(L^2)_2Co$ complexes resemble each other to a great extent. Thus both compounds were found to contain two H_2O molecules per formula unit and exhibited ΔH values (and thus also $\Delta H'$ values) of similar magnitudes. In both cases the dehydration took place in one step.

The L^1Ni complex, finally, was found to contain four molecules of H_2O per formula unit. The dehydration took place in two steps. Within the temperature interval 300–350 K two water molecules evaporated, and the last two molecules were lost between 365 and 405 K. The DSC and TG curves of the L^1Ni complex actually indicate that the last step consists of two overlapping processes. In connection with the dehydration the sample changed from blue to yellow. It is quite interesting to note that the $\Delta H'$ value for the two H_2O molecules evaporated in the lower temperature region is very similar to those observed for the Cu complexes while the $\Delta H'$ value associated with the last dehydration step resembles those observed for the $(L^2)_2Ni$ and $(L^2)_2Co$ complexes.

In nickel bis(picolinate) tetrahydrate[11] the Ni ions are octahedrally surrounded by two N atoms, two chelating carboxylic oxygens, and two oxygens of water molecules. The two remaining

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(22) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

Table IV. TG and DSC Results

	thermogravimetry					differential scanning calorimetry			
	weight change								
	exptl		calcd						
compd (L^xMe)	%	nH_2O/LM	nH_2O/LM	%	$T_{interval}$, K	ΔH, kJ/mol of $LM \cdot nH_2O$	$\Delta H'$, kJ/mol of $LM \cdot nH_2O$	T_{max}, K	$T_{interval}$, K
L^4Cu (M_r = 377.9)	16.3	n = 4.08	n = 4.00	16.0	300–345	179.3	44.8	332	300–340
L^1Cu (M_r = 462.00)	3.6	n = 0.96	n = 1.00	3.8	345–380	46.1	46.1	368	300–340
$(L^2)_2Cu$ (M_r = 504.11)	1.9	n = 0.54	n = 0.50	1.8	360–395	17.5	35.0	386	340–378
L^1Ni (M_r = 457.16)	6.8	n = 2.01	n = 2.0	6.8	300–350	90.7	45.4	340	300–355
	6.7	n = 1.98	n = 2.0	6.8	365–405	161.2	80.6	392	360–405
$(L^2)_2Ni$ (M_r = 499.27)	6.8	n = 2.02	n = 2.00	6.7	365–425	177.1	88.6	411	355–426
$(L_2)_2Co$ (M_r = 499.49)	6.7	n = 1.99	n = 2.0	6.7	355–405	150.7	75.4	399	353–409

water molecules form layers by means of hydrogen bonding. With the exception of the necessary cis arrangement of the N_2O_2 ligand atoms, our complex is expected to have a structure similar to that of nickel bis(picolinate) tetrahydrate.

Ghosh et al. have studied the dehydration processes of hydrated cobalt, nickel, and copper bis(picolinate).[23] The TG and DSC curves of the latter compound are very similar to those of $(L^2)_2Cu$, implying that both complexes contain 0.5 H_2O molecule per formula unit and exhibit similar ΔH values. The dehydration process of nickel bis(picolinate) tetrahydrate resembles that of the L^1Ni complex. Both complexes thus contain four H_2O molecules per formula unit, and the dehydration takes place in two steps, each step comprising two water molecules. The evaporation of water from the bis(picolinate) complex, however, takes place at a somewhat higher temperature. Finally the cobalt bis(picolinate) was found to contain four water molecules per formula unit, which are lost in two steps, 2.5 H_2O molecules in the first step and 1.5 in the second.

To the extent that the metal ions prefer octahedral coordination, the complexes must contain at least two molecules of water per formula unit, but otherwise there seems to be no direct correlation between the water content of the crystallized complex and the structure of the complex itself. However, available structural data indicate that the main role of water molecules is to stabilize the packing of these complexes in the crystalline state through hydrogen bonding.

Electronic Spectra. Electronic spectra of metal complexes were recorded between 11 000 and 25 000 cm^{-1}. In this region the deep blue complexes L^1Cu and L^4Cu showed bands at 15 924 cm^{-1} in ethanol (ϵ = 107 and 101 L mol^{-1} cm^{-1}, respectively). In chloroform L^1Cu absorbed at 16 340 cm^{-1} (ϵ = 101 L mol^{-1} cm^{-1}) while the blue-green complex L^3Cu had a band at 15 480 cm^{-1} in this solvent. Definitive conclusions about the stereochemistry of copper complexes from electronic spectra are usually not possible.[24] A deviation from planarity in copper complexes with N_2O_2 ligands is known, though, to cause absorption at lower energy.[25-28] Therefore, L^3Cu probably has a pseudotetrahedral structure, in accordance with the assumed sterically necessary deviation from planarity of the ligand. The complex $(L^2)_2Cu$ absorbed at 15 625 cm^{-1} in ethanol, which is close to the value reported for copper bis(picolinate),[14] and is supposed to have a planar trans structure.[6] In chloroform the absorption for this complex was shifted to 17 120 cm^{-1} with a considerably lower ϵ value (48 L mol^{-1} cm^{-1}), which may indicate a more symmetrical structure of this complex than of L^1Cu in chloroform.

The electronic spectrum of the nickel complex of L^1H_2, which is violet, showed bands at 13 514 cm^{-1} (ϵ = 20 L mol^{-1} cm^{-1}) and at 12 315 cm^{-1} (ϵ = 24 L mol^{-1} cm^{-1}) in ethanol, which is in accordance with the proposed octahedral structure.[29]

Not only high temperatures but also noncoordinating solvents are known to favor square-planar coordination in nickel complexes.[30] Indeed, when allowed to stand in chloroform, the purple nickel complex was transformed into a yellow complex with a band at 21 740 cm^{-1}, characteristic of a square-planar nickel complex.[29]

The electronic spectrum of the pink cobalt complex of L^1H_2 had a band at 20 408 cm^{-1} (ϵ = 24 L mol^{-1} cm^{-1}), indicating an octahedral structure,[29] which is also expected in analogy with the known structure of cobalt bis(picolinate).[31] The spectrum of the cobalt complex of L^3H_2 had a shoulder at 21 050 cm^{-1}.

Bis(picolinic acids) carrying additional coordinating groups are currently being prepared, and the effect of such groups on the coordinating properties of metal complexes will be investigated.

Acknowledgment. We are indebted to Professor Ingmar Grenthe for valuable discussions. This work was supported by the Swedish Natural Science Research Council and by the Swedish Board for Technical Development.

Registry No. L^1H_2, 111557-40-5; $L^1Cu \cdot H_2O$, 111557-49-4; $L^1Ni \cdot 4H_2O$, 111557-51-8; $L^1Co \cdot 2H_2O$, 111557-54-1; $(L^2)_2Cu \cdot 0.5H_2O$, 111557-50-7; $(L^2)_2Ni \cdot 2H_2O$, 111557-52-9; $(L^2)_2Co \cdot 2H_2O$, 111557-53-0; L^3H_2, 111557-41-6; L^3Co, 111557-55-2; L^3Cu, 111557-56-3; L^4H_2, 111557-43-8; $L^4Cu \cdot 4H_2O$, 111557-48-3; Cu, 7440-50-8; Zn, 7440-66-6; Ni, 7440-02-0; Co, 7440-48-4; Fe, 7439-89-6; Cd, 7440-43-9; 1,1-di-2-pyridylnonanol, 111557-35-8; 1,1-di-2-pyridylnonanol *N,N'*-dioxide, 111557-36-9; 1,1-bis(6-cyano-2-pyridyl)nonanol, 111557-37-0; 1,1-bis(6-cyano-2-pyridyl)-1-((trimethylsilyl)oxy)nonane, 111557-38-1; 1,1-bis(6-cyano-2-pyridyl)-1-methoxynonane, 111557-39-2; 1,1-bis(6-bromo-2-pyridyl)octene, 111557-42-7; heptylidenetriphenylphosphorane, 55367-56-1; 1,1-di-2-pyridylpropanol, 111557-44-9; 1,1-di-2-pyridylpropanol *N,N'*-dioxide, 111557-45-0; 1,1-bis(6-cyano-2-pyridyl)propanol, 111557-46-1; 1,1-bis(6-cyano-2-pyridyl)-1-methoxypropane *N,N'*-dioxide, 111557-47-2; di-2-pyridyl ketone, 19437-26-4; *n*-octylmagnesium bromide, 17049-49-9; bis(6-bromo-2-pyridyl) ketone, 42772-87-2; ethylmagnesium bromide, 925-90-6.

Supplementary Material Available: Full lists of intramolecular bond distances and bond angles, fractional atomic coordinates of the hydrogen atoms, and anisotropic thermal parameters (6 pages); structure factor tables (12 pages). Ordering information is given on any current masthead page.

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