Syntheses and Structures of Nickel(II) and Copper(II) Complexes of 2,6-Bis[(2-acetylphenyl)carbamoyl]pyridine: Effects of Molecular Structure on Crystal Lattice Architecture

T. Kawamoto,[†] **B. S. Hammes,**[†] **R. Ostrander,**[‡]
A. L. Rheingold,[‡] **and A. S. Borovik***[,†,§]

Departments of Chemistry, Kansas State University,
Manhattan, Kansas 66506, and University of Delaware,
Newark, Delaware 19716

Received October 16, 1997

Metal complexes that assemble into specific supramolecular structures in crystal lattices have generated considerable interest because of their potential use in developing new materials.[1] A variety of different synthetic methods have been recently reported[2] that produce intricate lattice architectures: these include coordination networks formed by polyfunctional organic ligands and transition metal salts[3] and supramolecular assemblies derived from helicates.[4] However, it is still difficult to reliably predict lattice structure because several factors, such as solvent, counterion(s), and the geometry of the ligands bonded to the metal ion(s), influence the assembly process. We have been investigating the effects of ligand geometry and solvent on the lattice structure for neutral transition metal complexes derived from the chelating ligands 2,6-bis[(2-R-phenyl)carbamoyl)]-pyridine (R = acetyl or carbamoyl).[5] These ligands contain a tridentate pyridyl diamidate chelate with appended groups having additional donors that can weakly interact with coordinated metal ions. The molecular structures of the complexes are determined by the orientations of the appended groups which in turn can direct the assembly process during crystallization to produce varied lattice architectures. This concept is illustrated herein by the syntheses and structural analyses of the Cu(II) and Ni(II) complexes of 2,6-bis[(2-acetylphenyl)carbamoyl]-pyridine, H_2**1**, a ligand which contains appended acetophenone groups.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. Elemental analysis of all compounds was performed by Desert Analytics, Inc., Tucson, AZ. All samples were dried in vacuo prior to analysis.

2,6-Bis[(2-acetylphenyl)carbamoyl]pyridine ($H_2$1). A solution of 2,6-pyridinedicarbonyl dichloride (1.0 g, 4.9 mmol) in 30 mL of THF was added dropwise to a solution of 2′-aminoacetophenone (1.5 g, 11 mmol) and triethylamine (2.0 g, 20 mmol) under a nitrogen atmosphere at 0 °C. When the addition was completed, the mixture was allowed to warm to room temperature and stirred an additional 1.5 h and volatiles were removed under reduced pressure. The residue was dissolved in 150 mL of ethyl acetate and extracted with two 150 mL portions of water and 100 mL of brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give a light yellow solid. Purification was accomplished by layering a concentrated CH_2Cl_2 solution of H_2**1** with cyclohexane to yield 1.4 g (69%) of H_2**1** as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 303 K, TMS): δ 13.13 (s, 2 H, OC−N*H*), 8.78 (d, 2 H, H_a), 8.46 (d, 2 H, H_e), 8.12 (t, 1 H, H_f), 7.91 (d, 2 H, H_d), 7.64 (t, 2 H, H_b), 7.23 (t, 2 H, H_c), 2.58 (s, 6 H, OC−C*H*$_3$). ^{13}C NMR (100.4 MHz, $CDCl_3$, 303 K): δ 200.7, 162.6, 149.4, 139.0, 139.1, 134.1, 131.0, 125.2, 125.0, 123.3, 122.0, 28.3. FTIR (CH_2Cl_2, cm^{-1}): ν_{NH}(amide) = 3350 (w), 3209 (w, br); ν_{CO}(amide) = 1690 (s), ν_{CO}(ketone) = 1660 (s). FTIR (KBr, cm^{-1}): ν_{NH}(amide) = 3330 (s), 3189 (w, br); ν_{CO}(amide) = 1689 (s); ν_{CO}(ketone) = 1658 (m), 1653 (m). Mp (uncorrected): 177−178 °C. MH^+ *m*/*e*: 402 (positive FAB).

[2,6-Bis[(2-acetylphenyl)carbamoyl]pyridine]nickel(II) (Ni1). The ligand H_2**1** (0.21 g, 0.53 mmol) was dissolved in 80 mL of hot methanol. KOH (0.092 g, 1.6 mmol) and $NiCl_2 \cdot 6H_2O$ (0.19 g, 0.80 mmol) were successively added to the reaction mixture. The solution was refluxed for 24 h and then allowed to cool to room temperature. A red precipitate formed and was collected by filtration. The precipitate was redissolved in CH_2Cl_2, and excess $NiCl_2 \cdot 6H_2O$ was removed by filtration. The resulting red solution was evaporated to dryness to afford a red solid, which was crystallized from hot toluene or methanol to give 0.14 g (55%) of Ni**1** as red crystals. Anal. Calcd for Ni**1**$\cdot H_2O$, $C_{23}H_{19}N_3NiO_5$: C, 58.02; H, 4.02; N, 8.83. Found: C, 58.14; H, 3.55; N, 8.90. ^{1}H NMR (400 MHz, $CDCl_3$, 303 K, TMS): δ 8.33 (d, 2 H, H_a), 8.04 (t, 1 H, H_f), 7.75 (d, 2 H, H_e), 7.68 (d, 2 H, H_d), 7.49 (t, 2 H, H_b), 7.11 (t, 2 H, H_c), 2.63 (s, 6 H, OC−C*H*$_3$). ^{13}C NMR (100.4 MHz, $CDCl_3$, 303 K): δ 202.4, 168.4, 151.2, 144.9, 141.1, 134.5, 130.9, 130.5, 126.6, 124.3, 123.18, 28.97. FTIR (CH_2Cl_2, cm^{-1}): ν_{CO}(ketone) = 1680 (m), 1653(m); ν_{CO}(amide) = 1635 (s). FTIR (KBr, cm^{-1}): ν_{CO}(ketone) = 1676 (m), 1649 (s); ν_{CO}(amide) = 1634 (s). λ_{max} ($CHCl_3$; ϵ, M^{-1} cm^{-1}): 326 (sh), 357 (10 200), 406 (sh), 423 (sh), 482 (2120), 528 (1320).

[2,6-Bis[(2-acetylphenyl)carbamoyl]pyridine]copper(II) (Cu1). A 0.10 g (0.25 mmol) sample of H_2**1** was dissolved in 40 mL of refluxing methanol. KOH (0.042 g, 0.76 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (0.075 g, 0.38 mmol) were successively added to the reaction mixture. The

---

* To whom correspondence should be addressed.

[†] Kansas State University.

[‡] University of Delaware.

[§] Current address: Department of Chemistry, University of Kansas, Lawrence, KS 66045.

(1) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F. In *Supramolecular Architecture*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1992; p 256. (c) *Transition Metals in Supramolecular Chemistry*; Fabbrizzi, L., Poggi, A., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1994.

(2) Selected examples: (a) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328. (b) Eichen, Y.; Lehn, J.-M.; Scherl, M.; Haarer, D.; Fischer, J.; DeCian, A.; Corval, A.; Trommsdorff, H. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2530. (c) Frey, W.; Schief, W. R., Jr.; Pack, D. W.; Chen, C.-T.; Chilkoti, A.; Stayton, P.; Vogel, V.; Arnold, F. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 4937. (d) Medina, J. C.; Gay, I.; Chen, Z.; Eschegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 365. (e) Saalfrank, R. W.; Stark, A.; Bremer, M.; Hummel, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 311. (f) Copp, S. B.; Subramanian, S.; Zaworotko, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1078.

(3) Recent reports: (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792. (c) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *374*, 792. (d) Robson, R. In *Comprehensive Supramolecular Chemistry*; Atwood, J., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Elsevier Science: Oxford, England, 1996; p 773. (e) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960.

(4) (a) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565. (b) Dietrich-Buchecker, C. O.; Sauvage, J.-M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 189. (c) Constable, E. D.; Elder, S. M.; Healy, J.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4590. (d) Piguet, C.; Bernardinelli, G.; Bocquet, B.; Quattropani, A.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 7440.

(5) (a) Kawamoto, T.; Prakash, O.; Ostrander, R.; Rheingold, A. L.; Borovik, A. S. *Inorg. Chem.* **1995**, *34*, 4294. (b) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. A.; Rheingold, A. L.; Borovik, A. S. *J. Am. Chem. Soc.* **1995**, *118*, 285.

S0020-1669(97)01318-9 CCC: $15.00

Table 1. Crystallographic Data for Ni**1**·$2H_2O$, Cu**1**·$0.5C_7H_8$

	Ni**1**·$2H_2O$	Cu**1**·$0.5C_7H_8$
empirical formula	$C_{23}H_{21}N_3NiO_6$	$C_{26.5}H_{21}CuN_3O_4$
fw	494.1	509.0
T (°C)	25	20
space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.655(4)	8.173(1)
b (Å)	7.449(3)	11.095(2)
c (Å)	24.432(8)	12.833(2)
α (deg)	90	93.72(3)
β (deg)	101.580(3)	103.18(1)
γ (deg)	90	98.91(1)
Z	4	2
V (Å^3)	2077.9(12)	1113.2(3)
ρ_{calc} (g/cm^3)	1.580	1.518
μ_{calc} (cm^{-1})	9.82	10.22
λ (Å)	0.71073	0.71073
$R(F_o)^a$	0.0351	0.0497
$R_w(F_o)^b$	0.0427	0.0723

^{a} $R = \sum|\Delta F|/\sum|F_o|]$. ^{b} $R_w = \sum w(\Delta F)^2/\sum wF_o^2$.

solution was refluxed for 24 h. After cooling, the methanol was removed under vacuum to give a green solid. The residue was dissolved in CH_2Cl_2, and the solution was filtered to remove any excess $Cu(CH_3COO)_2 \cdot H_2O$. The CH_2Cl_2 was removed under reduced pressure to afford a green solid, which was crystallized from hot toluene to yield 0.055 g (43%) of Cu**1** as green crystals. Anal. Calcd for Cu**1**·$0.5C_7H_8$, $C_{26.5}H_{21}CuN_3O_4$: C, 62.53; H, 4.16; N, 8.26. Found: C, 62.79; H, 4.03; N, 8.33. FTIR (CH_2Cl_2, cm^{-1}): ν_{CO}(ketone) = 1627 (s); ν_{CO}(amide) = 1617 (s). FTIR (KBr, cm^{-1}): ν_{CO}(ketone) = 1676 (m), 1649 (s); ν_{CO}(amide) = 1617 (s). λ_{max} ($CHCl_3$; ϵ, M^{-1} cm^{-1}): 356 (10 100). X-band EPR (1:1 toluene/CH_2Cl_2, 77 K): $g_{\parallel} = 2.21$, $g_{\perp} = 2.08$, $A_{\parallel} = 158$ G. X-band EPR (powder, 77 K): $g = 2.06$.

Physical Methods. ^{1}H and ^{13}C NMR spectra and NOE measurements were collected on a Bruker 400 MHz NMR spectrometer. Chemical shifts are reported in ppm relative to an internal standard of TMS. FTIR spectra were recorded on a Bio-Rad FTS-20 FTIR spectrometer interfaced to a PC computer and are reported in wavenumbers. UV−vis spectra were collected on an SLM-Aminco diode array spectrophotometer using a 1.0 cm Suprasil quartz cell. EPR spectra were collected using a Bruker TE_{102} cavity and a Bruker 200D-SRC control console (which housed a Bruker ER022 signal channel, a Bruker ER031 field controller, and a Bruker ER001 time base oscilloscope). The console was interfaced to a Bruker ER040 XR microwave bridge and a Varian V3603 magnet (powered by Varian model 907015-03 power supply and a Varian V-FR2503 fieldial magnetic field regulator). Spectra were collected at 77 K, and all g values reported are referenced to DPPH.

Crystallographic Structural Determinations. Single crystals of Ni**1**·$2H_2O$ and Cu**1**·$0.5C_7H_8$ were obtained under similar conditions using hot toluene as the solvent. Crystal data collection and refinement parameters for Ni**1**·$2H_2O$ and Cu**1**·$0.5C_7H_8$ are given in Table 1. The systematic absences in the diffraction data are uniquely consistent with the space group, $P2_1/c$ for Ni**1**·$2H_2O$ and $P\bar{1}$ for Cu**1**·$0.5C_7H_8$. For Cu**1**·$0.5C_7H_8$, $P\bar{1}$ was initially chosen, and this assignment was supported by the stable and chemically reasonable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The asymmetric unit of Ni**1**·$2H_2O$ contains two molecules of H_2O while that of Cu**1** has half a molecule of toluene. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Design Considerations and Syntheses. Figure 1 shows the design factors used in developing metal complexes of [**1**]$^{2-}$ and related ligands. Deprotonation of the pyridyl diamide center affords a *mer* chelate that becomes planar after coordination to a metal ion. This planar structure is caused by the rigidity of the pyridyl diamidate chelate and is independent of the coordinated metal ion. The molecular structure of the complexes is determined by the relative orientation of the groups appended from each amide nitrogen. The orientations of the appended groups are directed, to a large extent, by their interactions with the bonded metal. Each appended group is designed to contain additional donor atoms capable of binding to the metal ion. These donors are relatively weak Lewis bases whose interactions depend on the stereochemical preference of the coordinated metal ion, and *not* on the geometric requirements of the ligand.[6] For H_2**1**, acyl oxygen donors from the appended acetophenone groups are predisposed to furnish additional electron density to the coordinatively unsaturated metal center. A variety of molecular structures can therefore be obtained by binding metal ions with different coordination requirements. Moreover, these differences in molecular structure between complexes should result in varied lattice architectures. This is particularly true for complexes containing divalent metal ions of [**1**]$^{2-}$ which are neutral. The assembly of these complexes will be governed by intermolecular hydrogen bonds and π-stacking interactions.

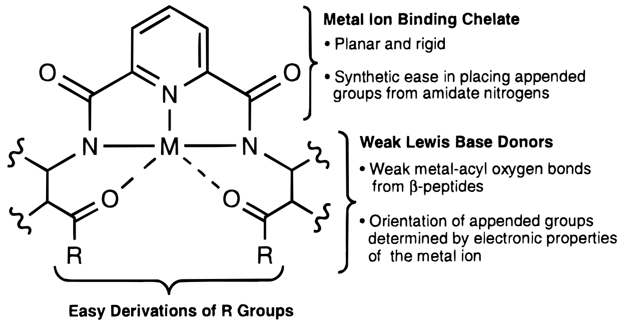

Figure 1. Schematic of the design concepts used in this study.

Molecular Structures. The structures of Ni**1** and Cu**1** were examined by single-crystal X-ray diffraction methods. Views of the molecular structures of Ni**1** and Cu**2** are found in Figures 2 and 3, and selected bond distances and angles are listed in Table 2. Both complexes have three of their coordination sites occupied by nitrogen donors from the diamidate−pyridyl chelate. In Ni**1** the geometry around the Ni(II) is approximately square planar, with the fourth donor provided by a carbonyl oxygen, O(4), from one of the appended acetophenone groups. The acyl oxygen coordination orients this group nearly coplanar with the rigid, tridentate chelate. The remaining acetophenone oxygen O(3) is pointed away from the Ni(II) center at a distance of ∼5.5 Å (vide infra).

In contrast to those in Ni**1**, both acetophenone oxygens in Cu**1** interact with the copper(II) center**,** producing a square pyramidal five-coordinate species with O(3) occupying the axial position. These oxygen donors are coordinated unsymmetrically to Cu(II), with distances of 2.357(3) and 1.933(3) Å for the Cu−O(3) and Cu−O(4) bonds, respectively. Dual coordination of carbonyl oxygens causes the appended acetophenone groups to orient on opposite faces of the plane formed by the Cu(II)−[pyridyl diamidate] chelate. The structural consequence of this displacement gives Cu**1** an overall helical morphology.[5,7]

---

(6) Representative papers: (a) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 172. (b) Wester, D.; Palenik, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 7565.

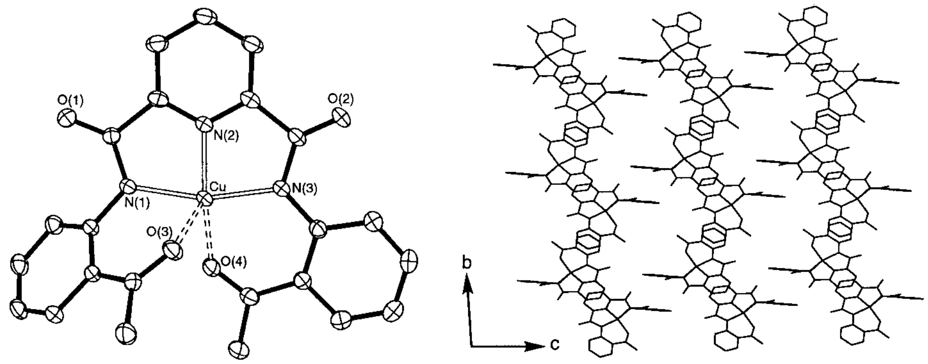

Figure 2. Thermal ellipsoid diagram of Cu**1** (left) and a portion of the crystal lattice for Cu**1** (view of the *b*,*c* plane) showing the open-framework structure. Solvent molecules have been omitted for clarity, and the ellipsoids are drawn at the 40% probability level.

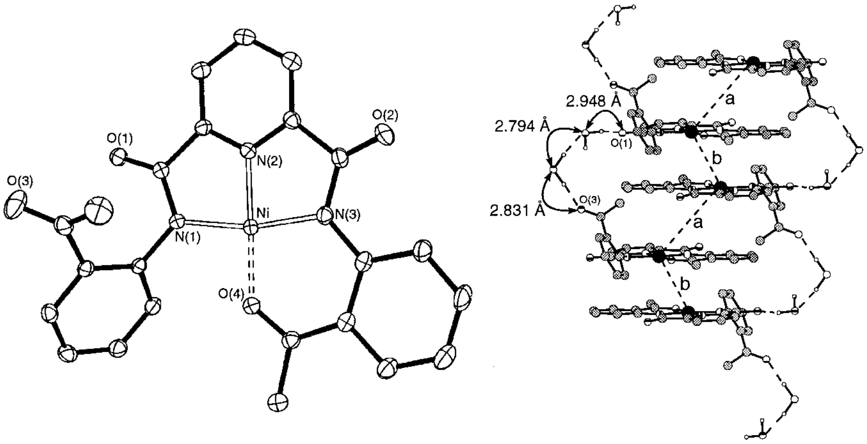

Figure 3. Thermal ellipsoid diagram of Ni**1** (left) and a portion of the crystal lattice for Ni**1** illustrating the hydrogen-bonding network used to stabilized the column motifs. Intraccolumnar Ni−Ni distances: *a*, 4.42 Å; *b*, 6.21 Å.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Ni**1** and Cu**1**

	Ni**1**	Cu**1**
M−N(1)	1.918(3)	1.981(3)
M−N(2)	1.805(2)	1.887(3)
M−N(3)	1.885(3)	1.980(3)
M−O(3)		2.355(3)
M−O(4)	1.828(2)	1.932(3)
N(1)−M−N(2)	82.7(1)	80.9(1)
N(1)−M−N(3)	167.7(1)	163.8(1)
N(1)−M−O(3)		78.0(1)
N(1)−M−O(4)	95.2(1)	102.8(1)
N(2)−M−N(3)	85.1(1)	83.0(1)
N(2)−M−O(3)		117.4(1)
N(2)−M−O(4)	177.5(1)	161.4(1)
N(3)−M−O(3)		109.6(1)
N(3)−M−O(4)	97.1(1)	92.6(1)
O(3)−M−O(4)		81.2(1)

The equatorial Ni−O(4) and Cu−O(4) bond distances are 1.828(3) and 1.932(3) Å, which are shorter than the apical Cu−O(3) bond length of 2.355(3) Å.[8,9] Comparison of these distances to those reported for other complexes with Ni(II)− and Cu(II)−ketonyl oxygen bonds (average M−O distance of ∼1.93 Å) suggests relatively strong equatorial M−O interactions are present in Ni**1** and Cu**1**. However, molecular modeling studies (CAChe) show that, for equatorial coordination of an acyl oxygen to the M(II)−[pyridyl diamidate] chelate, the oxygen donor must reside ca. 1.9 Å from the bound metal center. This inflexibility in the ligand system restricts all near-planar metal−carbonyl oxygen interactions; thus we propose that these short bond lengths in Cu**1** and Ni**1** are actually caused by the structural constraints imposed by $[\mathbf{1}]^{2-}$. This hypothesis is supported by two lines of structural evidence in Ni**1** which show that the Ni−O(4) interaction is indeed weak. First, the Ni−N(2) bond distance of 1.805 (2) Å is exceptionally short compared to those of known pyridine nitrogen−nickel bonds incorporated into two five-membered metallocycles (>1.95 Å).[10]

---

(7) Examples of metal complexes with mulitdentate ligands that form helical structures: (a) Lindoy, L. F.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1972**, 683. (b) Wester, D.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1975**, 74. (c) Lehn, J.-M.; Rigault, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095. (d) Williams, A. F.; Piquet, C.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1490.

(8) (a) Tandon, S. S.; Larkworthy, L. F. *J. Chem. Soc., Dalton Trans.* **1984**, 2389. (b) Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113. (c) Sheldrick, G. M.; Stotter, D. A. *J. Chem. Soc., Dalton Trans.* **1975**, 666. (d) Wiesemann, F.; Krebs, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1883. (e) Kastner, M. E.; Tang, K.; Birdsall, W. J. *Inorg. Chim. Acta* **1995**, *227*, 159. (f) Birdsall, W. J.; Long, D. P.; Smith, S. P. E.; Kastner, M. E.; Tang, K.; Kirk, C. *Polyhedron* **1994**, *13*, 2055. (g) Matt, D.; Huhn, M.; Fischer, J.; De Cian, A.; Kläui, W.; Tkatchenko, I.; Bonnet, M. C. *J. Chem. Soc., Dalton Trans.* **1993**, 1173. (h) Kwiatkowski, M.; Kwiatkowski, E.; Olechnowicz, A.; Ho, D. M.; Deutsch, E. *J. Chem. Soc., Dalton Trans.* **1990**, 2497.

(9) (a) Costes, J.-P.; Dahan, F.; Laurent, J.-P *Inorg. Chem.* **1985**, *24*, 1018. (b) Keturah, C.; Tasker, P. A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1057. (c) Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11357. (d) Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Nakamura, M.; Akiyama, S.; Kitagawa, S. *Inorg. Chem.* **1994**, *33*, 1284. (e) Costes, J.-P.; Serra, J.-F.; Kahan, F.; Laurent, J.-P. *Inorg. Chem.* **1986**, *25*, 2790. (f) Solans, X.; Aguiló, M.; Gleizes, A.; Faus, J.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, *29*, 775. (g) Scott, M. J.; Goddard, C. A.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 2558. (h) Vezzosi, I. M.; Zanoli, F. A.; Battaglia, L. P.; Corradi, A. B. *Inorg. Chim. Acta* **1985**, *105*, 13. (i) Goher, M. A. S.; Mak, T. C. W. *Inorg. Chim. Acta* **1985**, *99*, 223. (j) Mak, T. C. W.; Goher, M. A. S. *Inorg. Chim. Acta* **1986**, *115*, 17. Vezzoli, I. M.; Antolini, L. *Inorg. Chim. Acta* **1984**, *85*, 155.

This short bond length is consistent with a weak trans influence of O(4) on the Ni center. Moreover, short trans bond lengths have been documented in acyl Pd(II) and Pt(II) complexes.[11] Second, the C(22)−O(4) bond length of 1.260(4) Å is only slightly longer than that normally observed for a C═O bond (1.23 Å) but is still much shorter than the distance for a C−O single bond (1.43 Å).[12] This minor elongation of the C═O bond reflects the small decrease in the carbonyl bond order that occurs from the PhC═O- - -Ni interaction, which agrees with our FTIR measurements (see Experimental Section).

The major difference between the molecular structures of Ni**1** and Cu**1** is the orientation of the acetophenone groups containing O(3). In Ni**1**, this group is oriented such that the aryl ring is rotated 118.5° out of the coordination square plane. The acetyl oxygen O(3) is pointed away from the Ni(II) center and is hydrogen-bonded to one solvated water molecule (vide infra). However, in Cu**1**, where O(3) is coordinated to the Cu(II) center, this appended group is displaced only 48° from the plane of the pyridyl−diamide chelate. This structural difference has a significant influence on the assembly of the complexes in their respective crystal lattices.

Lattice Structures for Cu1 and Ni1. The Cu**1** complexes are arranged in coils that are aligned along the crystallographic *b* axis. These coils are stabilized by two π-stacking interactions with centroid−centroid distances of 3.92 and 4.45 Å. Adjacent coils interact via π-stacking interactions between the aryl rings of the apically coordinated acetophenone groups (i.e., the appended group containing O(3)) with a centroid−centroid distance of 3.74 Å. An open-framework lattice structure results (Figure 2 (right)) where the distance between adjacent set of stack rings is 7.74 Å. This space in the present structure of Cu**1** is filled with toluene molecules which come from the solvent used in crystallization.[13]

The Ni**1** complexes assemble into supramolecular columns that are positioned along the crystallographic *b* axis (Figure 3 (right)). The columns are stabilized by two hydrogen-bond networks that are on opposite sides of each column. The hydrogen-bond networks connect every other complex through repeated units consisting of two hydrogen-bonded water molecules. These pairs of water molecules in turn hydrogen-bond to O(3) of an appended acetophenone group from one complex and O(1) of a pyridyl diamidate chelate of an alternating complex. Additional columnar stabilization comes from stacking interactions between the coordination square planes of adjacent molecules where the average interplane distance is 3.75 Å. This arrangement of Ni**1** complexes results in two unique intraccolumnar Ni−Ni distances of 4.42 and 6.21 Å.

Summary. In this work, we have demonstrated that neutral transition metal complexes of 2,6-bis[(2-acetylphenyl)carbamoyl]pyridine can be used as building blocks to assemble varied supramolecular species in the solid state. The structures of complexes with this ligand are affected by the orientation of the acetophenone groups appended from the pyridyl diamidate chelates, which are controlled by their interactions with the metal centers. The modular design of 2,6-bis[(2-R-phenyl)carbamoyl]-pyridine (R = acetyl or carbamoyl) ligands allows for additional ligands to be generated having different appended groups. For example, we recently showed that appended groups containing hydrogen-bonded arrays can form complexes with helical structures.[5] These complexes also assemble into diverse lattice structures. Extension of this design concept to include appended redox-active groups and peptides will be reported in due course.

Acknowledgment. We thank NSF (Grant OSR-9255223), the NIH (Grant GM50781), and Kansas State University for financial support of this research.

Supporting Information Available: Tables of X-ray structural data for Ni**1** and Cu**1** (12 pages). Ordering information is given on any current masthead page.

IC9713184

---

(10) (a) Alyea, E. C.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1975**, *14*, 2491. (b) Wester, D.; Palenik, G. J. *J. Am. Chem. Soc.* **1975**, *96*, 7565. (c) Alcock, N. W.; Moore, P.; Reader, C. J.; Roe, S. M. *J. Chem. Soc., Dalton Trans.* **1988**, 2959. (d) Krüger, H.-J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955. (e) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *Organometallics* **1984**, *3*, 1003.

(11) (a) Wester, D.; Palenik, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 7565. (b) Roe, D. M.; Calvo, C.; Krishnamachari, N.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1975**, 125. (c) Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319. (d) Timken, M. D.; Sheldon, R. I.; Rohly, W. G.; Mertes, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4716. (e) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735.

(12) *CRC Handbook of Chemistry and Physics*, 53rd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1972; p F180.

(13) For examples of π-stacking interactions in supramolecular chemistry see: (a) Desiraju, G. D. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989. (b) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101 and references therein.