Inorg. Chem. **2003**, *42*, 6147–6152

Inorganic Chemistry

Article

Synthesis and Characterization of Two Polymorphic Crystalline Phases and an Amorphous Powder of Nickel(II) Bisimidazolate

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Received June 4, 2003

Nickel(II) bisimidazolate is polymorphic. Depending on the synthetic strategy adopted, two crystalline phases (α- and β-Ni(im)$_2$) or an amorphous material of the same composition can be prepared. The thermodynamically stable α-Ni(im)$_2$ phase, which can be prepared in water at elevated temperatures, contains a two-dimensional polymer (of nearly square meshes) with square-planar NiN$_4$ chromophores and exo-bidentate imidazolate ligands bridging nickel atoms that are ca. 5.73 Å apart. The β-Ni(im)$_2$ phase can be kinetically stabilized at lower temperatures, but the structural complexity and the lack of single crystals prevented its full structural characterization, even in the presence of an *indexed* powder diffraction pattern. The spectroscopic features of these crystalline phases are compared with those of the amorphous material.

Introduction

In a recent issue of *Inorganic Chemistry*, the synthesis and the crystal structures of polymeric iron, cobalt, and nickel pyrazolates appeared.[1] Because of the fortunate availability of good quality polycrystalline materials and the limited complexity of these systems, their crystal structures were solved and refined from X-ray powder diffraction (XRPD) data. Indeed, most of the known binary phases of M(pz)$_n$, M(im)$_n$, and M(pymo)$_n$[2] (Hpz = pyrazole, Him = imidazole, Hpymo = 2- or 4-hydroxypyrimidine) form only as powders, thus leaving XRPD as the only viable tool for structural characterization.[3] Ni(pz)$_2$ is polymorphic, since two structurally distinct phases containing the *same* one-dimensional motif built upon collinear chains of Ni^{2+} ions bridged by N,N′-exo-bidentate pyrazolates were found.[1] Polymorphic behavior is not uncommon in these kinds of materials[4] and, rather than being an annoying effect, was certainly helpful in recognizing subtle structural effects, as extensively discussed with respect to the (surprisingly) *pentamorphic* Cu(im)$_2$ species.[5]

During our continuous studies on this kind of system, which bear photomechanical,[6] magnetic,[7] anticorrosive,[8] or even antimicrobial[9] significance, we reported on the existence of an amorphous material of the composition Ni(im)$_2$,[10] as well as on the existence of a polycrystalline material of the same composition, which gave a rather complex, as yet uninterpreted, XRPD pattern. Aiming to better characterize this system, we resorted to different synthetic methods, which allowed us to prepare two crystalline Ni(im)$_2$ materials, hereafter labeled as the α- and β-polymorphs.

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10.1021/ic034619o CCC: $25.00

Results and Discussion

When aqueous or even organic solutions of $Ni(CH_3COO)_2$ are treated with excess imidazole and ammonia, a yellow precipitate of $Ni(im)_2$ formulation is typically obtained. Three different materials, hereafter labeled as α-, β-, or amorphous nickel bisimidazolate [*am*-$Ni(im)_2$], were identified from their room temperature (RT) XRPD traces and could be obtained as "monophasic" specimens only after proper tailoring of the syntheses; indeed, we have found that the actual experimental conditions such as solvent, temperature, concentrations, and, occasionally, stirring *all* affect the nature of the resulting materials.

For example, the use of *n*-butanol at reflux favors the precipitation of *am*-$Ni(im)_2$ while by refluxing the reactants in water, the highly crystalline α-phase is *selectively* formed. Amorphous, but analytically pure, $Ni(im)_2$ materials can also be obtained by employing $NiCl_2$ or $Ni(NO_3)_2$, instead of the nickel(II) acetate,[10] or by thermal decomposition at 260 °C of the $[Ni(acac)_2(im)_2]$ derivative (acac = acetylacetonate).[11] *am*-$Ni(im)_2$ can also be prepared by a two-step procedure, isolation of the polymeric $[Ni(Him)_2(im)(CH_3COO)]$ intermediate (as described in ref 10 or by "solventless" reaction of $Ni(CH_3COO)_2$ in molten pyrazole at ca. 120 °C), followed by its sublimation (and decompositon) at 200 °C with the aid of a heat gun.

In the reaction described above (nickel acetate/imidazole/ammonia), the β phase is recovered under aqueous conditions at room temperature, while single crystals of α-$Ni(im)_2$ could be obtained hydrothermally (150−180 °C, autogenous pressure). Thus, we can safely state that the formation of the amorphous material is a rather common occurrence, while the isolation of crystalline phases is a much rarer event.

The use of different starting materials, solvents, or procedures only slightly modified these results, in some cases affording mixtures of the two polycrystalline phases. For example, the use of $NiCl_2$ in water and of a Ni/Him ratio of 1/7, followed by addition of ammonia, allowed the isolation of a yellow material with a complex XRPD trace, now interpreted as a mixture of the α- and β-$Ni(im)_2$ phases (an intermediate, mononuclear species, formulated as $[Ni(im)_6]Cl_2$, was also detected).[10] If a strong base (NaOH) is used instead of aqueous ammonia, only the *am*-$Ni(im)_2$ material is recovered. Upon the use of different organic solvents (e.g., ethanol) and ammonia as base, no precipitation occurs and the solutions maintain the blue color typical of soluble hexacoordinated nickel(II) ions.

The analytical characterization of these materials suggested the existence of polymorphs (see Experimental Section), which were initially characterized by IR spectroscopy. The different materials possess slight differences in their absorption patterns, which are most prominent in the soft modes region (see Figure 1). As later confirmed by the XRPD analyses, the nonperiodic arrangement of the imidazolate ligands in *am*-$Ni(im)_2$ results in an IR absorption pattern somewhat similar to that of the "crystalline" β-phase (described below), while more significant differences (number of peaks and relative intensities) are observed for α-$Ni(im)_2$.

The availability of a single crystal of the α-$Ni(im)_2$ species from the hydrothermal synthesis allowed its structural characterization by conventional diffraction methods. In the crystals, nickel(II) ions, and N,N′-exo-bidentate imidazolate, ligands form two-dimensional arrays of nearly square meshes, stacked parallel to *c* (see Figure 2). The distance between adjacent metal atoms of ca. 5.73 Å is comparable with distances found in molecular species containing square-planar Ni(II) ions, such as the [Ni(5-methylimidazolate)(bis-(7-amino-4-methyl-5-aza-3-hepten-2-onato] cation,[12] but the rather small size of square-planar Ni(II) ions (Shannon's radius = 0.63 Å) means that the Ni−Ni distance is definitely lower than those found in polymeric compounds of similar nature (Cu···Cu in the 5.92−6.03 Å range).[5] The coordination about each metal is very close to square-planar (Ni−N 1.88 Å, trans N−Ni−N angles of 176.3°), as witnessed by the bright yellow color, typical for tetracoordinated d^8 Ni(II) ions of local D_{4h} symmetry.

Unfortunately, the *best* XRPD pattern of β-$Ni(im)_2$ in our hands (i.e., that of a pure β-phase with the narrowest diffraction peaks) still shows a structured background (reminiscent of partial contamination from amorphous material) and broad reflections (determined by an average crystal size near 450 Å), which prevented the full characterization of its structure by the ab initio XRPD technique, as we have done in the recent past on analogous species. However, based on the LeBail fit of the XRPD data shown in Figure 3, a common "reasonable" cell was independently determined by different methods (TREOR,[13] and TOPAS−R SVD[14]) and assigned orthorhombic symmetry ($a = 24.26$ Å, $b = 16.00$ Å, $c = 8.55$ Å, $V = 3319$ Å^3) with a tentative *Ibam* space group assignment based on systematic absences.

The apparent size of this unit cell, the broad features of the Bragg reflections, and the uncertainties on the space group assignment severely hindered our efforts to derive a satisfactory structural model. Thorough analysis by Patterson maps, direct methods, packing analysis, and particularly real space simulated annealing techniques[15] in *Ibam* or any of its proper subgroups (down to monoclinic symmetry) failed to provide a reasonable crystal structure.[16] For the sake of completeness, but equally unsuccessfully, other possible centering conditions or revised lattices were tested. Given the shape of the proposed cell, it is likely that, while *a*, *b*, and γ are known with extreme accuracy (the $hk0$, $h + k = 2n$ reflections are very clear), the third axis, *c*, is less certain, many peaks being possibly hidden by the large clustering already present at 2θ values near 30°. For comparison, the

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(15) As implemented in: TOPAS V2.0: General profile and structure analysis software for powder diffraction data. Bruker AXS, 2000, Karlsruhe, Germany.

(16) SHG measurements of powders of β-$Ni(im)_2$ (Kurtz-Perry powder technique, incident wavelength 1907 nm) gave null signals, thus suggesting, but not proving, its centrosymmetric nature.

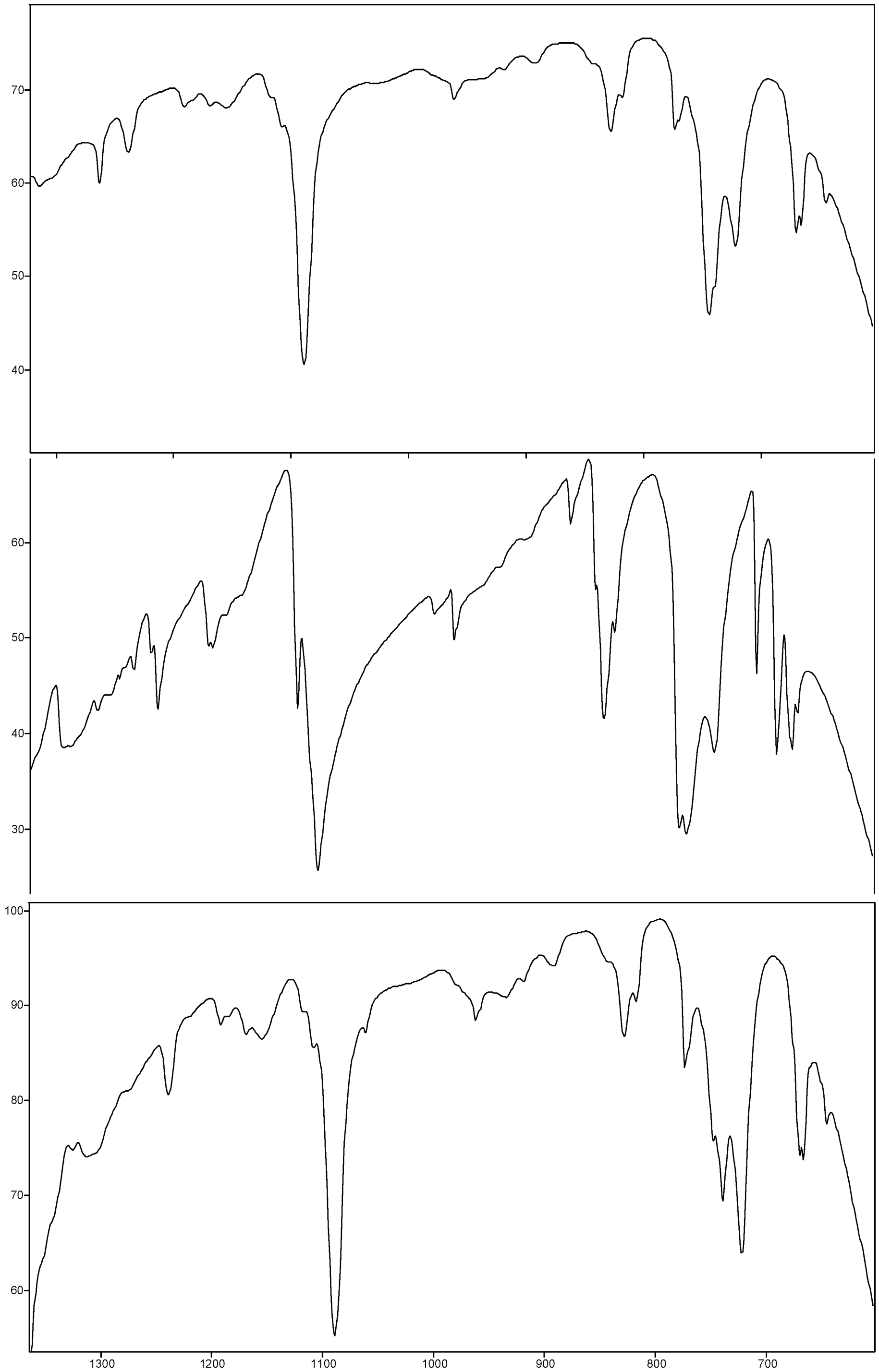

Figure 1. IR absorption spectra (Nujol mulls) in the 1300−600 cm^{-1} region, highlighting the spectral differences between *am*-, α-, and β-Ni(im)$_2$ (top to bottom).

XRPD traces of the three Ni(im)$_2$ forms are shown in Figure 4, from which the relative crystallinities of the three specimens can be appreciated. It can be seen that the approximate location of the very broad halos of *am*-Ni(im)$_2$ nearly match the most prominent peaks of the β-phase, thus suggesting a common structural motif that is not preserved in the crystalline α-Ni(im)$_2$ species. Roughly speaking, *it is likely that the amorphous material is a structural analogue* of β-Ni(im)$_2$, with particle size approaching 40 Å (rather than 450 Å), i.e., with coherent domains of less than *three* [β-Ni(im)$_2$] unit cell parameters.

The three different materials presented above possess different thermal stabilities. In agreement with the structural features described above, α-Ni(im)$_2$ is clearly a thermally robust polymer, since it was found to decompose only at $T > 515$ °C (peak value, onset near 480 °C), and is therefore comparable with cobalt and zinc (but not copper or iron) pyrazolates and pyrimidin-2-olates.[2] Thermogravimetric (TG) and differential scanning colorimetry (DSC) measurements showed that both the β-Ni(im)$_2$ and the *am*-Ni(im)$_2$ materials decompose above 450 °C (onsets near 410 °C) after a weight loss of ca. 5 and 6.5%, respectively, at $T < 220$ °C if freshly

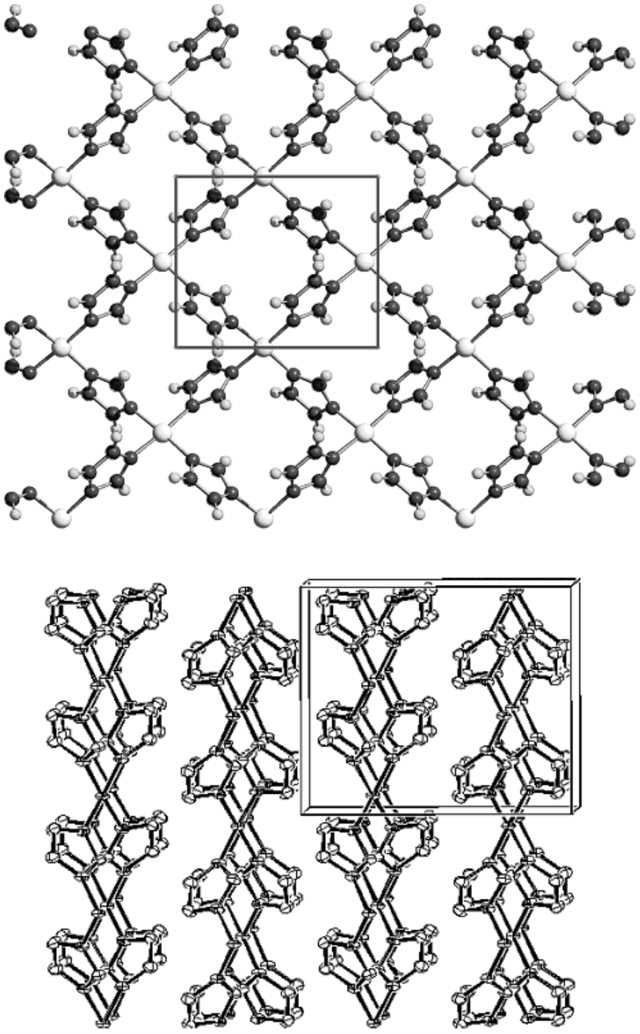

Figure 2. Top: Portion of the 2D polymeric layer of α-Ni(im)$_2$, viewed down (001). Horizontal axis is *a*. Large and small white spheres: nickel and hydrogen atoms, respectively. Carbon and nitrogen atoms in black. Relevant bond lengths (Å) and angles (deg) are Ni···Ni 5.728(1) Å, Ni−N 1.887(2) Å, N−Ni−N 90.53(6)°, 92.96(6)°, 176.32(6)° (Sluis, P. V. D.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194). Bottom: Packing of 2D layers, stacked along *c* (horizontal axis); H atoms omitted for clarity; thermal ellipsoids probability level, 50%.

prepared samples are employed. Notably, the thermal treatment of β-Ni(im)$_2$ and *am*-Ni(im)$_2$ did not improve their crystallinity, no significant changes of the (ex situ) XRPD traces obtained by heating just below their (rather high) decomposition temperatures could be observed, thus hampering efficient annealing of the sample or the observation of solid−solid transformations. In several previous works on similar coordination polymers, we have encountered fortunate cases where monotropic transitions led to the most stable phase by heating (either from hydrous species or anhydrous amorphous materials[2,17] or from other polycrystalline polymorphs).[4a] None of these transformations, however, was observed here.

The (continuous) loss of unknown material is not accompanied by significant peaks in the DSC traces and, together with the rather expanded lattice determined for β-Ni(im)$_2$ (assuming $Z = 16$), is consistent with a nanoporous material hosting solvent molecules in a nonstoichiometric fashion.[18] This effect seems to be further augmented in the amorphous powders, where an even larger number of guest molecules are present. Again, the thermal behavior and, particularly, the shapes of the DSC traces in the whole range examined (50−550 °C) favor the interpretation of the *am*-Ni(im)$_2$ as if it were an extremely disordered, but structurally analogous, β-Ni(im)$_2$ phase. Although high decomposition temperatures have previously been reported for late transition metal pyrimidinolates,[2] this thermal stability is unusually high for a hybrid inorganic−organic material,[19] suggesting that hybrid materials based on imidazolates or related molecules may offer thermal stability comparable to or even higher than carboxylates.

Conclusions

This paper reports on the polymorphic nature of nickel(II) bis-imidazolate, whose "supramolecular" structures (in both crystalline phases and in the amorphous material) depend on the synthetic method used. Monophasic samples could be obtained by tailored syntheses only after recognition that subtle effects of solvent, temperature, pressure, stirring, and other experimental conditions are at work. Efforts in the characterization of the β phase from XRPD have only led to an indexed diffraction pattern with a tentative space group assignment. Work can be anticipated in the direction of further structural and spectroscopic characterization (e.g., solid-state cross polarization magic angle spinning NMR studies), to highlight the anticipated supramolecular features of the β-phase.

The results presented above add important structural information to the rich and versatile structural chemistry of metal diazolates. While "conventional" local stereochemistry is maintained, the tendency of imidazolates to afford highly unpredictable, *variable*, connectivity and overall crystal topology is further illustrated,[20] a trend rarely shared among samples of similar stoichiometry.

Experimental Section

General. DSC and TG analyses were performed with the aid of Perkin-Elmer series 7 instruments under dinitrogen atmosphere at a 20° min^{-1} heating rate. IR spectra were recorded (Nujol mulls) on a Nicolet Avatar 360 FTIR spectrometer. Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory of the University of Milan.

Synthesis of Amorphous Ni(im)$_2$. To 40 mL of a *n*-butanol solution of imidazole (1.17 g, 17 mmol), solid nickel(II) acetate (500 mg, 2.83 mmol) was added (Ni/Him ca. 1:6). Heating the resulting deep-blue solution at reflux (ca. 120 °C) for 2 h resulted in the slow precipitation of a yellow solid. After cooling at RT, the solid was filtered, washed with butanol (2 × 20 mL) and acetone (3 × 30 mL), and then dried in a vacuum. Anal. Calcd for $C_6H_6N_4$-

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(17) Masciocchi, N.; Corradi, E.; Moret, M.; Ardizzoia, G. A.; Maspero, A.; La Monica, G.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 5648.

(18) Occasionally we measured a low analytical nitrogen content, possibly resulting from (partial) solvent contamination.

(19) Forster, P. M.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2002**, *41*, 457.

(20) For a recent example, see: Masciocchi, N.; Ardizzoia, G. A.; Brenna, S.; Castelli, F.; Galli, S.; Maspero, A.; Sironi, A. *Chem. Commun.* **2003**, 2018.

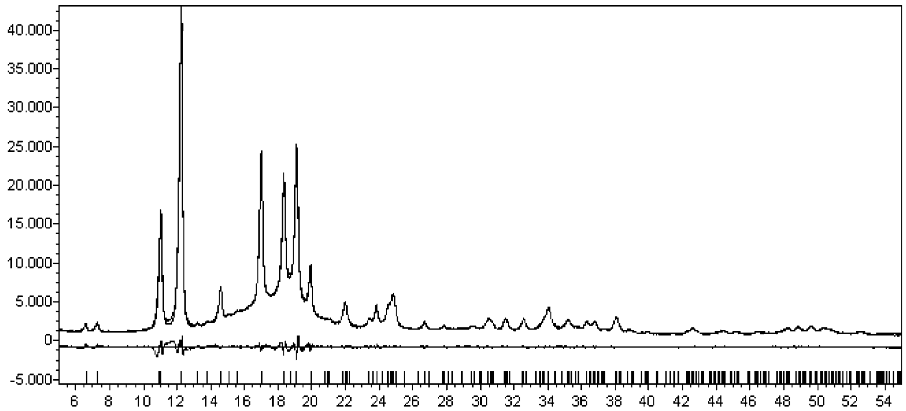

Figure 3. Plot of the XRPD pattern for β-Ni(im)$_2$. The experimental trace has been fitted by the LeBail method and the orthorhombic *Ibam* unit cell reported in the text. Difference plot and peak markers are at the bottom.

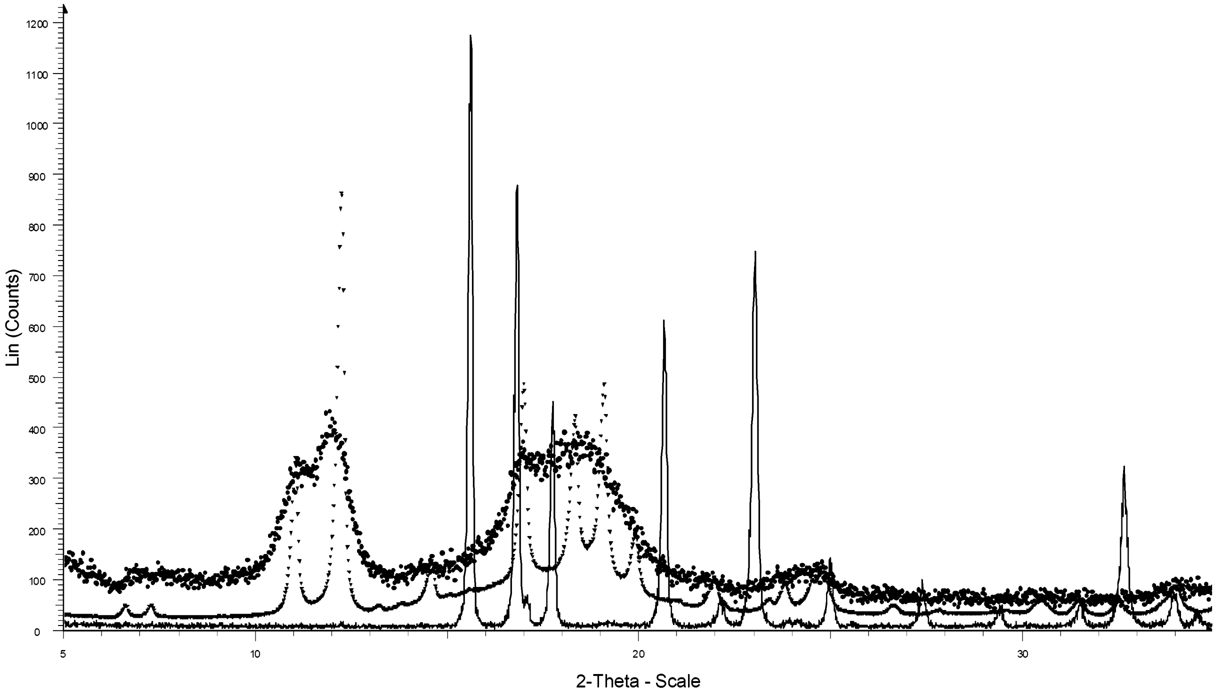

Figure 4. Plot of the low-angle section of the XRPD traces for Ni(im)$_2$. The sharp peaks (solid line) belong to the α-Ni(im)$_2$, while the featureless trace (top) refers to the amorphous material. The β-Ni(im)$_2$ phase, of nonnegligible, though imperfect, crystallinity (▼) shows broad Bragg peaks (as shown also in Figure 3).

Ni:[21] C, 37.31; H, 3.11; N, 29.01. Found: C, 38.15; H, 3.50; N, 27.15. Yield: 46%. Similar results were obtained on starting from NiCl$_2$ of Ni(NO$_3$)$_2$.

Synthesis of the α-Phase. This preparation exactly matches that of the amorphous material described above, except *water* replaces *butanol* as the solvent and the reflux temperature is 100 °C. After cooling at RT, the solid was filtered, washed with water (2 × 20 mL) and acetone (3 × 30 mL), and then dried in a vacuum. Anal. Calcd for C$_6$H$_6$N$_4$Ni: C, 37.31; H, 3.11; N, 29.01. Found: C, 37.47; H, 3.23; N, 28.95. Yield: 45%. Highly crystalline material, from which the sample studied by single-crystal X-ray diffraction was chosen, was obtained hydrothermally from the reaction of 0.25 g of Ni(OH)$_2$, 3.00 g of imidazole, and 5.1 g of H$_2$O at 180 °C in a 23-mL Teflon-lined autoclave. After the reaction proceeded for 3 days, the autoclave was cooled in air and the products were recovered by filtration and rinsed briefly with water. Yellow, elongated cubes of α-Ni(im)$_2$ were present, along with recrystallized imidazole. Reactions carried out with less imidazole, or at 150 °C, produced similar results, although unreacted Ni(OH)$_2$ was often present.

Synthesis of the β-phase. To 50 mL of an aqueous solution of nickel(II) acetate (500 mg, 2.83 mmol), solid imidazole was added (1.17 g, 17 mmol; Ni/Him ca. 1:6). To the resulting deep-blue solution, aqueous NH$_3$ (36% w/w, 3 mL) was then introduced. After the solution was allowed to stand for about 30 min, a yellow precipitate appeared over the course of 5 h, after which the rection was complete. Note that typically while stirring, mixtures of amorphous and polycrystalline materials are obtained. The yellow powders were then filtered, washed with water (4 × 30 mL) and acetone (2 × 30 mL), and then dried in a vacuum. Anal. Calcd for C$_6$H$_6$N$_4$Ni: C, 37.31; H, 3.11; N, 29.01. Found: C, 38.17; H, 3.48; N, 27.51. Yield: 24%. That this phase, in the absence of a reliable

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(21) A better matching between calculated and observed analytical contents can be envisaged for a nonstoichiometric material, close to the Ni(im)$_2\cdot{}^1/_8$ ButOH formulation, C$_{6.5}$H$_{7.25}$N$_4$NiO$_{0.125}$: Anal. Calcd (Found) C, 38.63 (38.15); H, 3.61 (3.50); N, 27.0 (27.15), which also accounts for ca. 5% weight loss by moderate heating. Similar considerations apply to the analytical content determined for the β-phase.

structural model, is indeed a polymorph of α-Ni(im)$_2$ is manifested by the convergence of a number of analytical data such as elemental analysis, thermal stability (proven by TG and DSC), absence of IR features attributable to extra ligands, and yellow color (typical for square planar nickel(ii) ions).

Crystallography. XRPD data were collected on a Bruker AXS D8 θ:θ diffractometer equipped with two sets of parallel (Soller) slits, a curved graphite monochromator in the diffracted beam, and Cu Kα radiation. The specimens were carefully layered on a quartz monocrystal (zero background plate) with the aid of an amyl acetate slurry. Indexing of the XRPD trace of *pure* β-Ni(im)$_2$ by TREOR[13] gave M(19) = 17, F(19) = 34 (0.008, 64), and the lattice parameters quoted below.

Conventional single-crystal analysis was performed on α-Ni(im)$_2$ using a Siemens SMART CCD diffractometer equipped with Mo Kα radiation (0.71073 Å). A small yellow single crystal was selected under a polarizing microscope, glued to a glass fiber, and diffraction data were collected using 90 s frames at RT. The structure was solved using direct methods and refined against $|F^2|$ using the SHELX-TL suite.[22] Hydrogen atoms were located in the Fourier map and refined with isotropic temperature factors fixed to 1.2 times that of the carbon atom to which they were bound. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as number 211709. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Rd., Cambridge CB21EZ, U.K. (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystal Data for α-Ni(im)$_2$. $C_6H_6N_4Ni$, fw 192.87 g mol^{-1}; orthorhombic, *Pbcn*, $a = 7.388(3)$ Å, $b = 8.755(4)$ Å, $c = 10.489(4)$ Å, $V = 678.4(5)$ Å^3; $Z = 4$; $D_{calc} = 1.888$ g cm^{-3}; R1 and wR2 0.0249, 0.0519 respectively, for 60 parameters and 819 unique data collected in the $3.61 < 2\theta < 28.26°$ range (Mo Kα radiation); R(int) = 0.0615, $\mu = 2.760$ mm^{-1}.

Crystal Data for β-Ni(im)$_2$. $C_6H_6N_4Ni$, fw 192.87 g mol^{-1}; orthorhombic, *Ibam*, $a = 24.26$ Å, $b = 16.00$ Å, $c = 8.55$ Å, $V = 3319$ Å^3; $Z = 16$; $D_{calc} = 1.544$ g cm^{-3}. No structural model available (see text).

Acknowledgment. This work was supported by the Chamber of Commerce of Como, the University of Insubria (Progetto di Ateneo Sistemi Poliazotati), and the MRL Program of the National Science Foundation under Award No. DMR00-80034. We thank Dr. A. Kern (Bruker AXS) for providing the β-version of the TOPAS-R software, the Dipartimento di Chimica Strutturale e Stereochimica Inorganica (University of Milano) for the use of equipment, G. A. Ardizzoia and A. Maspero (University of Insubria) and A. R. Burbank for helpful discussions.

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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[22] Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.