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Polymerization of $NiBr_2[P(CH_2CH_2CN)_3]_2$: a "Triply-Specific" Solid-State Reaction

Sir:

The reactivity of coordination complexes in the solid state has been little explored.[1] Because of the rather stringent directional requirements, the most interesting solid-state reactions of coordination complexes are undoubtedly polymerization processes.[2] Studies of the potentially topochemical polyreactions of monomeric coordination complexes, by analogy with other inorganic and organic systems,[3] can thus lead to an understanding of synthetic, dimensional, and symmetry-based criteria for the solid-state preparation of crystalline coordination polymers. Square-planar, red monomeric complexes of the type NiX_2CEP_2 (X = Cl, Br; CEP = $P(CH_2CH_2CN)_3$) are obtained as kinetic products at room temperature, and have been shown to undergo polymerization reactions in solution or in the solid state[4] to yield highly crystalline, blue, octahedral coordination polymers, insoluble in organic solvents and decomposed slowly by water. For $NiBr_2CEP_2$,[4a] we have examined the polymerization in acetone solution and in single crystals (Scheme I). Further, we find that the reaction is characterized by (a) product specificity, (b) stereospecificity, leading to formation of linear polymer, (c) "crystallographic specificity", and (d) highly anisotropic "front motion" through individual single crystals.

When either an acetone solution of monomer or individual single crystals of monomer moist with acetone are allowed to polymerize at various temperatures, the blue polymeric product is *always* contaminated with a green powder (~5%), which has defied characterization.[5] However, when dry individual single crystals are allowed to polymerize at temperatures below ~130 °C, only the blue polymeric product is formed. Thus, this reaction is readily product specific *only* in the solid state. While the rate of polymerization is slower (~1/6) in the solid state at room temperature and below, the rates are about equal at 80 °C, and the solid-state transformation is increasingly faster above the latter temperature.

To determine the probable geometrical course of the reaction, we have carried out complete three-dimensional x-ray structure analyses on single crystals of monomer and polymer grown from solutions of monomer:

monomer, orthorhombic,	→	polymer, monoclinic,
Pbca		$B2_1/c$[6]
$a = 13.169$, $b = 22.004$,		$a = 13.907$, $b = 21.055$,
$c = 8.487$ Å		$c = 8.496$ Å
$V = 2459.3$ Å^3		$\beta = 97.46°$, $V = 2466.7$ Å^3
R (all 1721 data) = 0.075		R (2127 data; $I > 2\sigma(I)$) = 0.031

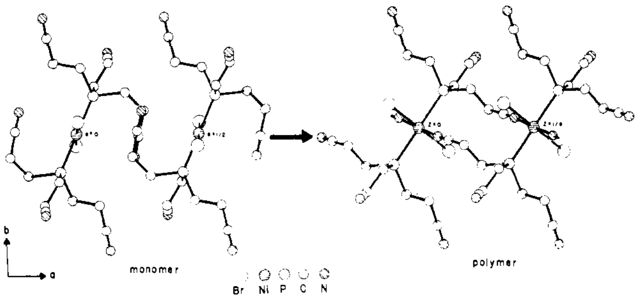
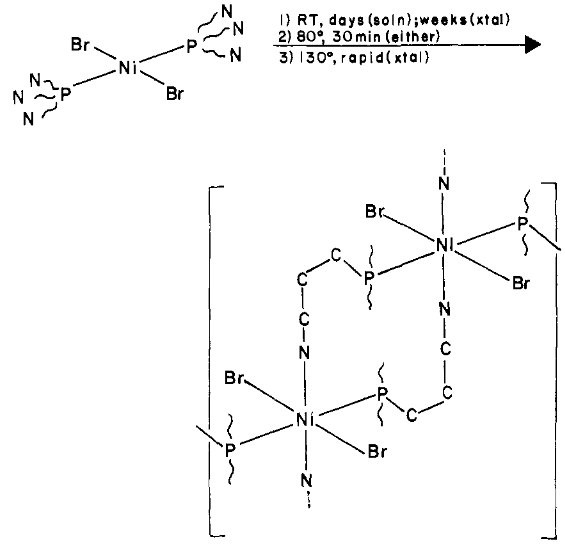


Figure 1. Pairs of square-planar reactant and octahedral product molecules viewed normal to the *ab* plane of the respective unit cells. Polymerization occurs in *ac* planes perpendicular to this view. No intermolecular bonds are present in the pure reactant phase.

Scheme I



In both the monomer and polymer phases, Ni atoms occupy the centers of symmetry (0,0,0), (½,0,½), (0,½,½), (½,½,0). The crystal structure of the product phase shows that only Ni complexes at (0,0,0) and (½,0,½) have reacted to form part of a repeating polymer chain, while Ni complexes at (½,½,0) and (1,½,½) have reacted to form a second polymer chain. This is a significant observation: since it can be shown that the solid-state reaction pathway is identical with that suggested by this structural study of reactant and solution-grown product (vide infra), we conclude that polymerization occurs only in specific *ac* planes in the crystal. Such a "layer-by-layer" reaction precludes cross-linking of polymer chains and may be expected to lead to the formation of rigorously linear polymer, as well as highly oriented crystalline product.

At temperatures >20 °C the crystals do not show well-defined front motion as the reaction proceeds; hence we have confined our initial studies of reacting crystals to temperatures near −5 °C. Crystals of the monomer are well-defined, wine-red, nearly opaque prisms, elongated along [001], with well-defined {010}, {100}, (111), ($\bar{1}$11), ($\bar{1}1\bar{1}$), and (11$\bar{1}$) faces. Reaction *always* begins on a single (100) face or on a pair of (100) faces; the reaction proceeds (over a 6-month period), with the first significant observation being a thin blue coloration of the entire (100) face. A very distinct blue reaction front then moves across the crystal, virtually parallel to the (100) face. X-ray diffraction studies of partially reacted crystals (5–60% complete) show that the reaction is topotactic,[7] and, further, that (a^*_{reactant}, a^*_{product}) and (b^*_{reactant}, b^*_{product}) are aligned. The c^* axis in the monoclinic product lies ~7.5° away from the c^* axis of the reactant phase (note that in the transformation from orthorhombic to monoclinic, β changes from

90 to 97.5°). However, for crystals where the solid-state reaction begins on a single (100) face, only one *new* c^* axis is observed, i.e., *twinning about* $[001]_{reactant}$ *does not occur* to a detectable extent. Thus, the first product which appears on a crystal face appears to determine, in a crystallographically specific manner, unit cell orientation in the product. Further, the established topotaxy demonstrates unequivocally that the phase of the solution-grown polymer crystals is identical with that formed by the solid-state reaction. We note that this strictly linear polymerization process appears to be different from other carefully studied examples,[3] (including the polymerization of $NiCl_2CEP_2$),[8] in which the polymer appears first in a solid solution with monomer, and crystallization/orientation of product may be effected via annealing.

The relationship between pairs of reactant and product molecules, chosen so as to be representative of the overall polymerization reaction, is presented in Figure 1, which demonstrates the spatial similarities between reactant and product. The reaction mechanism qualitatively involves polymerization in crystal *ac* planes, followed by repacking of the polymer along the *b* direction; further, it may be shown that motion of the centroids of the individual complexes during reaction defines the product *a* axis (and β angle of 97.5°). The direction of slowest front motion (i.e., along the *a* direction) is consistent with the observation that only the *a* axis of the reactant crystal must reorient to form the product pseudomorph.

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Supplementary Material Available: Atomic coordinates for $NiBr_2[P(CH_2CH_2CN)_3]_2$ monomer and polymer (2 pages). Ordering information is given on any current masthead page.

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(6) Coordinates: $\pm(x,y,z)$; $\pm(x,\frac{1}{2}-y,\frac{1}{2}+z)$; $\pm(\frac{1}{2}+x,y,\frac{1}{2}+z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$.
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Vibrational Circular Dichroism in Amino Acids and Peptides. 1. Alanine

Sir:

We report the first observation of vibrational circular dichroism (VCD) of an amino acid, alanine, which is both the simplest optically active amino acid and the smallest molecule for which vibrational optical activity has been reported. Previous VCD observations[1-4] have also reported signals in this region; however, for molecules containing more than one type of C–H bond, only tentative vibrational assignments have been made.[3] In alanine, the vibrational stretching modes of all four hydrogen atoms attached to carbon can be assigned without ambiguity from previous theoretical and experimental work[5-7] (see Table I). With the aid of these assignments, an interpretation of the VCD of alanine, based on a chiral perturbation of the degenerate asymmetric methyl stretching vibrations, is proposed. Degenerate methyl stretching modes in VCD may eventually prove to be sensitive probes of molecular configuration. Analogous behavior for the degenerate asymmetric methyl deformation modes as configurational probes in Raman optical activity have been reported by Hug et al.[8] and Barron.[9-11]

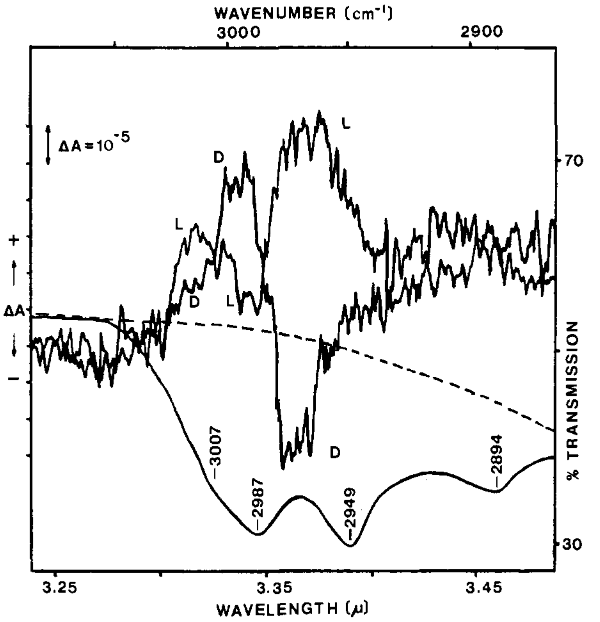

Figure 1. VCD and transmission spectra of saturated solutions of (*R*)-(−)-alanine-d_3 (D) and (*S*)-(+)-alanine-d_3 (L) in D_2O at 0.500-mm path length. The dashed line represents the D_2O background transmission spectrum; spectral band pass is ~17 cm⁻¹ at 2950 cm⁻¹. The individual VCD scans required a time of 4 h.

The instrument used in the VCD measurements reported here is similar to a unit described earlier.[3] The optical train consists of a 1000-W tungsten-halogen lamp (Sylvania 1000 Q/CL), a mechanical light chopper, a monochromator (Spex 1702), a $LiIO_3$ polarizer (Interactive Radiation, Inc.), a ZnSe photoelastic modulator,[12] a variable-path-length sample cell equipped with CaF_2 windows, and an InSb detector (Spectronix, Inc.). The electronic system for signal processing uses a variable-gain amplifier circuit and the three lock-in amplifier technique described earlier.[3] The VCD spectrum of camphor dissolved in CCl_4 has been obtained with comparable quality and signal magnitude using similar instrumental settings to previously published results.[3] In the present study, however, low transmission of the D_2O solutions necessitated long time constants to reduce the noise level. A high level of instrument stability allows spectra to be scanned reliably in times as long as 10 h.

Samples of D-alanine (Aldrich Chemical Co.), $[\alpha]^{25}{}_D$ −14° (*c* 10, 6 N HCl), and L-alanine (Calbiochem), $[\alpha]^{21}{}_D$ +14.5° (*c* 5.8, 1 N HCl), were dissolved in D_2O and boiled to dryness in vacuo to deuterate the amine function. The NH_3^+ vibrations, which otherwise may interfere with the C–H stretching modes, are shifted to ~2200 cm⁻¹; furthermore the amount of H_2O and HDO produced by the proton exchange was re-