

that the interlayer HPO_4^{2-} ions adjacent to the exchange $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions are much more subject to steric hindrance than those adjacent to the exchanged $\text{C}_6\text{H}_5\text{OPO}_3^{2-}$ ions. This may result in the exchange of one-fourth rather than half of the interlayer HPO_4^{2-} ions with $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions. If the steric factor is predominant in determining the exchanged amount, it is reasonable to conclude that the exchanged $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions can be ordered.

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Registry No. $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, 13772-31-1; $\text{C}_6\text{H}_5\text{PO}_3^{2-}$, 16486-11-6; HPO_4^{2-} , 14066-19-4; $\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.5}(\text{HPO}_4)_{1.5} \cdot 2\text{H}_2\text{O}$, 76900-20-4.

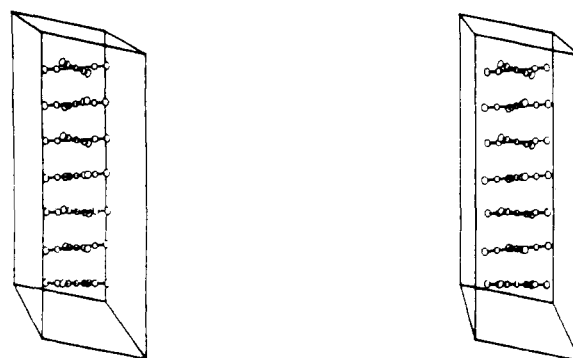


Figure 1. Stereoview into the narrow face (110) of a typical $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ crystal, showing a column of anions relative to the crystal morphology.

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Single-Crystal Polarized Specular-Reflectance Spectra of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. A One-Dimensional Solid-State Effect

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Square-planar complexes of d^8 transition-metal ions have been of interest recently because of their unusual spectral and electrical properties.¹ Tetracyanoplatinates are especially dramatic examples, due to the brilliant colors of divalent salts²⁻⁴ and the metallic characteristics of mixed-valence salts,^{1,5,6} grown from colorless aqueous solutions. Tetracyanopalladate(II) salts have shown effects similar to those of the platinum(II) salts except the transitions are limited to the ultraviolet region and thus are not as noticeable.^{2,7} Doubt has been expressed, however, about such a "solid-state effect" being present in tetracyanonickelates.² Polarized absorbance studies of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and other tetracyanonickelates⁸ have not observed solid-state effects of the same type found in the tetracyanoplatinates(II) and -palladates(II). A recent polarized specular reflection study involving $\text{BaK}_2[\text{Ni}(\text{C}-\text{N})_4]_2 \cdot 4\text{H}_2\text{O}$ ⁹ has shown that a strong solid-state effect is indeed observable in a tetracyanonickelate(II) salt. The purpose of this paper is to present polarized specular-reflectance spectra

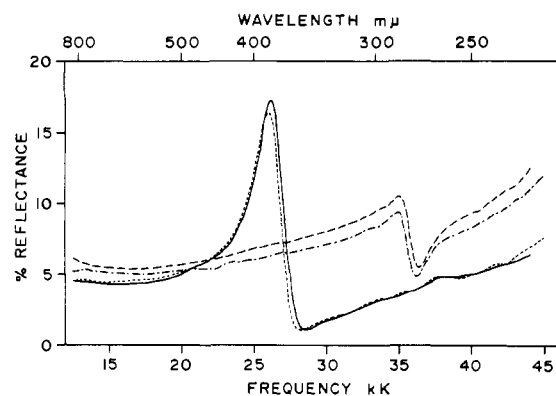


Figure 2. Polarized specular reflectance spectra of the (120) and (110) faces of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. Parallel to c axis (out-of-plane): ---, (120); —, (110). Perpendicular to c axis (in-plane): - · - ·, (120); · · · ·, (110).

of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ which clearly demonstrate a strong (>7000) solid-state band and to compare this band with the solid-state bands reported for the isomorphous analogues $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. The trend observed supports the view that the same effect is operating in this tetracyanonickelate as in the tetracyanopalladate and -platinates salts.

Experimental Section

$\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ was prepared by the addition of excess BaCl_2 to $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, followed by evaporation and recrystallization. Slow evaporation of aqueous solutions of this product yielded well-formed clear yellow-orange crystals $\sim 1 \times 0.6 \times 2$ mm, with highly planar surfaces suitable for specular reflection. The crystals were maintained in an atmosphere of 84% relative humidity at room temperature to avoid loss of waters of hydration.

Anal. Calcd for $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$: Ba, 36.90; Ni, 15.80; C, 12.90; N, 15.10; O, 17.20; H, 2.20. Found: Ba, 36.73; Ni, 16.01; C, 12.78; N, 15.10; O, 17.02; H, 2.19; K, <0.02 .¹⁰

Polarized reflection spectra were obtained on a microspectrophotometer described in detail elsewhere.¹¹ Measurements were made relative to an aluminum mirror and corrected for aluminum reflectivity.¹² Spectra were obtained with the electric vector aligned parallel (\parallel) and perpendicular (\perp) to the elongation axis of the crystal, on the (120) and (110) faces of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. For each face, measured on different sets of crystals, six of the best reflection spectra were averaged.¹³ The reflectance data were transformed into absorption-equivalent spectra through Kramers-Kronig analyses.¹⁴ The

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- (13) The "best" spectra were those with simultaneously the highest maxima and lowest minima, thus avoiding discrepancies due to poor crystal quality or misalignment of either the crystal or mirror.

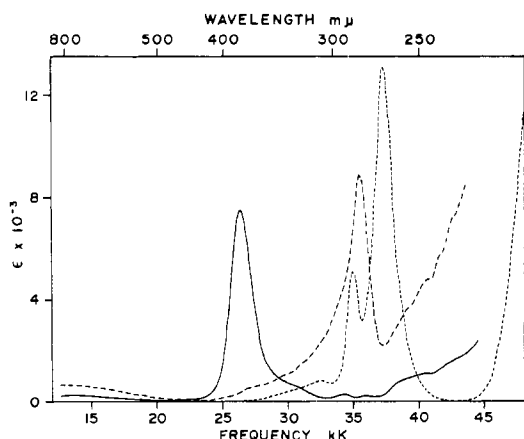


Figure 3. Polarized absorption spectra of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$: —, out-of-plane; --, in-plane on the (110) face; ---, solution spectrum of $\text{Ni}(\text{CN})_4^{2-}$.

close correspondence of the \parallel and \perp directions with the out-of-plane and in-plane molecular directions, respectively (see Figure 1), allowed the transformed crystal \perp and \parallel spectra to be identified as in-plane and out-of-plane spectra, respectively. These spectra were adjusted for solution equivalency by multiplying the \parallel spectrum by $1/3$ and the \perp spectrum by $2/3$ to account for the fixed nature of the crystalline vs. the random orientation of the solvated species.

Results and Discussion

$\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ is known to be monoclinic with 45° staggered, stacked planes having normals $4^\circ 46'$ from the c axis.¹⁵ We have determined, through correlating an $h,k,0$ Weissenberg photo with the crystal face orientations, that the elongated faces are (120) and (110). Figure 1 presents a stereoview of the crystal morphology with a single column of stacked $\text{Ni}(\text{CN})_4^{2-}$ planes, viewed normal to the (110) plane. It is evident, from Figure 1, that the two faces present similar orientations of molecular planes and that one should expect similar spectra, as opposed to $\text{CsKNi}(\text{CN})_4$ where planar orientations and thus spectra observed from adjacent faces are distinctly different.^{11,16} The polarized specular reflectance from the (110) and (120) faces are shown in Figure 2, and, as expected, the corresponding spectra on each face are nearly identical. The greater reflectivity from the (110) face appears to be primarily due to the better surface quality of the crystals used for those spectra. The slight tilt of the normals from the c axis does not affect the apparent dichroism of the crystal, as is evident from the reflection spectra, where the large \parallel reflection at $26.0 \times 10^3 \text{ cm}^{-1}$ shows no component in the \perp direction.

The absorption-equivalent spectra, transformed from the reflection data on the (110) face, are shown in Figure 3 with the solution absorption spectrum of $\text{Ni}(\text{CN})_4^{2-}$. The band at $26.1 \times 10^3 \text{ cm}^{-1}$ with an ϵ_{max} of 7130 in a region of no allowed solution transitions is evidence of a significant solid-state effect. This band, incidentally, seems to have been the cause of the high-energy opacity of the $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ crystals in absorption studies.⁸

Since $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ with a nickel-nickel distance of 3.36 \AA is isomorphous with $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ (Pd-Pd = 3.37 \AA)¹⁷ and $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ (Pt-Pt = 3.32 \AA),¹⁸ it would be interesting to compare the solid-state bands in the three compounds. Since the degree of spectral shift has been recognized

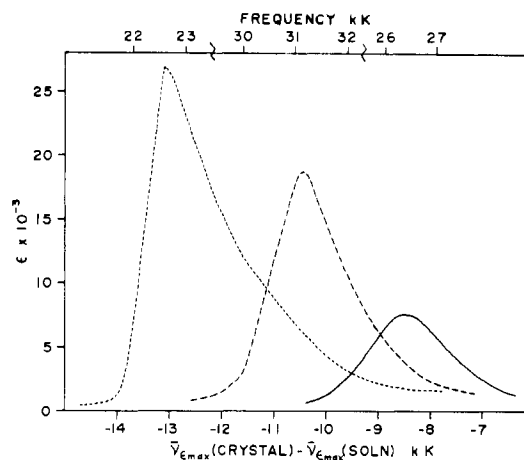


Figure 4. Out-of-plane polarized absorption spectra of solid-state band regions: $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, —; $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, --; $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, ---. The peak maxima are located according to the spectral shift upon crystallization. Pd and Pt data are from ref 7 and 9.

as an indication of the extent of solid-state perturbation, the bands will be positioned according to spectral shift upon crystallization. The solution origin of the solid-state band in $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ has been found to be $\sim 41.6 \times 10^3 \text{ cm}^{-1}$,⁷ for a spectral shift upon crystallization of $\sim -10.4 \times 10^3 \text{ cm}^{-1}$. From polarization evidence on the unstacked (and unperturbed) tetracyanonickelate salt $\text{CsKNi}(\text{CN})_4$ ¹¹ and following the results of a series of nickel glyoximes¹⁹ and a series of $\text{Pd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ salts,⁷ the out-of-plane polarized solution band at $34.9 \times 10^3 \text{ cm}^{-1}$, which disappears upon crystallization, may be tentatively identified as the origin of the solid-state band in $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, which would give a spectral shift of $-8.1 \times 10^3 \text{ cm}^{-1}$. The solution origin of the solid-state band in $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ has been identified as being the peak at $35.7 \times 10^3 \text{ cm}^{-1}$,⁷ for a spectral shift of $-13.1 \times 10^3 \text{ cm}^{-1}$ upon crystallization. These three solid-state bands are plotted in Figure 4 with their maxima positioned according to these spectral shifts (lower abscissa). The individual bands are plotted as absorption coefficient vs. wavenumber (upper abscissa). The spectral shape and degree of shift in the nickel complex is consistent with the trend which appears to have been established in the platinum and palladium complexes, indicating that the solid-state effect in the three complexes is of a similar nature.

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Kinetic Study of the Zinc Ion Catalyzed Hydrolysis of *O*-Acetyl-2-pyridinecarboxaldoxime

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A number of studies on metal ion catalyzed hydrolysis of esters have been reported and have provided valuable information on the roles of metal ions in hydrolytic metallo-enzymes.^{1,2} Metal ions are proposed to serve as superacids

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