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Crystal Structure and Spectra of Cesium Potassium Tetracyanonickelate(2−)

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Crystals of anhydrous cesium potassium tetracyanonickelate(2−) are triclinic, of space group $P\bar{1}$, with $a = 7.421$ (2) Å, $b = 8.626$ (4) Å, $c = 9.364$ (3) Å, $\alpha = 60.64$ (3)°, $\beta = 70.88$ (3)°, $\gamma = 70.88$ (3)°, and $Z = 2$. The final R factor is 6.1% for 1512 independent single-crystal X-ray diffractometer data. The structure consists of columns of square-planar $Ni(CN)_4^{2-}$ ions (average distances: Ni–C = 1.86 (1) Å, C–N = 1.15 (1) Å), with the column axis defined by Ni atoms spaced 4.30 Å apart. Each column is well separated from other columns by cations in six- (K^+) and ten-coordinate (Cs^+) cavities bounded by cyano ligands in which the nitrogen atoms display significant polar flattening. Two independent centrosymmetric complex anions stack alternately along each column, with the Ni(1) and Ni(2) square planes tilted ca. 36° with respect to the column axis and ca. 10° with respect to one another. Moreover, alternate square planes are staggered by a rotation about each normal of 35.5°. Reflectance measurements are consistent with the existence of noninteracting $Ni(CN)_4^{2-}$ ions in solid $CsKNi(CN)_4$, for they yield a spectrum which is essentially identical with that obtained from solution.

Introduction

Interest in square-planar complexes of d^8 transition-metal ions stems in part from their unusual solid-state spectral and electrical properties.[2-4] One example of a "solid-state effect" is the striking solution-to-solid color change observed in tetracyanoplatinates, which has been attributed to interplanar electronic interactions arising from the relatively close stacking (~3.3 Å) of the $Pt(CN)_4^{2-}$ planes.[3,5,6] In tetracyanoplatinates of mixed oxidation state, which display metallic luster and electrical conductivity, even closer stacking (~2.9 Å) is observed.[7-10]

A prominent spectral feature in crystalline tetracyanoplatinates and -palladates that contain small cations, e.g., $BaPt(CN)_4{\cdot}4H_2O$ and $BaPd(CN)_4{\cdot}4H_2O$, is a band which develops in the long-wavelength region of the charge-transfer spectrum.[6,11] The spectra of analogous nickel salts have not been as extensively studied, although solid-state effects are observed in $BaNi(CN)_4{\cdot}4H_2O$[12,13] and $K_2Ba[Ni(CN)_4]_2{\cdot}4H_2O$.[6] The relationships between solid-state effects, cation size, and the presence or absence of molecules of crystallization are also not well understood.

We have therefore undertaken a series of spectral and structural studies of tetracyanonickelate(2−) salts, the first of which is reported here for $CsKNi(CN)_4$. This is the first reported small-cation salt which has essentially identical solid and solution charge-transfer spectra.

Experimental Section

Crystal Preparation and Analysis. Single crystals of $CsKNi(CN)_4$ were prepared by slow evaporation of an aqueous solution of $Cs_2Ni(CN)_4{\cdot}4H_2O$ and $K_2Ni(CN)_4{\cdot}3H_2O$ in a 1:2 molar ratio. The solution was evaporated to near dryness and then the residue stored at 25 °C in a relative humidity of 55%. The desired clear crystals were harvested from a mixture of clear and opaque crystals. $K_2Ni(CN)_4{\cdot}3H_2O$ was recrystallized from commercially available material (K & K Laboratories), while $Cs_2Ni(CN)_4{\cdot}H_2O$ was prepared from an aqueous solution of Cs_2SO_4 and $BaNi(CN)_4{\cdot}4H_2O$. The latter was obtained from an aqueous solution of $K_2Ni(CN)_4{\cdot}3H_2O$ and excess $BaCl_2$.

Table I. Crystal Data for $CsKNi(CN)_4$

formula	$CsKNi(CN)_4$	
fw	334.8	
cryst size, mm³	ca. 0.15 × 0.30 × 0.60	
cryst system	triclinic	
space group	$P\bar{1}$	$I\bar{1}$
a, Å	7.421 (2)[a]	7.421 (2)[b]
b, Å	8.626 (4)	13.969 (5)
c, Å	9.364 (3)	8.604 (4)
α, deg	56.97 (3)	89.92 (3)
β, deg	60.64 (3)	78.16 (3)
γ, deg	70.88 (3)	90.02 (3)
V, Å³	436.5 (9)	873.0 (9)
formula units	2	4
d(obsd), g cm⁻³	2.57	
d(calcd), g cm⁻³	2.55	
μ(Mo Kα), cm⁻¹	6.8	
2θ range, deg	6.3–60	
reflctns measd ($I > 0$)	2260	
reflctns with $I > 3\sigma(I)$	1512	
variables refined	103	
R, %	6.1	
R_w, %	7.8	
GOF	1.91	

[a] Experimentally determined values used in data collection, structure solution, and refinement. [b] Derived values used in structure analysis.

Since the crystals were prepared in a heterogeneous solid mixture, great care was taken to identify the desired product. In addition to having a clear orange color, the crystals chosen were of uniform morphology. A preliminary polarized specular reflection spectrum of each crystal was obtained, and from a collection of such spectrally screened crystals, samples were chosen for detailed X-ray, spectral, and elemental analyses.

Analyses for nickel, cesium, and potassium were performed on a Varian-Techtron Model 1200 atomic absorption spectrophotometer. The Ni:Cs:K molar ratio was found to be 1.00:1.00:1.04. An analysis performed by Galbraith Laboratories for carbon and nitrogen yielded a C:N molar ratio of 1.00:1.01. The presence of $Ni(CN)_4^{2-}$ was confirmed by UV solution absorption spectroscopy.

X-ray Data. A bladelike crystal was attached to a glass rod and sealed in a thin-walled glass tube to exclude moisture. This assembly was then mounted on an Enraf-Nonius CAD-4 diffractometer equipped with pulse height analyzer, graphite monochromator, and Mo Kα

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Table II. Final Atomic Parameters for $CsKNi(CN)_4$

	$P\bar{1}$			$I\bar{1}$		
	x^a	y	z	x	y	z
K	2632 (5)	−139 (4)	4861 (4)	4993 (5)	2361 (3)	2500 (3)
Cs	6236 (2)	6267 (1)	1265 (1)	2 (2)	3766 (1)	7455 (1)
Ni(1)	0	0	0	0	0	0
C(1)	−2268 (22)	1456 (21)	951 (21)	−1065 (26)	1204 (15)	−253 (15)
N(1)	−3711 (21)	2242 (19)	1590 (19)	−1795 (24)	1916 (14)	−326 (14)
C(2)	1287 (21)	−324 (18)	1449 (18)	1850 (23)	563 (14)	886 (14)
N(2)	2112 (21)	−514 (17)	2297 (17)	3004 (22)	891 (14)	1406 (14)
Ni(2)	0	5000	5000	0	0	5000
C(3)	163 (20)	4028 (18)	3597 (18)	−1025 (23)	−1188 (13)	4785 (13)
N(3)	163 (21)	3402 (18)	2771 (19)	−1751 (24)	−1914 (14)	4685 (14)
C(4)	−2396 (20)	6437 (18)	4668 (17)	−1844 (22)	553 (13)	4116 (13)
N(4)	−3897 (19)	7279 (17)	4499 (18)	−3008 (22)	889 (13)	3610 (13)

	$U_{11}{}^b$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	283 (14)	380 (15)	394 (15)	109 (11)	−190 (12)	−255 (13)
Cs	418 (5)	309 (4)	317 (4)	8 (3)	−112 (4)	−133 (3)
Ni(1)	251 (11)	268 (11)	246 (11)	34 (9)	−106 (9)	−159 (9)
Ni(2)	209 (11)	230 (10)	275 (11)	64 (8)	−88 (9)	−150 (9)
C(1)	353 (75)	474 (82)	504 (85)	79 (62)	−206 (67)	−337 (73)
C(2)	322 (66)	312 (63)	318 (63)	29 (52)	−113 (54)	−208 (54)
C(3)	270 (63)	324 (64)	345 (66)	82 (51)	−147 (54)	−192 (56)
C(4)	267 (63)	311 (62)	273 (60)	53 (51)	−99 (51)	−144 (52)
N(1)	496 (78)	549 (79)	557 (81)	153 (63)	−173 (66)	−427 (72)
N(2)	587 (83)	358 (63)	399 (66)	−31 (57)	−222 (62)	−202 (55)
N(3)	517 (82)	456 (73)	512 (78)	127 (61)	−189 (66)	−329 (67)
N(4)	378 (68)	422 (68)	459 (72)	130 (55)	−169 (57)	−246 (60)

[a] Fractional coordinates × 10^4. [b] Anisotropic temperature factor is of the form $\exp(-2\pi^2 s\cdot U\cdot s)$ where $s = ha^* + kb^* + lc^*$ ($P\bar{1}$) and U is a symmetric tensor with components $10^{-4}U_{ij}$.

radiation (takeoff angle 3.5°). A preliminary survey of reflections established the crystal system as triclinic, and cell constants of the standard primitive reduced cell (Table I) were obtained by least-squares analysis of the positions of 15 precisely centered reflections. The crystal was oriented with the elongated ([0$\bar{1}$1]) direction nearly parallel to the φ axis of the instrument. The broad faces of the crystal belong to the {111} form, while smaller faces of the {100} and {011} forms were also well developed.

The intensities of reflections in four independent octants were measured by the $\omega/2\theta$ scan technique. Each scan range was computed as $2\theta = (2 + 2.1 \tan \theta)°$, with an additional 25% on either side of the θ(peak) for background measurement. From a rapid prescan (5° min^{-1}) of each reflection the integrated intensity $I = I_t - I_b$ was calculated, with I_t the total scan count and I_b the estimated background. Reflections with $I < 75$ were judged too weak to measure; for $2000 > I > 75$, the reflection was measured at a scan rate calculated to yield $I = 2000$ within a maximum scan time of 5 min; for $I > 2000$, the prescan measurement was accepted. Two general reflections were monitored at intervals of 50 reflections to detect crystal deterioration and instrument instability, while a third reflection was recentered every 100 reflections to detect crystal movement. Neither the crystal nor the instrument changed significantly during the data collection period.

The 2260 measured intensities were corrected for Lorentz and polarization (Lp) effects, but no absorption correlations were made. The variance in each intensity was approximated by $\sigma(I)^2 = I_t + I_b + (0.02I)^2$, while the variance in the structure amplitude was $\sigma(|F_o|)^2 = \sigma(I)^2/4ILp$.

Structure Solution and Refinement. The Cs and Ni atoms were located on a Patterson map, and successive difference Fourier maps revealed all remaining atomic positions. Full-matrix, weighted ($w = \sigma(|F_o|)^{-2}$), least-squares refinement with anisotropic thermal parameters for all atoms converged smoothly. No parameter shifted more than 0.4σ on the last cycle. This cycle also included 636 "less than" reflections, for which $I < 3\sigma(I)$ and $|F_c| > |F_o|$, but excluded five strong reflections which suffered extinction. A final difference map displayed the highest electron density (ca. 1 e $Å^{-3}$) in the vicinity of Cs. Attempts to refine two independent formula units in space group $P1$ failed to produce a more reasonable structural model.

The atomic scattering factors were those of Cromer and Mann,[14] and dispersion corrections for Cs and Ni were taken from ref 15. A listing of the final calculated and observed structure amplitudes is available (supplementary material).

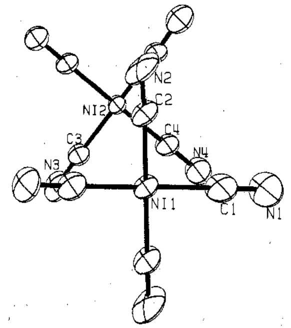

Figure 1. The two centrosymmetric $Ni(CN)_4^{2-}$ anions in $CsKNi(CN)_4$, viewed perpendicular to the Ni(1) plane.

Spectral Data. Single-crystal polarized specular reflection spectra were obtained with an instrument (similar to one described in detail elsewhere[16]) containing a tungsten–halogen lamp source, a Beckman DU monochromator, a Glan–Thompson prism polarizer, and a photomultiplier detector. This instrument was interfaced interactively to a Hewlett-Packard 3000 computer. Measurements were made relative to an aluminum mirror and corrected for aluminum reflectivity.[17] The reflection spectra were obtained on a broad face of the crystal ({110} in $I\bar{1}$; see discussion of morphology) with the electric vector of the incident light aligned either perpendicular or parallel to the elongation direction ([001] in $I\bar{1}$). Seven of the best[18] reflection spectra for each polarization were averaged prior to transformation of the reflection data into absorption parameters via Kramers–Kronig analyses.[20]

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(18) The reflection spectra with simultaneously the highest peaks and lowest troughs in the dispersion curves[19] were considered of highest quality. This avoided discrepancies due to misalignment of either the crystal or mirror which would produce uniformly low or high reflectivities.

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Table III. Interatomic Distances (Å) and Angles (Deg) in $CsKNi(CN)_4$

Ni(1)–C(1)	1.89 (2)		C(1)–Ni(1)–C(2)	91.8 (8)
Ni(1)–C(2)	1.87 (2)		C(3)–Ni(2)–C(4)	88.8 (7)
Ni(2)–C(3)	1.85 (2)		Ni(1)–C(1)–N(1)	176 (2)
Ni(2)–C(4)	1.86 (1)		Ni(1)–C(2)–N(2)	179 (1)
C(1)–N(1)	1.14 (2)		Ni(2)–C(3)–N(3)	177 (1)
C(2)–N(2)	1.14 (3)		Ni(2)–C(4)–N(4)	178 (1)
C(3)–N(3)	1.16 (3)			
C(4)–N(4)	1.15 (2)			
K---N(2)	2.80[c]	(2.82)[b]	K---N(2)–C(2)	156
K---N(4)(I)[a]	2.81	(2.82)	K---N(4)–C(4)	157
K---N(1)(I)	3.10	(3.07)	K---N(1)–C(1)	116
K---N(3)(II)	3.11	(3.07)	K---N(3)–C(3)	115
K---N(3)(III)	3.14	(3.17)	K---N(3)–C(3)	87
K---N(1)(IV)	3.17	(3.17)	K---N(1)–C(1)	87
Cs---N(1)(V)	3.31	(3.31)	Cs---N(1)–C(1)	125
Cs---N(3)(III)	3.31	(3.31)	Cs---N(3)–C(3)	126
Cs---N(4)(IV)	3.41	(3.48)	Cs---N(4)–C(4)	84
Cs---C(4)(VI)	3.48	(3.48)		
Cs---N(2)	3.41	(3.47)	Cs---N(2)–C(2)	83
Cs---C(2)	3.47	(3.48)		
Cs---N(1)(I)	3.45	(3.46)	Cs---N(1)–C(1)	100
Cs---N(3)(VII)	3.48	(3.46)	Cs---N(3)–C(3)	101
Cs---N(4)(VII)	3.53	(3.47)	Cs---N(4)–C(4)	99
Cs---N(2)(VIII)	3.53	(3.47)	Cs---N(2)–C(2)	99
Ni(1)---C(4)	3.61	(3.61)		
Ni(1)---N(4)	3.65	(3.61)		
Ni(2)---C(2)	3.61	(3.61)		
Ni(2)---N(2)	3.64	(3.61)		

[a] Symmetry operations in $I\bar{1}$ are as follows: (I) $1 + x, y, z$; (II) $-x, -y, 1 - z$; (III) $^1/_2 + x, ^1/_2 + y, -^1/_2 + z$; (IV) $^1/_2 - x, ^1/_2 - y, ^1/_2 - z$; (V) $^1/_2 - x, ^1/_2 - y, -^1/_2 - z$; (VI) $1 + x, y, z - 1$; (VII) $-x, -y, -z$; (VIII) $1 - x, -y, -z$. [b] Contact distances in parentheses are calculated on the basis of a nonspherical nitrogen atom model. [c] The esd of all contact distances is 0.01 Å.

Results and Discussion

The crystallographically independent unit consists of a K^+ ion, a Cs^+ ion (each in general positions), four cyano ligands with all eight C and N atoms in general positions, and two nickel half-atoms occupying different centrosymmetric positions. There are thus two independent half-anions in the crystal (Figure 1). Atomic parameters are listed in Table II and interatomic distances and angles in Table III.

The $Ni(CN)_4{}^{2-}$ anions are both exactly planar by symmetry and are very nearly square. The deviations of the C–Ni–C angles from 90° are not significant and, if real, can probably be attributed to packing forces. The cyanide ligands are linear to within experimental error, and neither the Ni–C bond lengths (average 1.86 (1) Å) nor the C–N bond lengths (average 1.15 (1) Å) differ significantly from their respective means. These values are consistent with measurements of other structures containing $Ni(CN)_4{}^{2-}$ anions.[12,21]

The crystal structure and morphology are obscured by the highly nonorthogonal shape of the primitive cell. Therefore all further discussion of the crystal structure will be in terms of a body-centered cell[22] of space group $I\bar{1}$. In this double cell, all heavy atoms occupy positions which are nearly or exactly in units of one-eighth. The two independent anions are stacked alternately along the [001] direction, the axis of elongation of the crystal. The Ni(1)–Ni(2) stacking distance is 4.30 Å.

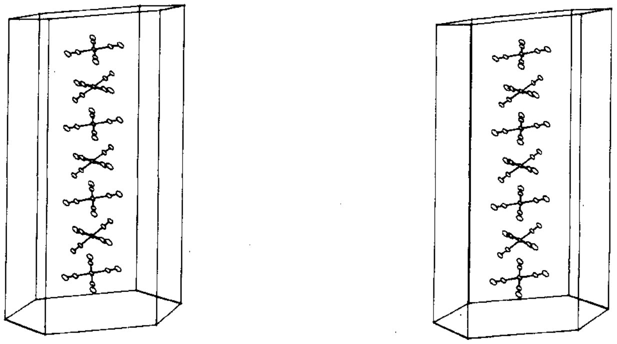

Figure 2. Stereoview into the broad ((110) in $I\bar{1}$) face of a typical $CsKNi(CN)_4$ crystal, showing a column of anions relative to the crystal morphology.

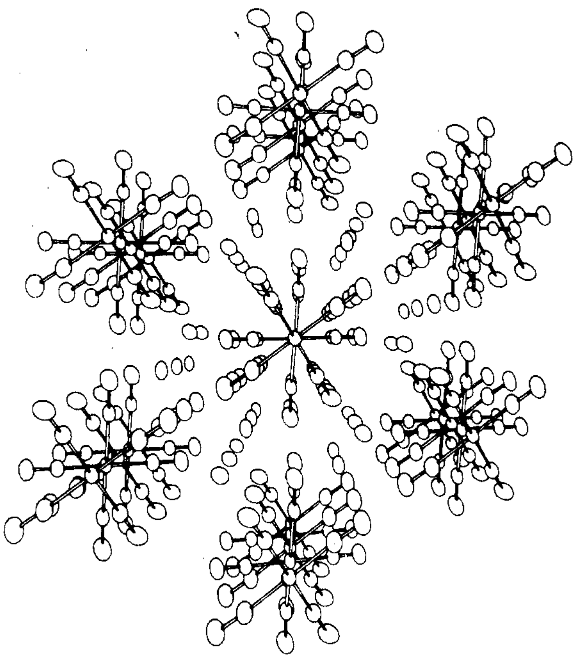

Figure 3. View down the direction of elongation ([0$\bar{1}$1] in $P\bar{1}$, [001] in $I\bar{1}$) in crystalline $CsKNi(CN)_4$ showing hexagonally packed columns of anions separated by Cs^+ and K^+ cations.

Adjacent pairs of square-planar anions are not aligned perpendicular to this column axis; their normals are tilted from the [001] direction by 35.92° (Ni(1)) and 35.80° (Ni(2)) and are also tilted by 10.12° with respect to one another. Further, the Ni(2) anions are rotated about their normal by 35.5° with respect to the Ni(1) anions. Thus, the columns contain alternating pairs of tilted, staggered $Ni(CN)_4{}^{2-}$ square-planar anions as illustrated in Figures 1 and 2.

The projection of the body-centered cell onto the (001) plane is, within experimental error, a rectangular cell with all heavy atoms at $x = 0$ or $x = {}^1/_2$. This arrangement produces strong orthorhombic pseudosymmetry (plane group *cmm*) which is violated only slightly by the CN ligands. Thus, it is not possible to distinguish significant differences in intensity between pseudosymmetric reflections on an *hk*0 Weissenberg photograph taken with Cu Kα radiation.

Each column of anions is surrounded by six other columns in a nearly hexagonal arrangement (Figure 3). Indeed, the three forms of the [001] zone which develop as crystal faces are just those planes which contain the highest densities of these columns: {110}, {010}, and {$\bar{1}$10}. Intercolumnar distances are 7.26 Å in (110) and ($\bar{1}$10) and 7.87 Å in (010); interfacial angles are (110)–(010) = 62.50° and (010)–($\bar{1}$10) = 62.55°.

The potassium ion resides in a distorted octahedral cavity bounded by six nitrogen atoms at distances ranging from 2.80

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(21) (a) S. S. Basson, L. D. C. Bok, and J. G. Leipoldt, *Acta Crystallogr., Sect. B*, **B25**, 579 (1969); (b) J. G. Leipoldt, S. S. Basson, and L. D. C. Bok, *ibid.*, **B26**, 361 (1970); (c) L. D. C. Bok, S. S. Basson, J. G. Leipoldt, and G. F. S. Wessels, *ibid.*, **B27**, 1233 (1971); (d) J. Ledent, *Bull. Soc. R. Sci. Liege*, **41**, 537 (1972).

(22) The transformation to body centered (I) from primitive (P) is as follows: $a_I = a_P$; $b_I = b_P + c_P - a_P$; $c_I = c_P - b_P$. Lattice constants are listed in Table I.

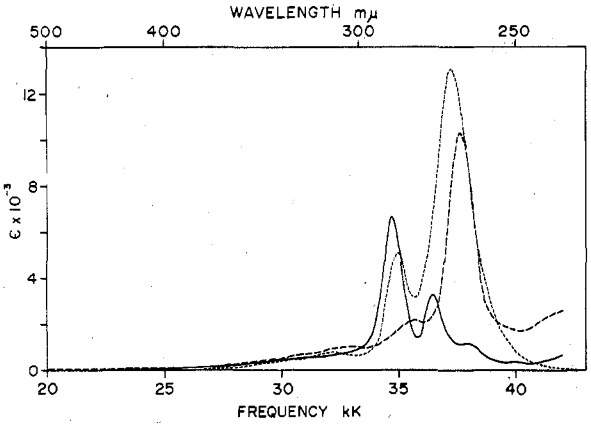

Figure 4. Polarized crystal spectra transformed from reflectance data on $CsKNi(CN)_4$: —, parallel to elongation axis [001]: ---, perpendicular to [001]. ··· indicates the solution spectrum of $Ni(CN)_4^{2-}$.

to 3.17 Å (next nearest neighbor, at 3.29 Å, is the carbon bonded to N(3)(III)). The cesium ion is in a cavity bounded by six nitrogen atoms and two complete cyano ligands at distances ranging from 3.31 to 3.53 Å (next nearest neighbor is a carbon atom at 3.82 Å); the six nitrogen atoms and the *midpoints* of the CN bonds occupy the eight vertices of a slightly distorted square antiprism. Each nickel atom makes contact ca. 3.6 Å above and below the plane with cyanide groups from adjacent anions (next nearest neighbor is Cs^+ at 4.25 Å). Such a wide range of contact distances (listed in Table III) suggests that the spherical atom model is not valid. The concept of polar flattening has been discussed in detail by Nyburg,[23] and when applied to the nitrogen atoms, the data in Table III come into suprisingly good agreement. In summary, only the nitrogen atoms are treated as oblate spheroids in which the distance from the nucleus to the contact (van der Waals) envelope, along a line ψ degrees from the C–N axis, is $R(\epsilon^2 \sin^2 \psi + \cos^2 \psi)^{-1/2}$. In this equation ϵ is the ellipticity, R is the envelope "radius" parallel to the C–N axis, and R/ϵ is the envelope radius perpendicular to the C–N axis. With the assumption that all other atoms are spherical and with the radius of the relatively nonpolarizable K^+ ion $R(K^+)$ fixed at 1.52 Å,[24] linear regression of the contact distances in Table III yields: $R(N) = 1.25$ (3) Å, $\epsilon = 0.76$ (2) Å, $R(C) = 1.65$ (2) Å, $R(Ni) = 1.92$ (2) Å, $R(Cs^+) = 1.83$ (1) Å. The root-mean-square deviation between observed and calculated contact distances in Table III is 0.02 Å.

The volume occupied by the $Ni(CN)_4^{2-}$ anion is calculated[25] to be ca. 100 Å^3, and the packing coefficient is 0.64. This value is a reasonable approximation to closest packing (0.74 for equal sized spheres). There are no large voids in the lattice.

The spectroscopic observations on the (110) face are presented in Figure 4 as polarized crystal spectra, adjusted for approximate solution equivalency,[26] together with the solution spectrum of the $Ni(CN)_4^{2-}$ ion. The crystal spectra are essentially equivalent to the solution spectrum, accounting for the principal features in solution and presenting no additional bands to the red of the solution absorptions. There is thus no solid-state effect in $CsKNi(CN)_4$.

The lack of a solid-state effect in this system is in contrast to the observation of such effects in other small-cation tetracyanonickelates[6] and is apparently due to the manner in which the anions interact. Models proposed for the solid-state effect include Frenkel exciton formation[27a,b] and metal d → p transitions.[27c] The former requires a close arrangement of parallel planes (which may be tilted from the metal–metal axis), and the latter requires close stacking of planes approximately normal to the metal chain. Three structural features exist in $CsKNi(CN)_4$ which would inhibit interplanar interactions according to the exciton and d → p models: (1) relatively large Ni–Ni distances (4.30 Å); (2) tilting of the $Ni(CN)_4^{2-}$ planes with respect to one another (~10°); (3) tilting of the planes with respect to the column axis (~36°). These structural parameters therefore represent collectively an upper limit to the misalignment of planes allowable for a solid-state effect to occur in tetracyanonickelates.

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Registry No. $CsKNi(CN)_4$, 74752-84-4; $Cs_2Ni(CN)_4$, 33517-38-3; $K_2Ni(CN)_4$, 14220-17-8.

Supplementary Material Available: Table IV listing final calculated and observed structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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(26) Solution equivalency requires that the absorption coefficients obtained from the Kramers–Kronig analysis be multiplied by $^2/_3$ for in-plane and $^1/_3$ for out-of-plane polarizations. The ⊥ and ‖ crystal polarization directions approximate the in-plane and out-of-plane directions as viewed from the (110) face, and thus approximate solution equivalency has been achieved by multiplying the ⊥ polarization by $^2/_3$ and the ‖ by $^1/_3$.

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