

The X-Ray Diffraction Analysis and Spectral Studies of Mixed Anionic (1 : 1) $\text{Cd}_3^{II}[(\text{Fe}^{III}/\text{Co}^{III})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$

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Refinement of the crystallographic structure of (1:1) $\text{Cd}_3^{II}[(\text{Fe}^{III}/\text{Co}^{III})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ (I) has been carried out by means of three-dimensional single-crystal X-ray diffractometry. This novel disordered mixed anionic complex crystallizes in the cubic space group $Fm\bar{3}m$ ($Z=1\ 1/3$) with $a_0=10.638(1)$ Å. Based on 166 unique reflections, the employed full-matrix least-squares method yielded a final reliability factor of $R=0.041$ ($R_w=0.047$) and a goodness-of-fit value (\sum_2) of 1.79. Indexed power diffraction data are reported and evaluated according to the quantitative figures-of-merit $F_{21}=114$ (0.007, 25) and $M_{20}=154.9$. A thermal gravimetric analysis revealed 14 water molecules per formula unit and the experimental density is $1.93(5)$ Mg m^{-3} [calc., $1.87(1)$ Mg m^{-3}]. The divalent Cd atoms are linked to the (1 : 1) mixed metal atoms by linear cyanide bridging. The disordered structure I is isomorphous with the hydrated cobalticyanides of Mn and Cd. A hydrogen-bonding network is set up within cavities of the crystal lattice created by the molecular disorder. Selective geometric parameters as well as conoscopic and IR spectral results are presented. © 1997 Academic Press

INTRODUCTION

Structure analyses of solid solutions of mixed cationic or mixed anionic complex cyanides are of basic interest from both the fundamental and practical points of view. They are of basic interest since it is possible to investigate the structural integrity of an entire transition or lanthanide series in the hexacyanide form. Additionally, as exemplified by the present work, perfect solid solution "mixed crystals" for the hexacyanides can be formed over a wide range of mixed transition or lanthanide compositions. This implies that it may be possible (within certain limits) to tailor the local crystal-field at the metal sites and hence, control the optical, magnetic, and other properties of ions in mixed hosts (1–3). From the practical point of view, these types of compounds display zeolitic and characteristic sieving properties that have been employed as electron scavengers and radionuclide sorbents in nuclear waste management (4, 5).

Initial studies of metal hexacyanocobaltates were conducted by James and Willand (6) who reported the amounts of hydration associated with microscopic crystals of several lanthanide complexes. Transition metal cobaltihexacyanide research dealing with physical properties was carried out by Cambi and Clerici (7) in the late 1920s. The determinations of unit cell constants of several $M_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ type complexes has been accomplished (8) where M represents divalent transition elements. Single-crystal analyses of some divalent transition metal hexacyanides by Ludi *et al.* (9–11) established the space group ($Fm\bar{3}m$) and a viable structural model. This model was improved by Beall *et al.* (12) employing both X-ray and neutron diffraction methods. The synthesis, spectroscopic, and single-crystal structural analyses of several disordered mixed cationic transition (Tr) metal hexacyanocobaltates, $Tr_{1.5}Zn_{1.5}[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, where $Tr = \text{Cd}, \text{Mn},$ and Co and the number of molecules in the unit cell equals $1\ 1/3$, have been completed (13). It has been shown that the cationic mixed metal systems of the mentioned hexacyanides (13) fit Beall *et al.*'s model (12) quite well and thus, lend further credence to the developed crystallographic model. The very first mixed anionic hexacyanide to be synthesized and studied structurally also crystallizes in the cubic space group $Fm\bar{3}m$ with $Z = 1\ 1/3$, $\text{Mn}_3^{II}[(\text{Co}^{III}/\text{Cr}^{III})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ (14). This laboratory deals primarily with synthesis and structural studies. Therefore, it has been deemed necessary to continue morphological and structural investigations of mixed anionic hexacyanide complexes and to verify further credibility of the model proposed by Beall *et al.* (12). The title compound I is the second disordered mixed anionic system ever to be synthesized and analyzed crystallographically.

EXPERIMENTAL

Using the appropriate molar ratios of the subject compound, clear cube-shaped single crystals were prepared by the U-tube slow diffusion method. Reagent grade CdCl_2 , $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_3\text{Co}(\text{CN})_6$ (commercially obtained) were

used without further purification as starting materials. Dilute solutions (0.01 M) of each of the interdiffusing constituents were prepared with triply distilled water. The floatation method was employed to determine the experimental density, $1.93(5) \text{ Mg m}^{-3}$ [calc., $1.87(1) \text{ Mg m}^{-3}$]. A thermal gravimetric analysis (TGA) revealed the loss of 14 water molecules per formula unit. A Perkin–Elmer TGS-1 thermal balance run at $2.5^\circ\text{C min}^{-1}$ while being purged with nitrogen (flow rate $25\text{--}30 \text{ cm}^3 \text{ min}^{-1}$) was used for the determination. An IR spectrum taken over the frequency range $4000\text{--}400 \text{ cm}^{-1}$, using the pressed-disk method (KBr pellet) on a Mattson Fourier Transform IR analyzer, yielded the following notable results: a very broad band at 3508 cm^{-1} with two distinct shoulders at approximately 3200 and 3100 cm^{-1} (all related to $\nu\text{-OH}$, H-bonding), three sharp peaks at 2146 , 2135 , and 2063 cm^{-1} ($\nu\text{-C}\equiv\text{N}$), a sharp peak at 1611 cm^{-1} ($\delta\text{-HOH}$), and two (Fe/Co)–C bending bands at 443 and 430 cm^{-1} . X-ray powder data were obtained by the use of a Siemens Debye–Scherrer cylindrical camera (114.6 mm, 292 K, under vacuum, Ni-filtered $\text{CuK}\alpha$ radiation, $\lambda_{\text{mean}} = 1.54184 \text{ \AA}$). Finely ground crystals of $\text{Cd}_3[(\text{Fe/Co})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ (**I**) were placed into a thin-walled glass capillary (0.2 mm). The unit cell constant was refined by entering measured S values (ring diameters) into a least-squares program (15) designed for X-ray powder diffraction data. This analysis program uses the Nelson–Riley extrapolation function (16) to determine lattice constants and their estimated standard deviations. The refined powder lattice parameter for the title compound is $10.6374(9) \text{ \AA}$ (see Table 1) with figures-of-merit values of $F_{21} = 114(0.007, 25)$ and $M_{20} = 154.9(17, 18)$. Table 2 presents the observed and calculated 2θ values (deg) with an average percentage deviation, the visually estimated relative intensities based on 100 as the strongest observed reflection, and the observed and calculated d spacings (Å). The average percentage deviation between observed and calculated d spacings is 0.044. A conoscopic examination, using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II, verified the optically isotropic character (isometric) and provided evidence of the optical homogeneity of the studied compound. A cube-like crystal selected on the basis of clarity and size ($0.13 \times 0.16 \times 0.20 \text{ mm}$) was mounted on an Enraf–Nonius CAD4-F automated diffractometer. Graphite monochromatized $\text{MoK}\alpha$ ($\lambda_{\text{mean}} = 0.71073 \text{ \AA}$) radiation was used. The orientation matrix and the initial cell parameter were obtained from a least-squares refinement of 25 carefully centered reflections (final single-crystal lattice constant at high θ angles, $> 20^\circ$, see Table 1). The ω – 2θ scan method, with a variable scan rate of $0.54\text{--}5.17^\circ \text{ min}^{-1}$ in ω , was used for intensity data collection. The data was collected in the range $3.0^\circ < 2\theta < 70.0^\circ$ ($h, -3 \rightarrow 17$; $k, -3 \rightarrow 12$; $l, -3 \rightarrow 17$) at a varied width of $1.15^\circ + 0.34 \tan \theta$. Three check reflections were monitored every 2 h of exposure time. Since there were only random

TABLE 1
Experimental and Statistical Data Summary

	Powder	Single crystal
System	Cubic	Cubic
Space group	$Fm\bar{3}m$ (No. 225)	$Fm\bar{3}m$ (No. 225)
$a/\text{Å}$	10.6374(9)	10.638(1)
$V/\text{Å}^3$	1203.7(3)	1203.9(2)
M_r	1016.7	1016.7
Z	1.3333	1.3333
$D_o/\text{Mg m}^{-3}$	1.93(5)	1.93(5)
$D_c/\text{Mg m}^{-3}$	1.87(1)	1.87(1)
T/K	292	292
Radiation	$\text{CuK}\alpha$	$\text{MoK}\alpha$
$F(000)/e^-$		657
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$		2.64
Transmission range		
min.		0.8674
max.		0.9996
$\Delta\theta/^\circ$		1.5–35.0
Unique reflections		166
$R, R_w (R_{\text{int}})^a$		0.041, 0.047 (0.043)
GOF (Σ_2)		1.79
Data-to-parameters ratio		8.7:1

^a $R = \sum ||F_o| - F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / w|F_o|^2]^{1/2}$, and the minimized quantity was $\sum w||F_o| - |F_c||^2$ where the weighting factor $w = [\sigma^2(F) + 0.0003F^2]^{-1}$.

variations from the mean intensity values, the reliability of the electronics, the X-ray intensity measurements, and the crystal stability were declared true. All resultant data were corrected for Lorentz and polarization effects and an empirical absorption correction (19) was also applied; see Table 1 for transmission range. After averaging redundant data ($R_{\text{int}} = 0.087$), 166 reflections were found to be unique and were used in the full-matrix least-squares structural refinement (20). An $N(Z)$ analysis (cumulative probability distributions relative to centrosymmetry test) provided evidence that the studied system is centrosymmetric in nature. Examination of the treated data revealed systematic absences that are consistent with the cubic space group $Fm\bar{3}m$ ($hkl: h + k, h + l, k + l = 2n + 1; Okl: l = 2n + 1; hhl: h + l = 2n + 1$; and $h00: h = 2n + 1$). Since the disordered structure **I** is isomorphous with the hydrated cobaltcyanides of Mn and Cd, the initial metal atomic positions were taken from the work of Beall *et al.* (12). Difference Fourier mapping revealed the positions of all other nonhydrogen atoms. A secondary extinction correction was applied ($5.0 \times 10^{-4} e^{-2}$) and after several cycles of anisotropic refinement, reliability factors were finalized ($R = 0.041$, $R_w = 0.047$). The goodness-of-fit value was 1.79. Experimental and statistical data are summarized in Table 1. The final difference Fourier map revealed a peak of $0.85 e^- \text{ \AA}^{-3}$ in the vicinity of the Cd atom which is quite common.

TABLE 2
X-ray Powder Diffraction Data for I

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_0$ (deg)	$2\theta_c$ (deg)	<i>I</i> / <i>I</i> ₀	<i>d</i> ₀ (Å)	<i>d</i> _c (Å)
1	1	1	14.426	14.421	30	6.140	6.142
2	0	0	16.674	16.667	100	5.317	5.319
2	2	0	23.650	23.656	80	3.762	3.761
3	1	1	27.828	27.819	25	3.206	3.207
2	2	2	29.077	29.077	2	3.071	3.071
4	0	0	33.700	33.702	40	2.6596	2.6594
4	2	0	37.825	37.821	40	2.3785	2.3787
4	2	2	41.599	41.591	10	2.1710	2.1714
5	1	1	44.250	44.243	5	2.0469	2.0472
4	4	0	48.401	48.404	5	1.8806	1.8805
5	3	1	50.775	50.775	5	1.7981	1.7981
6	0	0	51.550	51.550	5	1.7729	1.7729
6	2	0	54.549	54.560	5	1.6823	1.6820
6	2	2	57.476	57.464	2	1.6034	1.6037
4	4	4	60.273	60.278	2	1.5355	1.5354
6	4	0	63.026	63.012	5	1.4749	1.4752
6	4	2	65.674	65.685	2	1.4217	1.4215
7	3	1	67.673	67.645	2	1.3845	1.3850
8	0	0	70.850	70.863	1	1.3300	1.3298
7	3	3	72.775	72.769	2	1.2995	1.2996
8	2	2	75.899	75.892	1	1.2536	1.2537

Note. Average percentage deviation ($\Delta 2\theta$) in $2\theta = 0.016$. Average percentage deviation (Δd) in *d* spacing = 0.044.

Elsewhere, the map showed only a random fluctuating background. Obviously, hydrogen atom positions were not found. Atomic scattering factors and anomalous dispersion correction factors were taken from the "International Tables" (21). The resultant atomic coordinates with equivalent isotropic displacement coefficients are presented in Table 3. Tables of observed and calculated structure factors are available from the authors (D.F.M.).

TABLE 3
Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^2$) with e.s.d.'s in Parenthesis

Atom	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Cd	1.000	0.000	0.500	0.000	2.8(1)
Fe	0.333	0.000	0.000	0.000	1.2(1)
Co	0.333	0.000	0.000	0.000	3.5(1)
C	0.667	0.000	0.1789(7)	0.000	3.4(1)
N	0.667	0.000	0.286(1)	0.000	6.7(2)
O(1)	0.333	0.000	0.279(5)	0.000	13.1(9)
O(2)	0.333	0.000	0.000	0.000	2.2(1)
O(3)	0.167	0.172(3)	0.172(3)	0.172(3)	18.4(20)
O(4)	0.500	0.250	0.250	0.250	9.6(9)

^a Equivalent isotropic thermal parameters [*U*_{eq}] are defined as one-third the trace of the orthogonalized *U*_{*ij*} tensor.

DISCUSSION

The disordered mixed anionic solid solution (1:1) $\text{Cd}_3^{II}[(\text{Fe}^{III}/\text{Co}^{III})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ best fits the cubic space group *Fm* $\bar{3}m$ (No. 225), *Z* = 11/3. This one and one-third formula units per cell has been well established and confirmed by many research groups (9, 12–14, 22–24). This structural model proposed by Beall *et al.* (12) can accommodate 12 to 15 water molecules quite well in similar transition metal hexacyanides. Figure 1(a) is a perspective view of the molecular packing within the unit cell and represents both disordered and ordered positions of the structure. The ordered arrangement is depicted by the cationic Cd atoms being cyanide bridged to the mixed (Fe/Co) anionic metal atoms. The disordered unit arrangement occurs when a $[(\text{Fe}/\text{Co})(\text{CN})_6]^{3-}$ counter anion is vacant. The disordering (by vacancies) forms channels within the structure lattice. In this case, O(1) atoms coordinate to the Cd atoms, filling the octahedral arrangement about the Cd atoms, O(2) occupies the site of the (Fe/Co) atom at the 0, 0, 0 site, and O(3) atoms are positioned tetrahedrally about O(2). This structural arrangement sets up a hydrogen-bonding network. Figure 2 is a stereoview of I, from $-1/2$ to $+1/2$ along the crystallographic axes. According to the results of the TGA study, the loss of water molecules varied between 13 and 15, averaging at 14 which was the obtained experimental value for most runs. This varying was attributed to humidity dependence, also observed for a similar compound in the work of Güdel (25). The positional set 8c (1/4, 1/4, 1/4) where O(4) is located is the more plausible site for humidity dependent water molecules; see Table 3.

The divalent Cd atoms are octahedrally coordinated as are the (Fe/Co) atoms. As mentioned, linear cyanide bridging links the metal atom components with the cyanide ligands oriented with nitrogen toward the Cd atoms which are in position set 4*b* with an occupancy of 1.0. The anionic (Fe/Co) atoms are positioned in 4*a* with an occupancy of 1/3 for each (a total of 2/3 occupancy at this site). The carbon and nitrogen atoms are located in Wyckoff position 24*e* (0, *x*, 0) where *x* \approx 0.18 and 0.29 for C and N atoms, respectively. The Cd–N and Cd–O bond distances are 2.28(1) and 2.36(2) Å, respectively, and the Fe–C and Co–C bond lengths are 1.904(8) Å. These and the C \equiv N distance [1.14(1) Å] are internally consistent (see Table 4) and in

TABLE 4
Bond and Contact Distances (Å) with e.s.d.'s in Parenthesis for (1:1) $\text{Cd}_3^{II}[(\text{Fe}^{III}/\text{Co}^{III})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$

Cd–N	2.276(11)	Cd–O(1)	2.36(2)
Fe–C	1.904(8)	O(1)–O(2)	2.96(3)
Co–C	1.904(8)	O(1)–O(3)	2.82(3)
C–N	1.139(13)	O(2)–O(3)	3.16(2)

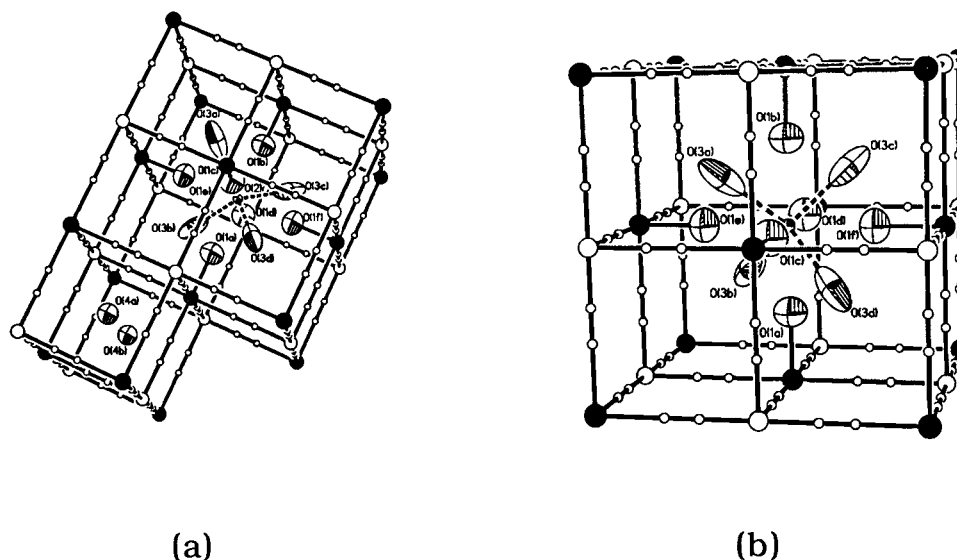


FIG. 1. (a) A representation of the disordered and ordered portions of **I**. (b) A close-up perspective view, from $-1/2$ to $+1/2$ along the crystallographic axes, of the arrangement of the oxygen atoms when a $[(\text{Fe}/\text{Co})(\text{CN})_6]^{3-}$ counter anion is vacant (causing disorder) in the structural lattice. The cyanide groups bridge the cationic Cd atoms and the mixed (Fe/Co) anionic metal atoms. O(1) is bonded to the Cd atoms; O(2) is located in the center of the formed cage; O(3) atoms are positioned tetrahedrally about O(2) as depicted in (b) by connecting the O(3) atoms to O(2) which are not bonded; and O(4) water molecules merely occupy interstitial space (zeolitically). The (●) symbol represents the Cd atoms, the (o) symbol represents the carbon and nitrogen atoms, and the (O) symbol represents the (Co/Fe) atoms. The water oxygen atoms displacement ellipsoids are shown at 50% probability.

good agreement with experimental values published in the Cambridge Structure Data Center (26) and in BIDICS (27). The intermoiety oxygen–oxygen contact lengths are significantly different. The respective O(1)⋯O(2), O(1)⋯O(3), and O(2)⋯O(3) contact distances are 2.96(3), 2.82(3), and 3.16(2) Å; see Table 4. These differences can be attributed to different degrees of hydrogen bonding. Studies by Brown (28) on the geometry of hydrogen bonding have demon-

strated that O⋯O intermolecular distances of 2.73 Å (or less) are related to strong hydrogen bonds and that, as the oxygen–oxygen contact distance increases, the hydrogen bonds become progressively weaker. Beyond 3.3–3.4 Å, H-bonding does not exist. These conclusions are based on the assumption that no specific geometric constraints are present in the system of interest. The structural results of this study of compound **I** suggests the possibility of three types of H-bonding which could be further indicated by the IR results (mentioned in the Experimental section). Recall a very broad strong band at 3508 cm^{-1} (that could be related to a moderately strong H-bond, O⋯O = 2.82 Å) with two distinct shoulders at 3200 and 3100 cm^{-1} (that may attest to O⋯O contact distances of 2.96 and 3.16 Å, respectively). It appears that no H-bonding exists between O⋯N (the contact distance is 3.967 Å). Other studies related to mixed solid systems are in progress, since such systems have become interesting in many areas of the scientific community at large.

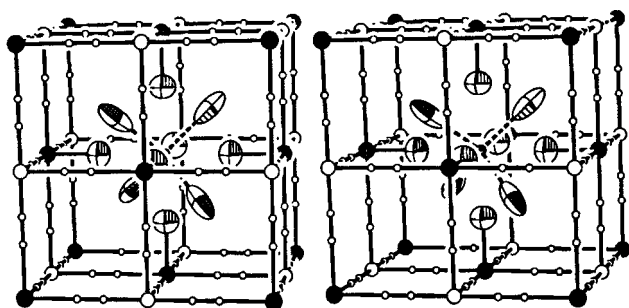


FIG. 2. A stereoview of compound **I**, from $-1/2$ to $+1/2$ along the crystallographic axes emphasizing the hydrogen-bonding network. The (●) symbol represents the Cd atoms, the (o) symbol represents the carbon and nitrogen atoms, and the (O) symbol represents the (Co/Fe) atoms. The water oxygen atoms displacement ellipsoids are shown at 50% probability.

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