

Synthesis, Spectroscopic and Single-Crystal Structural Investigations of Several Mixed Metal Hexacyanocobaltate Dodecahydrates

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Single crystals of $Tr_{1.5}Zn_{1.5}[Co(CN)_6]_2 \cdot 12H_2O$ (where divalent $Tr = Cd, Mn,$ and Co) have been synthesized by the slow diffusion method. Each mixed metal complex crystallized in the cubic space group $Fm\bar{3}m(O_h^5)$, No. 225) with respective lattice constants of 10.5312(6), 10.3265(7), and 10.2566(14) Å. The disordered structures contain $1\frac{1}{2}$ molecules in each unit cell. All atoms in each system are disordered and the divalent Tr/Zn atoms are linked to the Co atoms by cyanide bridging. Anisotropic refinements of the structures using a full-matrix least-squares program yielded reliability factors of 0.038, 0.034, and 0.034, respectively. Important bond lengths are presented as well as the results from optical, thermal gravimetric, and infrared studies. © 1994 Academic Press, Inc.

INTRODUCTION

James and Willand (1) initiated studies of metal hexacyanocobaltates. Their reported work dealt with the amount of hydration associated with microscopic crystals of several lanthanide complexes. In the late 1920s, transition-metal cobaltihexacyanide research related to physical properties was carried out by Cambi and Clerici (2). Magnetic properties of $Fe_3[Co(CN)_6]_2 \cdot 12H_2O$ were reported in 1956 by Bozorth *et al.* (3). This work was followed by the determination of unit cell constants (FCC) of several $M_3[Co(CN)_6]_2 \cdot 12H_2O$ type complexes where M represents divalent transition elements (4, 5). Morphological and structural investigations of heavy-metal ferro-, ferri-, and cobalticyanides were reported by Milligan *et al.* (6) employing electron diffraction, infrared, isobaric dehydration, Mössbauer, and powder X-ray diffraction methods. Single-crystal analyses of some divalent transition-metal hexacyanides by Ludi *et al.* (7-9) established the space group ($Fm\bar{3}m$) and a viable and sound structural model. This model was improved by Beall *et al.* (10) employing both X-ray and neutron diffraction methods. Beall's model (10) was tested by X-ray diffraction studies of several divalent-metal cobaltihexacyanide hydrates (11-13). A structural analysis of 1:1 gadolinium-ytterbium orthophosphate (14) has shown that a mixed metal

system tends to maintain the same structural geometry as the pure phase of either system.

In the present work, structural data for several mixed metal hexacyanides are presented to provide a basis for future solid-state chemical investigations dealing with the process of the structural integration and association of diverse cations so as to develop a better understanding of semipermeable membranes and to verify further credibility of the model proposed by Beall *et al.* (10).

EXPERIMENTAL

Clear colorless single crystals of $Cd_{1.5}Zn_{1.5}[Co(CN)_6]_2 \cdot 12H_2O$ (I), $Mn_{1.5}Zn_{1.5}[Co(CN)_6]_2 \cdot 12H_2O$ (II), and $Co_{1.5}Zn_{1.5}[Co(CN)_6]_2 \cdot 12H_2O$ (III) were prepared by the U-tube slow diffusion method using very dilute aqueous solutions containing stoichiometric amounts of chlorides of the mixed cations [Cd (I)/ Zn (II), Mn (II)/ Zn (II), and Co (II)/ Zn (II)] and $K_3Co(CN)_6$. These interdiffusing components were obtained commercially (ACS grade) and were used without any further purification. The respective crystal sizes used in the data collections were $0.391 \times 0.409 \times 0.446$ mm, $0.353 \times 0.446 \times 0.484$ mm, and $0.197 \times 0.213 \times 0.311$ mm.

Conoscopic examinations of single crystals of I, II, and III verified the isotropic nature (cubic) of each system. Crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II was employed for the optical studies. A Perkin-Elmer TGS-1 thermobalance (TGA) was used to determine the thermal dehydration (run at $2.5^\circ C \text{ min}^{-1}$ while purging the balance with N_2 , $20 \text{ cm}^3 \text{ min}^{-1}$). The analyses yielded the dehydration of 12.0 water molecules per formula unit for I, II, and III. Infrared spectral data were obtained on a Mattson Cygnus 100 FTIR analyzer over a frequency range of $4000-400 \text{ cm}^{-1}$ using the KBr pellet technique. The spectra displayed the following relevant absorption peaks for I, II, and III: sharp free OH stretching bands at approximately 3650 cm^{-1} , very broad-strong bands with shoulders between 3475 and 3200 cm^{-1} (ν -OH, H-bonding), sharp peaks at about 2170 cm^{-1} (ν -

C≡N) and 1610 cm⁻¹ (δ-HOH), as well as Co–CN(δ) and Co–C(ν) bonding bands at approximately 670 and 450 cm⁻¹, respectively.

Single crystals of **I**, **II**, and **III**, selected on the basis of optical purity, were mounted on glass fibers and transferred to goniometer heads which, in turn, were placed on an automated diffractometer (Enraf-Nonius CAD-4F) equipped with a dense graphite monochromator (take-off angle of 5.8°). Using MoK_α radiation (0.71073 Å), the orientation matrices and unit cell dimensions (final lattice constants at high θ angles) for each data set were obtained from least-squares refinements of 25 randomly selected and accurately centered reflections. Data were then collected over the range of 3.0° < 2θ < 70.0° (*h*:0 → 16, *k*:0 → 16, *l*:0 → 16) using the ω – 2θ scan technique at a scan rate between 0.46 and 3.44° min⁻¹ which was determined by a fast prescan of 3.44° min⁻¹. Two check reflections for each data set showed no significant intensity changes. Thus, the reliability and stability of the electronic hardware and the crystals were verified. Reflections having less than 75 counts above background during the prescan were considered to be unobserved. Intensities having *I* > 3σ(*I*) were used in the structure refinements. Experimental and statistical data are listed in Table 1 for compounds **I**, **II**, and **III**.

Systematic absences revealed the appropriate space group assignment (*hkl*: *h* + *k*, *h* + *l*, *k* + *l* = 2*n* + 1; *0kl*: *k*, *l* = 2*n* + 1; *hhl*: *h* + *l* = 2*n* + 1; and *h00*: *h* = 2*n* + 1). All data were corrected for Lorentz and polariza-

tion factors as well as for absorption effects. Absorption corrections were applied using an empirical absorption method (15); see Table 1 for transmission ranges. Additional examinations of the collected reflections in each data set employing an *N*(*Z*) analysis (cumulative probability distribution relative to centrosymmetry) also provided further evidence of the presence of a center of symmetry as did a negative pyroelectric test. The data were averaged (*R*_{int}, see Table 1), and initial atomic positions for the metal atoms (isomorphic substitution) were taken from the pure isostructural metal hexacyanocobaltate dodecahydrates (10, 11). Other nonhydrogen atoms were revealed by difference Fourier mapping. Each structure was initially refined isotropically using a full-matrix least-squares program (16). Anisotropic refinements and the application of secondary extinction corrections (*g*) yielded final reliability factors based on *R* = ΣΔ*F*/Σ*F*₀ and *R*_w = Σ√*w* Δ*F*/Σ√*w* *F*₀, where Δ*F* is defined as ||*F*₀| – |*F*_c||. The weighting factor *w* is defined as the reciprocal of the square of the standard deviation of *F*₀, σ⁻²(*F*₀). The occupancies of the disordered atoms were refined and did not deviate appreciably from the set values. The final difference Fourier maps were virtually featureless revealing only random background fluctuations. Anomalous dispersion correction factors and scattering factors for each atom were obtained from the usual source (17). Final atomic positions, occupancies, and anisotropic thermal parameters with estimated standard deviations are listed in Table 2.

TABLE 1
Crystal Data and Statistical Summaries

	I	II	III
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	<i>Fm</i> $\bar{3}$ <i>m</i>
<i>a</i> /Å	10.5312(6)	10.3265(7)	10.2566(14)
<i>V</i> /Å ³	1167.98	1101.18	1078.97
<i>M</i> _r	912.96	826.75	832.75
<i>Z</i>	1.3333	1.3333	1.3333
<i>D</i> _x /Mg m ⁻³	1.730	1.662	1.709
<i>F</i> (000)/(e ⁻)	596	550	554
μ(MoK _α /mm ⁻¹)	2.92	2.68	2.91
Transmission range			
min.	0.9385	0.8579	0.9783
max.	0.9993	0.9994	0.9999
Δθ/°	1.5–35.0	1.5–35.0	1.5–35.0
<i>T</i> /K	292	292	292
<i>R</i> _{int}	0.027	0.019	0.011
<i>R</i>	0.038	0.034	0.034
<i>R</i> _w (<i>R</i> _{all})	0.039(0.058)	0.033(0.046)	0.033(0.048)
<i>g</i> /(10 ⁻⁶ e ⁻²)	7.1(10)	8.8(12)	11.0(10)
Observed data [<i>I</i> > 3σ(<i>I</i>)]	163	123	124
Goodness of fit (Σ ₂)	2.72	2.19	2.44
Residual/(e ⁻ Å ⁻³)			
min.	-0.087	-0.136	-0.285
max.	0.156	0.123	0.218

TABLE 2
Atomic Positional Parameters and Anisotropic Displacement Coefficients ($\text{\AA} \times 10^3$) for I, II, and III

Atoms	Occupancy	x	y	z	U(11)	U(22)	U(33)
Compound I							
Cd	1/2	0.5	0.5	0.5	3.12(2)	—	—
Zn	1/2	0.5	0.5	0.5	3.12(2)	—	—
Co	2/3	0.0	0.0	0.0	3.03(4)	—	—
C	2/3	0.0	0.0	0.1795(8)	5.2(2)	—	3.4(3)
N	2/3	0.0	0.0	0.2877(8)	10.0(4)	—	2.9(3)
O(1)	1/3	0.0	0.0	0.283(4)	24(2)	—	13(4)
O(2)	1/3	0.0	0.0	0.0	11.0	—	—
O(3)	1/8	0.221(3)	0.221(3)	0.221(3)	10(2)	—	—
O(4)	1/3	0.25	0.25	0.25	7(1)	—	—
Compound II							
Mn	1/2	0.5	0.5	0.5	3.18(3)	—	—
Zn	1/2	0.5	0.5	0.5	3.18(3)	—	—
Co	2/3	0.0	0.0	0.0	2.70(3)	—	—
C	2/3	0.0	0.0	0.183(1)	4.0(1)	—	3.5(2)
N	2/3	0.0	0.0	0.295(1)	7.6(2)	—	2.5(2)
O(1)	1/3	0.0	0.0	0.300(3)	29(2)	—	8(1)
O(2)	1/3	0.0	0.0	0.0	10.8	—	—
O(3)	1/8	0.200(6)	0.200(6)	0.200(6)	18(1)	—	—
O(4)	1/3	0.25	0.25	0.25	12(2)	—	—
Compound III							
Co(1)	1/2	0.5	0.5	0.5	2.53(3)	—	—
Zn	1/2	0.5	0.5	0.5	2.53(3)	—	—
Co	2/3	0.0	0.0	0.0	1.72(3)	—	—
C	2/3	0.0	0.0	0.1824(5)	3.2(1)	—	2.0(2)
N	2/3	0.0	0.0	0.2954(5)	6.9(2)	—	1.0(2)
O(1)	1/3	0.0	0.0	0.315(3)	23(1)	—	23(2)
O(2)	1/3	0.0	0.0	0.0	15.0	—	—
O(3)	1/8	0.158(5)	0.158(5)	0.158(5)	14(1)	—	—
O(4)	1/3	0.25	0.25	0.25	15(3)	—	—

Note. The form of the anisotropic thermal parameter is $\exp[-2\pi^2\{U(11)h^2a^{*2} + U(22)k^2b^{*2} + U(33)l^2c^{*2} + 2U(12)hka^*b^* + 2U(13)hla^*c^* + 2U(23)klb^*c^*\}]$.

DISCUSSION

The structural characterizations of the subject cobalt-hexacyanide compounds have shown that these mixed $(Tr/Zn)_3[Co(CN)_6]_2 \cdot 12H_2O$ solid solutions are isomorphous with pure phases of divalent metal hexacyanocobaltate dodecahydrates which crystallize in the cubic space group model $Fm\bar{3}m$. Figure 1 is a representative perspective view of the molecular packing within the unit cell. The bridging cyanide ligands between the metal atoms are oriented with the carbon atoms toward the anionic cobalt atoms; see Fig. 1. These anionic cobalt atoms are in Wyckoff position 4a at 0, 0, 0 with $\frac{2}{3}$ occupancy. Carbon and nitrogen atoms are also disordered and are located in positional set 24e (0, 0, x), each of

which has an occupancy of $\frac{2}{3}$. The disordered cationic metal atoms are also positioned at a special site with $\frac{1}{2}$ occupancy, set 4b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). All metal atoms are six-coordinated octahedrally. Since $Z = 1\frac{1}{3}$ and the formula of each compound contains 12 water molecules, 16 oxygen atoms must be assigned proportionally. There are 8 coordinated water molecules per unit cell (0, 0, x at $\frac{1}{3}$ occupancy) and 8 uncoordinated water molecules which are located at three positions. Wherever the cyanide ligands are disordered in the structure, the coordinated water molecules, O(1), are bonded to the cationic metal atoms forming a cage within which the uncoordinated water molecules O(2) and O(3) are found. Oxygen atoms O(2) account for $1\frac{1}{3}$ of the 8 uncoordinated water molecules located at 0, 0, 0 and are held in position by hydrogen

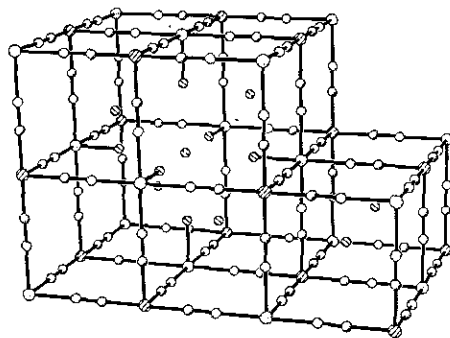


FIG. 1. A representative perspective view of the unit cell ($Z = 1.33$). Note the cyanide bridging between the cationic mixed metals, \odot , and the cobalt anionic metal atoms, \ominus . O(1) is bonded to the cationic metal atoms, O(2) is located in the center of the cage, O(3) is positioned tetrahedrally about O(2), and O(4) is merely occupying space, zeolitically (bottom of figure).

bonding to the O(1) water molecules. Oxygen atoms O(3) account for another 4 uncoordinated water molecules (at special site 32f; x, x, x) and are also positioned by hydrogen bonding to the O(1) water molecules. O(3) atoms are tetrahedrally arranged about O(2). Figure 2 is a representative stereoscopic drawing of the disordered arrangement within the structural units. The oxygen-oxygen contact distances between O(1) \cdots O(2) and O(1) \cdots O(3) are presented in Table 3 as well as the O(2) \cdots O(3) contact distances. It is highly improbable that hydrogen bonding can exist between O(2) \cdots O(3) in compounds **I** and **II**. However, hydrogen bonding between these water molecules is more than probable in compound **III**; O(2) \cdots O(3) is 2.85 Å. It has been shown by Brown (18) that the

TABLE 3
Bond and Contact Distances (Å) with E.S.D.'s in Parentheses
for **I**, **II**, and **III**

	I	II	III
Zn-N	2.236(7)	Zn-N 2.116(6)	Zn-N 2.113(5)
Cd-N	2.236(7)	Mn-N 2.116(6)	Co(1)-N 2.113(5)
Co-C	1.890(6)	Co-C 1.881(6)	Co-C 1.874(5)
C-N	1.139(8)	C-N 1.166(9)	C-N 1.142(7)
Zn-O(1)	2.29(3)	Zn-O(1) 2.10(3)	Zn-O(1) 1.88(2)
O(1)-O(2)	2.98(2)	O(1)-O(2) 3.07(3)	O(1)-O(2) 3.15(3)
O(1)-O(3)	3.18(4)	O(1)-O(3) 3.26(2)	O(1)-O(3) 2.77(1)
O(2)-O(3)	3.76(2)	O(2)-O(3) 3.86(2)	O(2)-O(3) 2.85(2)

strength of hydrogen bonds is dependent upon O \cdots O intermoiety contact distances. Strong hydrogen bonds, assuming no geometric constraints, have contact distances of approximately 2.73 Å or less. As contact distances increase, hydrogen bonds become increasingly weaker, and beyond approximately 3.3 Å, hydrogen bonding does not exist. The range of intermoiety oxygen-oxygen contact distances in this study (**I**, **II**, and **III**) varies considerably, signifying strong to very weak hydrogen bonds (2.77 to 3.26 Å, see Table 3). Infrared data presented in the experimental section lend credence to the X-ray diffraction analyses. That is to say, strong broad peaks with pronounced shoulders, located between 3475 and 3200 cm^{-1} , attest to the presence of hydrogen bonding and that the shoulders can be related to a different type of hydrogen bonds. Similar observations have been encountered and verified in neutron structure analyses of $\text{In}(\text{OH})_3$ and $\text{Lu}(\text{OH})_3$ (19, 20). A neutron diffraction anal-

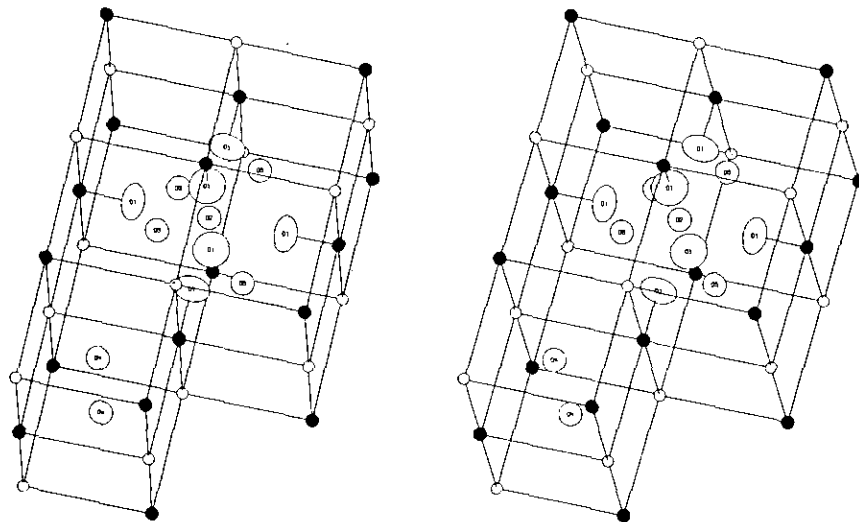


FIG. 2. A representative stereoview of **I**, **II**, and **III** displaying the disordered section of the unit cell. \bullet represents the cationic mixed metals and \circ designates anionic cobalt atoms.

ysis of **I**, **II**, or **III** would help clarify any questions related to hydrogen bonding. At this time, crystals are being sought that are large enough for neutron diffraction studies. Uncoordinated oxygen O(4) is related to a zeolitic type water molecule and is also located at a special positional set ($8c; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) with an occupancy of $\frac{1}{3}$ which accounts for the final $2\frac{2}{3}$ water molecules. This water molecule, O(4), merely occupies space and is positioned at a distance greater than 3.7 Å from its nearest neighbor, see Fig. 1. This free water molecule is also evidenced by the IR studies, sharp free OH stretches at approximately 3650 and at 1610 cm^{-1} (δ -HOH).

The Co-C and $\text{C}\equiv\text{N}$ bond distances are quite reasonable when making comparisons to other published experimental values (5, 7, 8, 10, 21-23). All experimental bond distances in **I**, **II**, and **III** are in good agreement with published values found in BIDICS (24) and in the Cambridge Structure Database (25). The accuracy of the experimentally determined values in this work is expected to provide invaluable data for further investigations dealing with mixed systems, since these type of compounds are considered to be true molecular sieves. Further, this work also lends credence to the proposed model and crystallographic conclusions developed by Beall *et al.* (10).

SUPPLEMENTARY MATERIALS

Additional materials comprising all bond distances and angles, thermal parameters, and structure factor amplitudes for **I**, **II**, and **III** are available from the authors (D.F.M.) on request.

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