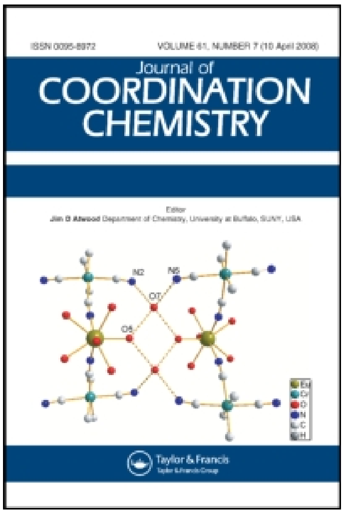

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X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS AND CHARACTERIZATIONS OF THREE MIXED ANIONIC HEXACYANO COMPLEXES

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The mixed anionic complexes, $Cd_3^{II}[(Cr^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$, $Co_3^{II}[(Co^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$, and $Pd_3^{II}[(Cr^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$, crystallize in the cubic centrosymmetric space group *Fm*$\bar{3}$*m* (No. 225) with $a_0 = 10.884(1)$, $10.396(1)$, and $10.455(2)$ Å, respectively. The disordered structures contain 1 1/3 molecules in the unit cell. Full-matrix least-squares refinements yielded final reliability (*R*) index factors of 0.040, 0.050, and 0.069 with 'goodness-of-fit' (GOF, Σ_2) values of 1.26, 1.25, and 1.11, respectively. All metal atoms in each compound are six-coordinate octahedral and the cationic divalent metal atoms are linked to the (1 : 1) mixed trivalent metal atoms by cyanide bridging. Networks of hydrogen-bonding are setup within cavities of the crystal lattices (created by molecular disordering). Characterization of each hexacyano complex includes physical property determinations, conoscopic studies, I.R. spectroscopic identifications, and thermal gravimetric analyses (TGA). Selective bond distances and angles are tabularized.

Keywords: Mixed transition/iridium complexes; X-ray structure; hexacyanides; iridium(III)

INTRODUCTION

The use of iridium in the chemical industry has, in the past, been restricted to production of limited amounts of specialty compounds.[1] Due to prevailing low prices of the element in recent years, the development of new applications for iridium has been advanced. Specifically, a new iridium-based

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catalyst is being used in the production of acetic acid.[1] Modern ion-exchange membrane processes require new and novel technological systems. Iridium(III) forms a large number of octahedral complexes including cyanide ligands.

Since $[Ir(CN)_6]^{3-}$, like $[Co(CN)_6]^{3-}$, is a low-spin d^6 complex, it is likely that a number of substituted Ir(III) hexacyano complexes can exist. Much work has been accomplished related to cyanide complexes of cobalt(III).[2–6] X-ray and neutron diffraction investigations of Mn and Cd cobaltihexacyanide dodecahydrates by Beall *et al.*[7] established an improved model for Prussian blue analogues with $Z = 1\ 1/3$ and the space group being $Fm\bar{3}m$. In our group, structural analyses of solid solutions of mixed systems of metal complex hexacyanides have become of basic interest, since it is possible to tailor the local crystal-field strength at the metal sites. Control of magnetic, optical and other properties of mixed systems may then be achieved. Cyanide complexes also exhibit zeolitic and characteristic sieving properties as well as being electron scavengers, ion exchangers and radionuclide sorbents, which are used in nuclear waste management.[8,9] Current interest in mixed transition metal systems, focused on morphological and structural investigations, has sparked research not only in mixed cationic systems but also in mixed anionic hexacyanides. To our knowledge, the title compounds are the first mixed iridium anionic systems ever to be synthesized and crystallographically analyzed.

EXPERIMENTAL

Clear, cube-like, single crystals of the mixed anionic complexes, $Cd_3^{II}[(Cr^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$ (**I**), $Co_3^{II}[(Co^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$ (**II**), and $Pd_3^{II}[(Cr^{III}/Ir^{III})(CN)_6]_2 \cdot 13H_2O$ (**III**), were prepared by the ‘U-tube slow-diffusion’ method. Molar ratios of the anionic components were accurately controlled. The dilute (0.01 M) interdiffusing constituents were prepared with triply distilled water and the reagents were obtained commercially (ACS grade). Harvested crystals of **I**, **II**, and **III** were taken directly from the mother liquors before peripheral studies and single-crystal analyses were performed. Experience has shown that many transition metal cyanide complexes may partially dehydrate when allowed to remain at ambient conditions for any length of time. The flotation method using bromoform and bromobenzene was used to obtain experimental pyknometric densities, see Table I. Thermal dehydration results were obtained on a Perkin-Elmer TGS-1 thermal balance. After many measurements, the

TABLE I Crystal data and summaries of compounds **I**, **II**, and **III**

	I	**II**	**III**
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
Crystal size (mm)	0.25 × 0.27 × 0.71	0.17 × 0.17 × 0.17	0.20 × 0.26 × 0.30
M_r	1127.8	974.2	1109.8
a/(Å)	10.884(1)	10.396(1)	10.455(2)
V/(Å^3)	1289.4(2)	1123.4(2)	1142.8(3)
Z	1.3333	1.3333	1.3333
D_c/(mg m^{-3})	1.936	1.924	2.149
F(000) (e$^-$)	708	628	700
$\mu(\text{MoK}_{\bar{\alpha}})/\text{mm}^{-1}$	5.350	5.920	5.738
$\Delta 2\theta/°$	3.0–70.0	3.0–70.0	3.0–70.0
Scan range (ω,°)	$1.15 + 0.34 \tan\theta$	$1.15 + 0.34 \tan\theta$	$1.15 + 0.34 \tan\theta$
T/K	292	292	292
Unique reflections	106	109	106
R_{int}	0.040	0.064	0.016
R, R_w	0.040, 0.119	0.050, 0.062	0.069, 0.180
$R_{\text{all data}}$	0.054	0.071	0.115
$g/(10^{-4}\text{e}^{-2})$	2(3)	19(3)	3(2)
GOF (Σ_2)	1.26	1.25	1.11

resultant data revealed that each complex contained 13.0 water molecules per formula unit. The instrument was run at 2.5°C min^{-1} while nitrogen purged the system. A Mattson Fourier Transform IR spectrometer was employed utilizing a frequency range of 4000–400 cm^{-1} (KBr pellet method). Notable spectral absorption peaks for **I**, **II**, and **III** are: sharp free stretching bands at *ca.* 3610 cm^{-1} (unbonded, ν-OH), very strong broad bands at approximately 3400 cm^{-1} with distinct shoulders at 3200 cm^{-1} (all related to intermolecular hydrogen bonding, ν-OH), three sharp peaks at *ca.* 2150 cm^{-1} (ν-C≡N), sharp peaks at 1620 cm^{-1} (δ-HOH), and metal-C bands at approximately 450 cm^{-1}.

Conoscopic examinations, using crystal rotations between two crossed polarizers on a Zeiss Photomicroscope II, verified the optical isometric character of the studied systems and provided evidence of the optical homogeneity of each. Cube-like crystals were mounted on an Enraf-Nonius CAD4-F autodiffractometer. All data were collected at 292 K using $\text{MoK}_{\bar{\alpha}}$ radiation ($\lambda_{\text{mean}} = 0.71073$ Å). Intensities were measured for **I**, **II**, and **III** in the (ω–2θ mode at varied rates of 1.18–4.12° min^{-1} in the 2θ range of 3.0–70.0° (h: 0–16, k: 0–16, l: 0–16). Crystal stabilities and electronic hardware reliability were verified by monitoring three check reflections in each data set as a function of time (every 2 h of exposure time, < 2.0%). Total independent intensity data for **I**, **II**, and **III** were 128 ($R_{\text{int.}} = 0.040$), 128 ($R_{\text{int.}} = 0.055$) and 165 ($R_{\text{int.}} = 0.016$), respectively of which 106, 109, and 106 with $F > 4.0\sigma(F)$ were included in the structure refinements. All intensity data were corrected for Lorentz and polarization effects after which absorption corrections were applied. Final lattice constants were obtained at high θ angles, > 20°. Experimental and statistical data are summarized in Table I.

Examination of the treated data revealed systematic absences (for **I**, **II**, and **III**) that are consistent with the cubic centrosymmetric space group $Fm\bar{3}m$ (hkl: $h+k, h+l, k+l=2n+1$; $0kl$: $l=2n+1$; hhl: $h+l=2n+1$; and $h00$: $h=2n+1$). The initial metal atomic positions were taken from the structural analysis of $Mn_3[(Co/Cr)(CN)_6]_2 \cdot 14H_2O$.[4] Difference Fourier mapping yielded the atomic positions of all other non-hydrogen atoms. At this point, isotropic refinements confirmed the correctness of the model and after several cycles of anisotropic refinements while applying secondary extinction corrections (g), final residual index factors were obtained (R, R_w, R_{all}: 0.040, 0.119, 0.054 for **I**, 0.050, 0.062, 0.071 for **II**, and 0.069, 0.080, 0.115 for **III**).[10] The index factors, R and R_w, are defined as, $R=\Sigma\Delta F/\Sigma F_o$ and $R_w=[\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$ where $\Delta F=||F_o|-|F_c||$ and $w=\sigma^{-2}(F_o)$. The 'goodness-of-fit' parameter is defined as $\Sigma_2=\mathrm{GOF}=[\Sigma w(\Delta \mathrm{F})^2/N_G]^{1/2}$ where ΔF and w have been defined above and $N_G=(N_o-N_v)$, N_o is the number of independent observations and N_v is the number of varied parameters in each refinement. Final residual density maps revealed some density in the vicinity of the heavy metal atoms, which is quite reasonable for heavy metal atom complexes. Elsewhere, the maps were featureless revealing only random fluctuating backgrounds. The minimized quantity in each refinement was $\Sigma w(|F_o|-|F_c|)^2$ and the weighting function $w=[\sigma^2(F)+BF^2]^{-1}$ where $B=8.6\times10^{-3}$ for (**I**), 1.0×10^{-3} for (**II**), and 5.0×10^{-3} for (**III**). $N(Z)$ analyses (cumulative probability distributions relative to centrosymmetry test) provide further evidence that the investigated systems are centrosymmetric in nature. The presence of any additional symmetry in **I**, **II**, and **III** was ruled out by employing the program MISSYM.[11] Atomic scattering factors and anomalous-dispersion correction factors for all non-hydrogen atoms were taken from Ibers and Hamilton.[12] Final atomic positions and equivalent isotropic thermal parameters with estimated standard deviations are listed in Table II. Tables of observed and calculated structure factors are available from the authors (D.F.M.)

RESULTS AND DISCUSSION

Table III lists bond lengths and pertinent bond angles for **I**, **II**, and **III**. Figure 1 is a representative molecular view of the three cyanide-bridged

TABLE II Atomic coordinates and equivalent isotropic thermal parameters (Å^2 × 10^2) for I, II, and III with esd's in parentheses

Atoms	*Occ.*	*x*	*y*	*z*	U_{eq}[a]
$Cd_3[(Cr/Ir)(CN)_6]_2 \cdot 13H_2O$ (I)					
Cd	1.000	0.0000	0.5000	0.0000	3.5(1)
Cr	0.333	0.0000	0.0000	0.0000	2.6(1)
Ir	0.333	0.0000	0.0000	0.0000	1.7(2)
C(1)	0.667	0.0000	0.1813(3)	0.0000	4.2(1)
N(1)	0.667	0.0000	0.2875(4)	0.0000	6.1(2)
O(1)	0.333	0.0000	0.2762(1)	0.0000	8.1(3)
O(2)	0.333	0.0000	0.0000	0.0000	0.9(1)
O(3)	0.167	0.1930(3)	0.1930(3)	0.1930(3)	10.5(6)
O(4)	0.333	0.2500	0.2500	0.2500	11.6(2)
$Co_3[(Co/Ir)(CN)_6]_2 \cdot 13H_2O$ (II)					
Co	1.000	0.0000	0.5000	0.0000	3.9(1)
Co	0.333	0.0000	0.0000	0.0000	6.4(2)
Ir	0.333	0.0000	0.0000	0.0000	1.6(1)
C(1)	0.667	0.0000	0.1852(3)	0.0000	4.1(3)
N(1)	0.667	0.0000	0.2958(2)	0.0000	4.7(1)
O(1)	0.333	0.0000	0.2880(2)	0.0000	4.2(3)
O(2)	0.333	0.0000	0.0000	0.0000	18.4(2)
O(3)	0.167	0.1914(3)	0.1914(3)	0.1914(3)	30.5(4)
O(4)	0.333	0.2500	0.2500	0.2500	14.2(3)
$Pd_3[(Cr/Ir)(CN)_6]_2 \cdot 13H_2O$ (III)					
Pd	1.000	0.0000	0.5000	0.0000	2.4(1)
Cr	0.333	0.0000	0.0000	0.0000	3.2(2)
Ir	0.333	0.0000	0.0000	0.0000	3.7(2)
C(1)	0.667	0.0000	0.1909(4)	0.0000	3.3(3)
N(1)	0.667	0.0000	0.3007(3)	0.0000	3.2(3)
O(1)	0.333	0.0000	0.2856(4)	0.0000	10.1(1)
O(2)	0.333	0.0000	0.0000	0.0000	7.7(1)
O(3)	0.167	0.1913(1)	0.1913(1)	0.1913(1)	10.7(1)
O(4)	0.333	0.2500	0.2500	0.2500	9.1(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

complexes showing the crystallographic numbering scheme. The crystal lattice of these systems is disordered containing $1\frac{1}{3}$ molecules in the unit cell. This value of one and one-third molecules per unit cell has been well established by several crystallographic research groups.[7,13–15] The crystallographic data of the title mixed anionic hexacyano complexes best fit the face-centered cubic (fcc) space group *Fm$\bar{3}$m* (No. 225). The improved model proposed by Beall *et al.*[7] has been successfully employed by this research group for the last two decades. The model can accommodate 12–15 water molecules in the crystal lattice quite well. The proposed model shows that the divalent cationic atoms (Cd, Co, and Pd) are six-coordinate octahedral as are the (Tr/Ir) atoms (Tr = Cr and Co). Cyanide bridging oriented with the nitrogen atoms toward the cationic atoms (placed in positional set 4c

TABLE III Bond and contact distances (Å) for **I**, **II**, and **III** with esd's in parentheses

I		**II**		**III**	
Cd–N	2.313(4)	Cd–N	2.121(2)	Pd–N	2.083(3)
Cd–O(1)	2.436(1)	Cd–O(1)	2.203(3)	Pd–O(1)	2.241(4)
Ir–C	1.973(3)	Ir–C	1.944(3)	Ir–C	1.996(4)
Cr–C	1.973(3)	Co–C	1.944(3)	Cr–C	1.996(4)
C–N	1.156(3)	C–N	1.150(3)	C–N	1.148(2)
O(1)–O(2)	3.006(1)	O(1)–O(2)	2.992(2)	O(1)–O(2)	2.986(4)
O(1)–O(3)	3.106(3)	O(1)–O(3)	2.986(3)	O(1)–O(3)	2.995(4)
O(2)–O(3)	3.638(3)	O(2)–O(3)	3.444(3)	O(2)–O(3)	3.464(1)
O(3)–N	3.144(4)	O(3)–N	3.014(2)	O(3)–N	3.056(2)
O(4)–N	> 4.0	O(4)–N	> 4.0	O(4)–N	> 4.0

with full occupancy of 1.0) links the metal atom components. For compounds **I**, **II** and **III**, the (Tr/Ir) atoms are located at set 4a with an occupancy of 1/3 for each Tr (Cr or Co) and Ir atom (a total of 2/3 occupancy at this site). The Wyckoff position 24e (0, x, 0; where x is *ca.* 0.185 and 0.290) accommodates the carbon and nitrogen atoms, respectively. The lattice of each compound has vacancies and a high degree of disorder which is depicted in Figures 1 and 2. These vacancies form channels by systematic absences of the $[(\mathrm{Tr/Ir})(\mathrm{CN})_6]^{3-}$ counteranions in the structures. When this disorder occurs, oxygen O(1) completes the octahedral arrangement about the cationic atoms and a network of H-bonding is set up. Water oxygen O(2) is positioned at the center of the formed cavity where the mixed (Tr/Ir) atoms are normally located (0, 0, 0; 4a). Each species at the same site [O(2) and (Tr/Ir)] was held constant while the other was refined and then, conversely refined. O(3) is tetrahedrally arranged about O(2) which completes the H-bonding network within the created vacancies. The highly zeolitic O(4) water molecules occupy interstitial space at positional set 8c (1/4, 1/4, 1/4), see Table II. Using an additional occupancy of 1/6 at this site (8c) permits the addition of one water molecule into the lattice. In compounds **I**, **II**, and **III**, the T.G.A. results affirmed 13 waters of hydration in each. The observed smooth dehydration thermograms are explained by the detailed hydrogen-bonding network associated with the structural model.[7] It is this network that is important in stabilizing the nonbonded and the coordinated water molecules, O(1). Hence, when the zeolitic water molecules begin to leave the crystal lattice, the coordinated water molecules, O(1), are destabilized and dehydration continues in a smooth manner as observed for **I**, **II**, and **III**.

Hydrogen bonding and electrostatic cohesive forces are of paramount importance in the network of the crystal lattices of these complexes. The strength of hydrogen bonds has been shown by Brown[16] to be dependent

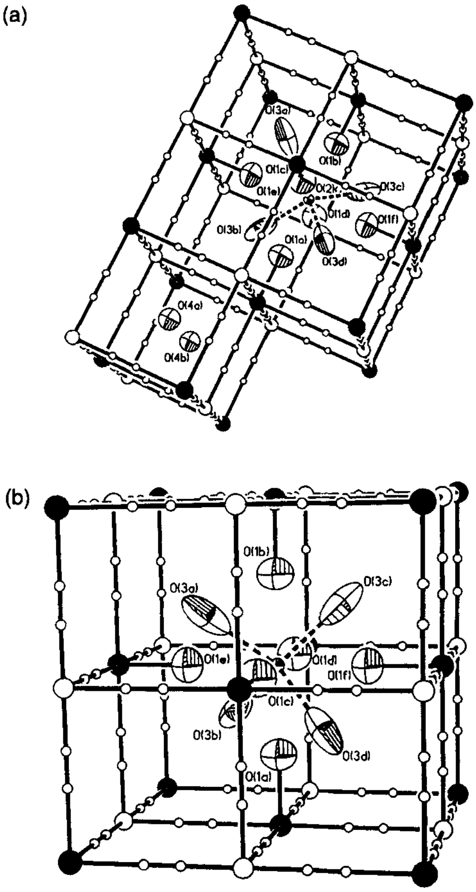

FIGURE 1 (a) A representative view of I, II, and III related to the disordered and ordered portions. (b) A close-up perspective view (from −1/2 to +1/2 along the crystallographic axes) of the arrangement of the oxygen atoms when a $[(Tr/Ir)(CN)6]^{3-}$ counter anion is vacant, causing disorder in the structural lattice. The cyanide groups bridge the cationic atoms and the mixed (Tr/Ir) anionic atoms; O(1) is bonded to the cationic atoms; O(2) is located in the center of the formed cage; O(3) atoms are positioned tetrahedrally about O(2) as depicted in (a) and (b) by connecting the O(3) atoms to O(2) by dash lines; and O(4) water molecules merely occupy interstitial space (zeolitically). The (●) symbol represents the cationic atoms, the (o) symbol represents the carbon and nitrogen atoms, and the (O) symbol represents the (Tr/Ir) anionic atom. The water oxygen atoms (displaced ellipsoidally) are seen at 50% probability.

upon the O···O interatomic contact distances and O–H···O angles, assuming no geometric constraints. Strong H-bonds have O···O lengths of 2.73 Å or less and as the contact distance increases, the H-bonding becomes progressively weaker. Note the different intermoiety oxygen–oxygen contact distances in Table III. Beyond a distance of 3.4 Å, H-bonding is

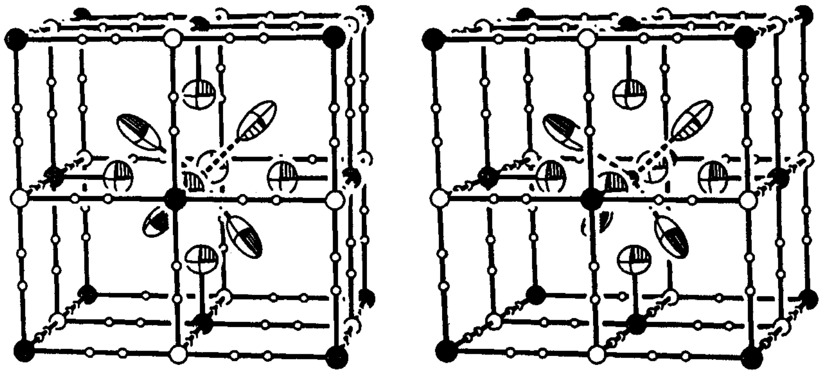

FIGURE 2 A representative stereodrawing (from −1/2 to +1/2 along the crystallographic axes) of **I**, **II**, and **III**.

insignificantly weak. The infrared spectra of **I**, **II**, and **III** lend credence to different degrees of hydrogen bonding (see the Experimental section); strong broad bands at 3400 cm^{-1} with distinct shoulders at 3200 cm^{-1} indicate weak and very weak hydrogen bonding. Further, the I.R. spectra of complexes **I**, **II**, and **III** show three bands in the range of 2100–2200 cm^{-1}. Two extremely sharp narrow bands at 2150 and 2140 cm^{-1} with a distinct shoulder at 2100 cm^{-1} can be assigned to intermetallic linear cyanide bridging and suggest that the cyanide ligands are displaying two coordination modes.[17]

The Cd–O, Co–O, and Pd–O distances of 2.436(1), 2.203(3), and 2.241(1) Å are within range of the summation of the radii of Cd [CN = 6, 0.95(1) Å], Co [CN = 6, 0.74(1) Å], Pd [CN = 6, 0.86(1) Å] and that of oxygen 1.38(1) Å, all obtained from the work of Shannon.[18] The mean C≡N bond length of 1.151(3) Å (range in the three structures, 1.148–1.156 Å) is also in direct accord with the sum of the triple bond radii of C and N atoms (0.603 and 0.55 Å, respectively) found in the work of Pauling.[19] The same holds true for the Cr–C, Co–C, and Ir–C (mean) bond distances in **I**, **II**, and **III**, 1.973(3), 1.944(3) and 1.996(4) Å, respectively, when compared to single bond covalent radii also obtained from the *Nature of the Chemical Bond*,[19] r(Cr, Co, and Ir) + r(C) = 1.95(2), 1.93(2), and 2.04(2) Å. Finally, all bond distances in **I**, **II**, and **III** are in agreement with experimental published values found in the Cambridge Structure Database[20] and in BIDICS.[21]

Interest in these mixed cyanide-bridged complexes will continue due to their possible ability to function as models for evaluating molecule–membrane interactions and molecular transport in permselective membranes. Both selectivity and permeation rate of species of interest can be strongly influenced by molecular structure of exchange host. The development of new materials with such possibilities is always of interest to this research laboratory.

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Supplementary Data

Anisotropic thermal parameters, complete bond distances and angles, and structure factor data for complexes **I**, **II**, and **III** are available from the authors (D.F.M.).

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