JOURNAL OF SOLID STATE CHEMISTRY **140,** 140–144 (1998)
ARTICLE NO. SC987813

BRIEF COMMUNICATION

Structural and Spectral Studies of Two Mixed Anionic (1 : 1) $Cd_3^{II}[(Tr^{III}/Cr^{III})(CN)_6]_2 \cdot 15H_2O$ Complexes (Tr = Co, Fe)

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Received November 11, 1996; in revised form February 12, 1998; accepted February 27, 1998

The crystal structures of (1:1) $Cd_3^{II}[(Co^{III}/Cr^{III})(CN)_6]_2 \cdot 15H_2O$(I) and $Cd_3^{II}[(Fe^{III}/Cr^{III})(CN)_6]_2 \cdot 15H_2O$(II) have been determined by the single-crystal diffraction method. These novel mixed anionic systems crystallize in the cubic space group $Fm\bar{3}m$ (No. 225) with $a_0 = 10.650(2)$ and $10.898(2)$ Å, respectively. The disordered structures contain $1\frac{1}{3}$ molecules in the unit cell. Full-matrix least-squares refinements of I and II yielded final reliability (R) factors of 0.027 ($R_w = 0.034$) and 0.036 ($R_w = 0.045$) with goodness-of-fit (GOF, Σ_2) values of 1.09 and 1.22 based on 146 and 124 unique reflections, respectively. All metal atoms are six-coordinated octahedrally and the cationic divalent Cd atoms are linked to the (1 : 1) mixed metal atoms by cyanide bridging. A hydrogen-bonding network is set up within cavities of the crystal lattices (created by molecular disorder). Powder diffraction data are reported and evaluated according to quantitative figures-of-merit for I and II ($M_{20} = 140.4$ and 205.9, respectively). Thermal gravimetric analysis revealed 15 water molecules per formula unit in each complex. Conoscopic and infrared spectral results, as well as selected bond distances and angles, are presented.

INTRODUCTION

Many divalent metal hexacyanochromates (III) have been studied using powder X-ray diffractometry (1). It was concluded that these compounds belong in either space group $Fm\bar{3}m$ or $F432$ with $Z = 2$. Güdel (2) corrected the number of molecules in the unit cell to $Z = 1\frac{1}{3}$, and a disordered model was developed by Ludi *et al.* (3). X-ray and neutron diffraction investigations of Mn and Cd cobaltihexacyanide dodecahydrates by Beall *et al.* (4) established an improved model and verified that $Z = 1\frac{1}{3}$ and that the space group was $Fm\bar{3}m$. Several synthetic, spectroscopic, and single-crystal structural studies of disordered mixed cationic transition (Tr) hexacyanometallates where *Tr* equals Mn, Co, and Cd have been completed (5). In the past and to our knowledge, mixed anionic hexacyanometallates have not been synthesized or crystallographically analyzed. The very first mixed anionic cyanometallates are (1 : 1) $Mn_3^{II}[(Co^{III}/Cr^{III})(CN)_6]_2 \cdot 14H_2O$ (6) and (1 : 1) $Cd_3^{II}[(Fe^{III}/Co^{III})(CN)_6]_2 \cdot 14H_2O$ (7). These organometallic complexes fit and lend credence to the Beall model (4).

Interest in the rapidly developing field of molecular magnetism (8, 9) due to the use of nanomagnetic materials in information storage has fostered the present study of **I** and **II**, so that crystallographic results may be incorporated into such information storage studies. Research by Sato *et al.* (10) has demonstrated the application of molecular magnetism to molecular electronics. Morphological and structural studies of **I** and **II** are considered necessary for those in the scientific community who tailor molecular compounds for specific applications in magnetic memory devices (8, 9), especially organometallic magnetic materials (11).

EXPERIMENTAL

Clear, cube-like single crystals of **I** and **II** were prepared by the U-tube slow diffusion procedure. 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** and **II** were taken directly from the mother liquors before peripheral studies and single-crystal analyses were performed in order to prevent premature dehydration. Experience has shown that many transition metal cyanide complexes may partially dehydrate when allowed to remain at ambient conditions for any length of time and that some cyanometallates are sensitive to changes in humidity. Thermal dehydration results were obtained on a Perkin-Elmer TGS-1 thermal balance. After many measurements, it was concluded that each complex contained 14.7–14.9 water molecules per formula unit. The instrument was run at 2.5°C min^{-1} while

0022-4596/98 $25.00

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** and **II** are: sharp, free-stretching bands at about 3610 cm^{-1} (unbonded, ν-OH); very strong, broad bands at 3500 cm^{-1} with a distinct shoulder at 3200 cm^{-1} (all related to intermolecular hydrogen bonding, ν-OH); three sharp peaks at 2150, 2140, and 2100 cm^{-1} (ν-C≡N); sharp peaks at 1620 cm^{-1} (δ-HOH); and (Co/Cr)–C and (Fe/Cr)–C bands at approximately 450 cm^{-1}. Powder X-ray diffraction (PXD) patterns were indexed in the cubic space group $Fm\bar{3}m$ with respective resultant cell parameters of 10.6497(9) Å and 10.8989(8) Å (see Table 1). A Siemens Debye-Scherrer cylindrical camera (114.6 mm, 292 K, under vacuum) was employed using Ni-filtered Cu$K\bar{\alpha}$ radiation, $\lambda_{mean} = 1.54184$ Å. The figure-of-merit values for complex **I** are $F_{20} = 82(0.009, 26)$ (12) and $M_{20} = 140.4$ (13) and for complex **II**, $F_{23} = 126(0.007, 25)$, $F_{20} = 128(0.007, 21)$, and $M_{20} = 205.9$.

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 Mo$K\bar{\alpha}$ radiation ($\lambda_{mean} = 0.71073$ Å). Final lattice constants were obtained at high θ angles, $> 20°$. Intensities were measured in the ω–2θ mode at a varied rate of 0.56–5.17° min^{-1} in the 2θ ranges 3.0°–70.0° (h : 0–17, k : 0–12, ℓ : 0–17, for both compounds). Total respective intensity data for **I** and **II** were 767 and 820, of which 172 and 186 were independent and 146 and 124 with $F > 4.0\sigma(F)$ were included in the structure refinements. All intensity data were corrected for Lorentz and polarization effects, after which empirical absorption corrections (14) were applied (min and max transmission factors for **I** and **II**: 0.8841, 0.9995 and 0.9025, 09988, respectively). Examination of the treated data revealed systematic absences (for both **I** and **II**) that are consistent with the cubic space group $Fm\bar{3}m$ (hkℓ: h + k, h + ℓ, k + ℓ = 2n + l; 0kℓ : ℓ = 2n + l; hhℓ : h + ℓ = 2n + l; and h00 : h = 2n + l). The initial metal atomic positions were taken from the structural analysis of $Mn_3(Co/Cr)(CN)_6]_2 \cdot 14H_2O$ (6). Difference Fourier mapping yielded the atomic positions of all other nonhydrogen 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}: 0.027, 0.034, 0.039 for **I** and 0.036, 0.045, 0.075 for **II**) (15). Atomic scattering factors and anomalous-dispersion correction factors for all nonhydrogen atoms were taken from Ibers and Hamilton (16). The resultant atomic coordinates with equivalent isotropic displacement coefficients are given in Table 2. Tables of observed and calculated structure factors are available from the authors (D.F.M.).

TABLE 1
Experimental and Statistical Summaries of I and II

	I	**II**
Empirical formula	$Cd_3CrCoC_{12}N_{12}O_{15}H_{30}$	$Cd_3CrFeC_{12}N_{12}O_{15}H_{30}$
Formula weight	1030.6	1027.5
Crystal system	cubic	cubic
Space group	$Fm\bar{3}m$ (No. 225)	$Fm\bar{3}m$ (No. 225)
Crystal size (mm)	0.115 × 0.164 × 0.197	0.082 × 0.164 × 0.180
a (Å), single crystal	10.650(2)	10.898(2)
a (Å), powder (Cu$K\bar{\alpha}$)	10.6497(9)	10.8998(8)
V ($Å^3$)	1207.9(3)	1294.3(3)
Z	1.3333	1.3333
D_c (g cm^{-3})	1.889	1.755
μ (Mo$K\bar{\alpha}$) (mm^{-1})	2.526	2.301
F(000)	668	665
$\Delta\theta$ range (°)	1.5–35.0	1.5–35.0
R_{int}	0.017	0.040
R (R_w, R_{all})	0.027 (0.034, 0.039)	0.036 (0.045, 0.075)
Unique refl.	146	124
g (e^{-2}) ($\times 10^{-4}$)	8.7(1)	0.8(1)
No. variable para.	19	19
Data-to-para. ratio	7.7 : 1	6.5 : 1
GNFT (Σ_2)	1.09	1.22

TABLE 2
Atomic Coordinated and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^2$) for I and II with esd's in Parentheses

Atoms	Occ.	x	y	z	U_{eq}[a]
$Cd_3[(Co/Cr)(CN)_6]_2 \cdot 15H_2O$ (**I**)					
Cd	1.000	0.000	0.500	0.000	3.3(1)
Co	0.333	0.000	0.000	0.000	1.7(1)
Cr	0.333	0.000	0.000	0.000	3.0(1)
C(1)	0.667	0.000	0.1875(9)	0.000	3.8(2)
N(1)	0.667	0.000	0.293(1)	0.000	11.1(4)
O(1)	0.333	0.000	0.284(2)	0.000	7.0(2)
O(2)	0.333	0.000	0.000	0.000	11.3(9)
O(3)	0.167	0.167(6)	0.167(6)	0.167(6)	25(3)
O(4)	0.667	0.250	0.250	0.250	15.2(7)
$Cd_3[(Fe/Cr)(CN)_6]_2 \cdot 15H_2O$ (**II**)					
Cd	1.000	0.000	0.500	0.000	3.9(1)
Fe	0.333	0.000	0.000	0.000	3.7(1)
Cr	0.333	0.000	0.000	0.000	2.6(1)
C(1)	0.667	0.000	0.1875(9)	0.000	4.2(3)
N(1)	0.667	0.000	0.293(1)	0.000	9.0(5)
O(1)	0.333	0.000	0.284(2)	0.000	7.7(5)
O(2)	0.333	0.000	0.000	0.000	18(1)
O(3)	0.167	0.167(6)	0.167(6)	0.167(6)	22(2)
O(4)	0.667	0.250	0.250	0.250	19(2)

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

RESULTS AND DISCUSSION

One of the goals of this investigation was to ascertain whether other cubic hydrated divalent metal (mixed-anionic)hexacyanometallates (III) conform to the disordered model proposed by Beall *et al.* (5). In particular, since the title compounds (**I** and **II**) have more than 12 water molecules in the formula unit, testing the model's versatility was deemed necessary. This goal has been accomplished; the model accommodates 12 to 15 water molecules quite well. The crystallographic data of $Cd_3^{II}[(Tr^{III}/Cr^{III})(CN)_6]_2 \cdot 15H_2O$ where $Tr = $ Co and Fe best fit the face-centered cubic (fcc) space group $Fm\bar{3}m$ (No. 225) with $Z = 1\frac{1}{3}$. This value of one and one-third molecules per unit cell has been well established by several crystallographic research groups (2–7, 17–19). Measured intensities solve equally well for 14 or 15 water molecules. However, the TGA results (see experimental section) were consistently greater than 14 water molecules per formula unit. Therefore, 15 water molecules were used in the refinements. It is quite clear that the site for O(4) water molecules is the most zeolitic in nature, i.e., humidity-dependent, which is in accordance with the work of Güdel (2). The positional set 8c $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ where water oxygen atoms O(4) are located is the more plausible site for humidity-dependent water molecules (see Table 2). Using an additional occupancy of $\frac{1}{6}$ at this site (8c) permits the addition of one water molecule into the lattice. Table 3 presents bond and contact distances for compounds **I** and **II**.

The divalent cationic atoms (Cd) are six-coordinated octahedrally, as are the (*Tr*/Cr) atoms. Cyanide-bridging oriented with nitrogen atoms toward the Cd atoms (placed in positional set 4c with an occupancy of 1.0) links the metal atom components. For both compounds **I** and **II**, the (*Tr*/Cr) atoms are located at set 4a with an occupancy of $\frac{1}{3}$ for each *Tr* (Co or Fe) and Cr atom (a total of $\frac{2}{3}$ occupancy at this site). Wyckoff position 24e (0, *x*, 0, where *x* is about 0.19 and 0.29) accommodates the carbon and nitrogen atoms, respectively. The lattice of each compound has vacancies and a high degree of disorder (see Figs. 1 and 2). These vacancies form channels by systematic absences of the $[(Tr/Cr)(CN)_6]^{3-}$ counteranions in the structures. When this disorder occurs, oxygen O(1) completes the octahedral arrangement about the Cd 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*/Cr) atoms are normally located (0, 0, 0; 4a). Each atom at the same site 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

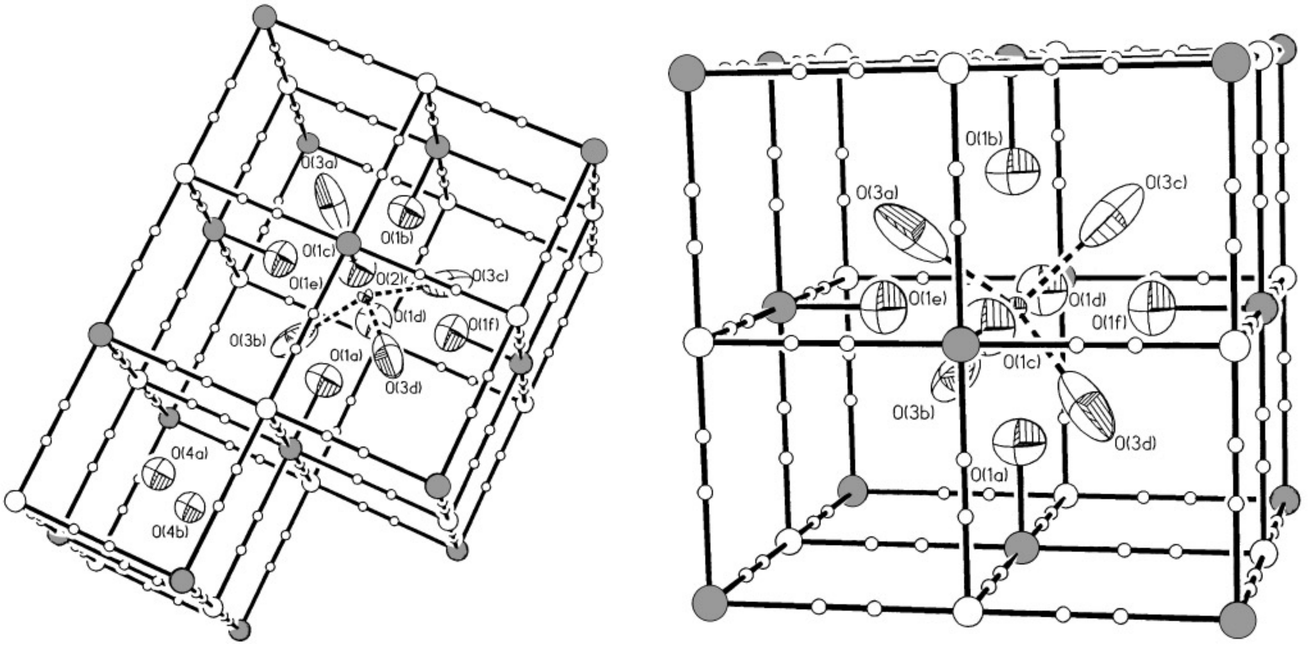

FIG. 1. (a) A representative view of **I** and **II** related to the disordered and ordered portions. (b) A close-up perspective view (from − 1/2 to + 1/2 along the crystallographic axes) of the arrangement of the oxygen atoms when a $[Tr/Cr)(CN)_6]^{3-}$ counter anion is vacant, causing disorder in the structural lattice. The cyanide groups bridge the cationic Cd atoms and the mixed (*Tr*/Cr) anionic 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 (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 Cd atoms, the (○) symbol represents the carbon and nitrogen atoms, and the (◯) symbol represents the (*Tr*/Cr) anionic atom. The water oxygen atoms (displaced ellipsoidally) are seen at 50% probability.

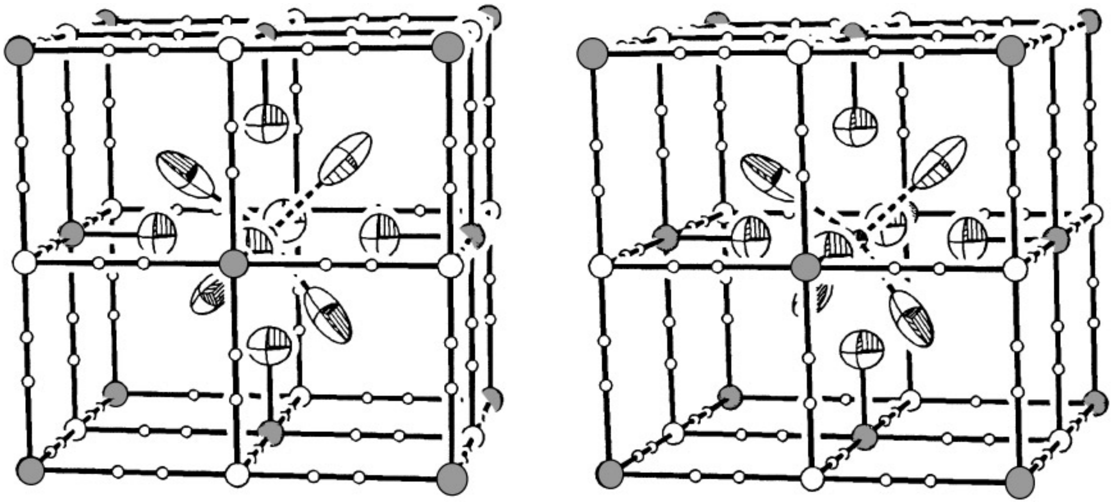

FIG. 2. A representative stereodrawing (from $-\frac{1}{2}$ to $+\frac{1}{2}$ along the crystallographic axes) of **I** and **II**.

occupy interstitial space and are positioned by electrostatic forces. The strength of hydrogen bonds has been shown by Brown (20) to be dependent on the $\mathrm{O}\cdots\mathrm{O}$ interatomic contact distances, assuming no geometric constraints. Strong H-bonds have $\mathrm{O}\cdots\mathrm{O}$ 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 3. Beyond a distance of 3.4 Å, H-bonding with all probability does not exist. The infrared spectra of **I** and **II** lend credence to different degrees of hydrogen bonding (see the experimental section, a strong broad band at 3500 cm^{-1} with a distinct shoulder at 3200cm^{-1}). Further, the IR spectra of the complexes (**I** and **II**) show three bands in the range 2100–2200 cm^{-1}: two extremely sharp, narrow bands at 2150 and 2140 cm^{-1}, which suggest that the cyanide ions are displaying two coordination modes, and a narrow, sharp shoulder at 2100 cm^{-1}, all of which can be assigned to intermetallic linear cyanide bridging (21).

The respective Cd–N and Cd–O bond lengths are 2.264 and 2.339 Å in **I** and 2.259 and 2.360 Å in **II**. The (Tr/Cr) bond distance in **I** is (CO/Cr)–C = 1.915 Å and in **II**, (Fe/Cr)–C = 2.043 Å. The difference in these bond lengths is related to the difference in unit cell parameters. However, the equidistant Tr–C and Cr–C lengths within **I** and **II** are due to the comparable ionic radii of Cr, Fe, and Co (for VI coordination) found in the work of Shannon (22). All bond distances in both compounds are internally consistent (see Table 3) and in agreement with experimentally determined distances found in BIDICS (23) and the Cambridge Structure Data Center (24). Specifically, the cyanide bond lengths (in **I** and **II**) are in very good agreement with the summation of the involved triple bond radii of carbon (0.603 Å) and nitrogen (0.55 Å) atoms found in the work of Pauling (25). Crystallographic and spectroscopic studies dealing with mixed solid systems (cationic and/or anionic) are in progress and will continue in this group, since such systems have become of great interest to the scientific community at large in many areas.

TABLE 3
Bond and Contact Distances (Å) for I and II with esd's in Parentheses

$Cd_3[(CO/Cr)(CN)_6]_2 \cdot 15H_2O$ (**I**)		$Cd_3[(Fe/Cr)(CN)_6]_2 \cdot 15H_2O$ (**II**)	
Cd–N	2.264(9)	Cd–N	2.259(9)
Cd–O(1)	2.339(13)	Cd–O(1)	2.360(15)
Co–C	1.915(7)	Fe–C(1)	2.043(2)
Cr–C	1.915(7)	Cr–C	2.043(9)
C–N	1.146(11)	C–N	1.146(15)
O(1)–O(2)	2.99(2)	O(1)–O(2)	3.09(2)
O(1)–O(3)	2.94(4)	O(1)–O(3)	2.87(5)
O(2)–O(3)	3.4(1)	O(2)–O(3)	3.1(1)
O(3)–N	2.96(4)	O(3)–N	2.91(5)
O(4)–N	> 4.0	O(4)–N	> 4.0

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of this research, in part, by the Robert A. Welch Foundation (Grant AA-0668) and the Baylor Research Committee.

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