

Synthesis, Peripheral Studies, and Structural Investigation of (1 : 1) $Mn_3^{II}[(Co^{III}/Cr^{III})(CN)_6]_2 \cdot 14H_2O$

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The crystal structure of (1 : 1) $Mn_3^{II}[(Co/Cr)(CN)_6]_2 \cdot 14H_2O$ has been determined by single-crystal diffractometry and refined by the full-matrix least-squares method to yield $R = 0.030$ and $R_w = 0.036$ based on 114 unique reflections. This first studied mixed anionic hexacyanide crystallizes in the cubic system (space group $Fm\bar{3}m$, No. 225) with $a = 10.470(1)$ Å. The disordered structure contains $1\frac{1}{2}$ molecules in the unit cell. The experimental density is $1.61(1)$ $Mg\ m^{-3}$ (calculated, 1.620 $Mg\ m^{-3}$). A thermal gravimetric analysis yielded 13-14 water molecules per formula unit. All metal atoms are six-coordinated octahedrally and linkage between the cationic and the (1 : 1) mixed anionic metals is accomplished by cyanide bridging. Conoscopic and infrared spectral results are presented as well as important bond and contact distances. © 1994 Academic Press, Inc.

INTRODUCTION

Structure analyses of solid solutions of mixed cation metal complex cyanides have become of basic interest since it may be possible to tailor the local crystal-field strength at the metal sites. Control of magnetic, optical, and other properties related to these mixed systems may then be achieved. Further, cyanide complexes of the lanthanide and transition series, as well as of mixed metal systems, exhibit zeolitic and characteristic sieving properties; some are electron scavengers, ion exchangers, and radionuclide sorbents used in nuclear waste management (1, 2).

The first double salt ferrocyanide containing a lanthanide atom, $CeKFe(CN)_6$, was prepared in 1909 by Robinson (3). This work was followed by that of Prandtl and Mohr (4), who synthesized several double salts of alkali-lanthanide ferrocyanides, where the alkali metals were sodium and potassium. Studies of the zeolitic properties of ferrocyanides of the transition (*Tr*) metals were conducted by Seifer (5-7). His work included X-ray powder diffraction analyses of the double salt compounds. However, the most widely studied polycyanides are the hexacyanides (prussides) of the transition elements. Within many of these compounds, channels are formed

by the systematic vacancies of the $[Tr^{III}(CN)_6]^{3-}$ counteranions in the structure lattices. Their pore sizes are ca. 6×9 Å (8). Such is the case for $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$ (9).

Wyckoff (10) has described members of the $A^{II}[B^{III}(CN)_6]_2 \cdot xH_2O$ type to be cubic and face-centered. Many divalent metal hexacyanochromates (III) were studied by Ferrari *et al.* (11) using X-ray powder diffraction. This group concluded that there were two molecules in the unit cell of $Cd_3[Cr(CN)_6]_2$ hydrate and that the space group was $Fm\bar{3}m$ or $F432$. The value of $Z = 2$ was later corrected by Güdel (12) and Milligan *et al.* (9) to $Z = 1\frac{1}{2}$ and the space group was also defined by the latter as $Fm\bar{3}m$. Studies of this isostructural series and current interest in mixed transition metal systems, focused on morphological and structural investigations, have sparked interest in studying not only mixed cationic systems but also mixed anionic hexacyanides. To our knowledge the title compound, $Mn_3^{II}[(Co^{III}/Cr^{III})(CN)_6]_2 \cdot 14H_2O$, is the first mixed anionic system ever to be crystallographically analyzed.

EXPERIMENTAL

Clear cube-shaped single crystals of the title compound were prepared by the U-tube slow diffusion method. Starting materials [$MnCl_2$, $K_3Co(CN)_6$, and $K_3Cr(CN)_6$] were purchased commercially (reagent grade) and were used without further purification. Dilute solutions (0.01M) of each of the interdiffusing constituents were prepared with triply distilled water. Synthesis and preliminary analyses were carried out at 292 K. The flotation method using bromobenzene and 1,1,2,2-tetrabromoethane was employed to determine the experimental density, $1.61(1)$ $Mg\ m^{-3}$ (calc. 1.620 $Mg\ m^{-3}$). A Perkin-Elmer TGS-1 thermobalance run at $2.5^\circ C\ min^{-1}$ while being purged with nitrogen (flow rate $25-30\ cm^3\ min^{-1}$) was used for the thermal analysis. After several runs, the thermal dehydration result showed that between 13 and 14 water molecules per formula unit were lost. An infrared spectroscopic study using the pressed KBr pellet technique over a frequency range of $4000-400\ cm^{-1}$ was carried out on a Mattson

TABLE 1
Experimental and Statistical
Data Summary

System	Cubic
Space group	<i>Fm</i> $\bar{3}$ <i>m</i> (No. 225)
<i>a</i> /Å	10.470(1)
<i>V</i> /Å ³	1147.7
<i>M</i> _r	840.17
<i>Z</i>	1.3333
<i>D</i> _o /Mg m ⁻³	1.61(1)
<i>D</i> _c /Mg m ⁻³	1.620
<i>F</i> (000)/e ⁻	563
μ (MoK α)/mm ⁻¹	1.869
Transmission range	
min.	0.900
max.	1.233
$\Delta\theta$ /°	1.5–35.0
<i>T</i> /K	292
Unique refl.	114
<i>R</i> _{int}	0.019
<i>R</i> (<i>R</i> _w)	0.030(0.036)
<i>g</i> /(10 ⁻⁶ e ⁻²)	6.5(2)
Goodness of fit (Σ_2)	2.14
Residual density/e Å ⁻³	
min.	-0.231
max.	0.128
Shift/error	
max./(10^{-3})	1.19
avg./(10^{-4})	4.90

Fourier transform IR instrument. The spectrum displayed the following relevant absorption peaks: a sharp free OH stretching band at 3650 cm⁻¹, a very broad and strong band at 3422 cm⁻¹ with a shoulder (broad) at approximately 3200 cm⁻¹ (both ν -OH, H-bonding), a very sharp peak at 2164 cm⁻¹ (ν -C \equiv N), a sharp peak at 1611 cm⁻¹ (δ -HOH), and a (Co/Cr)-C bonding band at 450 cm⁻¹. Crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II was used in a conoscopic examina-

tion of single crystals of the title compound. The study provided evidence that the single crystals were not twinned and that the crystals were optically isotropic in nature (a cubic system).

A cube-like crystal (prism dimensions 0.15 × 0.21 × 0.18 mm) selected on the basis of optical homogeneity was placed in a capillary and mounted on a Enraf-Nonius CAD4-F autodiffractometer which was equipped with a dense graphite monochromator, takeoff angle of 5.8° (MoK α , 0.71073 Å, 292 K). The orientation matrix used for data collection and the initial cell parameters (final lattice constant at high θ angles, >20°) were obtained from a least-squares refinement of 25 randomly selected and accurately centered reflections. Measured intensities of the data were collected by the ω -2 θ scan technique at a scan speed of 0.41–3.44° min⁻¹ in ω , determined by a fast prescan of 3.44° min⁻¹. Data were collected in the range 3.0 < 2 θ < 70.0° at a varied scan width of 1.10° + 0.344 tan θ . The crystal stability and electronic hardware reliability were verified by monitoring three check reflections as a function of time every 2 hr of exposure time (< 2.0% deviation). Reflections having less than 75 counts above background during the prescan were deemed unobserved. Lorentz and polarization corrections, as well as an empirical absorption correction (13), were applied to the collected data set; see Table 1 for transmission range. A total of 2845 intensity measurements was collected (*h*: 0 → 16, *k*: 0 → 16, *l*: 0 → 16). After averaging (*R*_{int} = 0.019), 165 were independent and 114 with *F* > 6.0 σ (*F*) were retained and used in the full-matrix least-squares refinement (14). Experimental and statistical data are summarized in Table 1.

Examination of the reduced and averaged data revealed systematic absences which are consistent with space group *Fm* $\bar{3}$ *m* (*hkl*: *h* + *k*, *h* + *l*, *k* + *l* = 2*n* + 1; 0*kl*: *l* = 2*n* + 1; *hhl*: *h* + *l* = 2*n* + 1; and *h*00: *h* = 2*n* + 1). An *N*(*Z*) cumulative probability distribution test provided

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters
(Å² × 10³) with ESD's in Parenthesis

Atom	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Mn	1.000	0.5	0.5	0.5	3.12(3)
Co	0.333	0.0	0.0	0.0	2.02(6)
Cr	0.333	0.0	0.0	0.0	1.31(6)
C	0.667	0.0	0.0	0.1815(3)	3.0(2)
N	0.667	0.0	0.0	0.2921(4)	10.2(4)
O(1)	0.333	0.0	0.0	0.276(1)	6.5(6)
O(2)	0.333	0.0	0.0	0.0	24(4)
O(3)	0.167	0.208(3)	0.208(3)	0.208(3)	16(1)
O(4)	0.500	0.25	0.25	0.25	15(3)

^a Equivalent isotropic thermal parameter (*U*(eq)) is defined as one-third the trace of the orthogonalized *U*_{ij} tensor.

further evidence of centrosymmetric symmetry. Initial metal atomic positions were taken from the work of Milligan *et al.* (9). Difference Fourier mapping revealed the location of all other nonhydrogen atoms. Several cycles of refinement while varying the anisotropic thermal parameters and applying a secondary extinction correction (*g*) yielded final residual index factors and the "goodness-of-fit" value (Σ_2). The reliability factors are defined as $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ and $R_w = \frac{\sum \sqrt{w} ||F_o| - |F_c||}{\sum \sqrt{w} |F_o|}$, where *w* (the weighting factor) is specified as $\sigma^{-2}(|F_o|)$. The largest and mean shift/error values were 1.2×10^{-3} and 4.9×10^{-4} , respectively. A final difference Fourier map was virtually featureless, revealing only a random fluctuating background; see Table 1. Atomic scattering factors for all atoms and their anomalous-dispersion corrections were taken from the work of Ibers and Hamilton (15). The resultant atomic positions and equivalent isotropic displacement coefficients are given in Table 2. Tables of observed and calculated structure factors are available from D.F.M.

DISCUSSION

The crystallographic data of (1:1) $\text{Mn}_3[(\text{Co}/\text{Cr})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ best fit a face-centered cubic lattice, space group No. 225 (*Fm3m*), with one and one-third formula units per cell. This value of $Z = 1\frac{1}{3}$ has been well established by several groups (9, 12, 16–19) for similar transition metal hexacyanides. The structural model proposed by Beall *et al.* (18) can accommodate 12 to 15 water molecules quite well. The collected intensity data solve equally well for 13 or 14 water molecules, slightly better

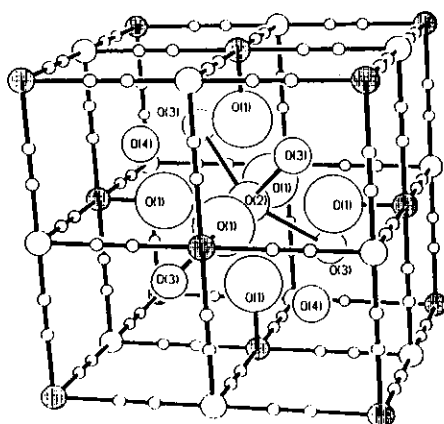


FIG. 1. A perspective view, from $-\frac{1}{2}$ to $+\frac{1}{2}$ along the crystallographic axes, of the arrangement of the oxygen atoms when the $[(\text{Co}/\text{Cr})(\text{CN})_6]^{3-}$ counter anion in the structural lattice is vacant. The cyanide bridges between the cationic (Mn) metal atoms and the mixed (Co/Cr) anionic metal atoms; O(1) is bonded to the Mn atoms; O(2) is located in the center of the formed cage; O(3) is positioned tetrahedrally about O(2), as depicted by connecting the O(3) atoms to O(2) which are not bonded; and O(4) merely occupies interstitial space.

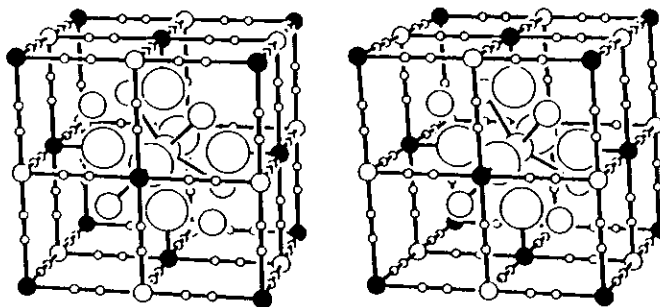


FIG. 2. A stereoscopic drawing, from $-\frac{1}{2}$ to $+\frac{1}{2}$ along the crystallographic axes, of (1:1) $\text{Mn}_3[(\text{Co}/\text{Cr})(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$.

for the latter but not significantly so, according to the Hamilton \mathcal{R} significance test (20). However, since our thermal gravimetric analysis results were consistently greater than 13 water molecules per formula unit, 14 water molecules were used in the refinement. The variation between 13 and 14 water molecules was attributed to humidity dependence, which is in accord with the work of Güdel (12). The positional set $8c (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, where O(4) is located, is the more plausible site for a humidity dependent water molecule.

The lattice shows random vacancies and a high degree of disorder. A depiction of the disorder is seen in Figs. 1 and 2. The vacancies form channels by the systematic absences of the $[(\text{Co}/\text{Cr})(\text{CN})_6]^{3-}$ counteranions in the structural lattice. When this occurs, oxygen O(1) completes the octahedral coordination about the Mn atoms and a network of hydrogen bonding is set up. Oxygen O(2) is located in the center of the cavity where the mixed (Co/Cr) atoms would normally be found (0, 0, 0; Wyckoff position 4a). O(3) is tetrahedrally arranged about O(2) and O(4) occupies interstitial space. Note that the intermolecular oxygen–oxygen contact distances are significantly different. The $\text{O}(1) \cdots \text{O}(2)$ and $\text{O}(1) \cdots \text{O}(3)$ distances are 2.895(8) and 3.157(8) Å, respectively. This difference can be attributed to different degrees of hydrogen bonding. The strength of a hydrogen bond has been shown by Brown (21) to be dependent upon the $\text{O} \cdots \text{O}$ interatomic distances, assuming no geometric constraints. Strong hydrogen bonds have $\text{O} \cdots \text{O}$ contact distances of 2.73 Å or less. However, as the contact distance increases, the hydrogen bonding becomes progressively weaker and beyond an $\text{O} \cdots \text{O}$ distance of 3.3–3.4 Å, H-bonding does not exist. The IR results (mentioned in the experimental section) also suggest the presence of two different strengths of hydrogen bonding. The strong, broad band at 3422 cm^{-1} attests to hydrogen bonding, while the broad shoulder located approximately at 3200 cm^{-1} may be associated with weaker H-bonding [$\text{O}(1) \cdots \text{O}(3)$]. No hydrogen bonding is present between $\text{O}(2) \cdots \text{O}(3)$ or $\text{N} \cdots \text{O}(3,4)$. It appears that since O(4) is completely out

TABLE 3
Bond and Contact Distances (Å) with ESD's
in Parenthesis

Mn-N	2.177(6)	O(1)-O(2)	2.895(8)
Co-C	1.900(3)	O(1)-O(3)	3.157(8)
Cr-C	1.900(3)	O(2)-O(3)	3.764(8)
C-N	1.159(3)	O(3)-N	3.755(8)
Mn-O(1)	2.340(6)	O(4)-N	3.728(8)

of hydrogen bonding range (>3.8 Å from its nearest neighbor), the water molecule associated with O(4) is positioned by electrostatic attraction.

Table 3 lists the bond and contact distances for the title compound. All bond lengths are internally consistent and in good agreement with experimental values published in the Cambridge Structure Data Centre (22) and in BIDICS (23). Specifically, the C≡N bond length of 1.159(3) Å is in especially 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 (24). Finally, since mixed systems are becoming of great interest in many areas of the scientific community, it has been deemed necessary to continue synthesizing and structurally analyzing mixed cyanide complexes of both the transition and lanthanide series.

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