

Synthesis, Spectroscopic, and Structural Studies of Two Mixed Transition Metal Complexes

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The crystal structures of the mixed transition-metal nitrosylpentacyanoferrate trihydrates have been determined from three-dimensional single-crystal X-ray diffraction data. These polynuclear cyanides crystallize in the monoclinic space group $P2_1/n$ ($Z = 4$) with lattice parameters of $a = 7.385(1)$, $b = 14.905(3)$, $c = 10.810(2)$ Å, $\beta = 91.54(2)^\circ$; and $a = 7.4109(3)$, $b = 14.9430(9)$, $c = 10.8423(6)$ Å, $\beta = 91.570(4)^\circ$ for 1:1 (Cd/Mn) and 1:1 (Cd/Zn)[Fe(CN)₅NO] · 3H₂O, respectively. The final least-squares full-matrix refinements, based on 1978 and 2026 unique reflections, yielded reliability factors equal to 0.048 and 0.044, respectively. The mixed cation centers are six-coordinated, with five cyanide ligands and one water molecule in an octahedral arrangement. The Fe atoms also display octahedral symmetry with five cyanide ligands and one nitrosyl group. The distorted octahedral metal centers, which are geometrically arranged in a staggered fashion, are united by cyanide bridging. Two of the three water molecules which are uncoordinated occupy channels in the crystal lattice and are held in position by hydrogen bonding to the coordinated water molecule, O(1). Important bond distances and angles are presented and appropriately discussed. Conoscopic, infrared, thermogravimetric, and crystallographic results are reported. © 1993 Academic Press, Inc.

Introduction

The continuation of a general study of series of isomorphous complex cyanides of the transition and lanthanide metals is viewed from both fundamental and practical points of view. It is of basic interest since it is possible to investigate the structural chemistry of the entire transition and lanthanide series in the hexacyanide and nitrosylpentacyanide forms. Solid solutions of "mixed cation metal crystals" for both systems can be formed over a wide range of mixed transition and/or rare-earth compositions. Within certain limits, this suggests that it may be possible to tailor the local crystal-field strength at the metal sites and in that connection, control the magnetic, optical, and other properties related to mixed forms. From a practical point of view, these materials exhibit zeolitic and characteristic

sieving properties which have been applied as cation exchangers, electron scavengers, and as radionuclide sorbents in nuclear waste management (1, 2).

The first citation in the literature which dealt with the chemistry of sodium nitroprusside was by Playfair (3) in 1848. The structural analysis of this compound was not done until 1963 (4) after which many of groups I and II nitroprussides were studied by means of single-crystal diffractometry. Interest in other metal nitrosylpentacyanoferrates brought about a series of spectral and X-ray powder diffraction studies. For transition metal salts of the formula $M^{II}[\text{Fe}(\text{CN})_5\text{NO}] \cdot n\text{H}_2\text{O}$, where $M^{II} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Zn}$, the compounds were classified as face-centered cubic and that of the Cu^{II} analogue was categorized as a primitive cubic or tetragonal unit cell (5). Recently, it was found that $\text{Zn}[\text{Fe}$

(CN)₅NO] · 3H₂O crystallized in the rhombohedral space group $R\bar{3}$ on a hexagonal lattice, that Fe[Fe(CN)₅NO] · 3H₂O crystallized in the monoclinic space group $P2_1/n$, that Cu[Fe(CN)₅NO] · 2H₂O crystallized in the orthorhombic space group $Pnma$, and that only Co[Fe(CN)₅NO] · 5H₂O crystallized in the face-centered cubic space group $Fm\bar{3}m$ (6–9).

The most widely studied polycyanides are the prussides (hexacyanides). Within many of the transition metal hexacyanides, channels are formed by systematic vacancies of the [Fe(CN)₆]³⁻ counteranion in the structure lattice, pore sizes of ca. $6 \times 9 \text{ \AA}$ (10). However, in the case of the nitroprussides, transition metal complexes generally possess no vacancies. Channels in these compounds are the result of unbridged nitrosyl groups (6) and the formed channels are considerably smaller ($\sim 5.2 \times 5.4 \text{ \AA}$) than those of the hexacyanides. This phenomenon offers a greater selectivity in the separation of small molecules (i.e., when employing these compounds as molecular sieves). Current interest in mixed transition and lanthanide metal systems, focused upon morphological and structural investigations, has prompted this work.

Experimental

Clear light-red crystals of Cd_{0.5}Mn_{0.5}[Fe(CN)₅NO] · 3H₂O (**I**) and Cd_{0.5}Zn_{0.5}[Fe(CN)₅NO] · 3H₂O (**II**) were synthesized using the proper stoichiometric amounts of commercially obtained (analytical reagent grade) CdCl₂, MnCl₂, ZnCl₂, and Na₂[Fe(CN)₅NO] · 2H₂O. The "slow-diffusion U-tube" method was employed. As a precaution, the diffusion tube apparatuses were stored in the dark and after two to three months of aging, crystals large enough for single-crystal analysis were observed. Experience has proven that many of the transition metal nitrosylpentacyanides cannot be air dried or remain undamaged at ambient conditions for any length of time. Consequently, after harvesting, crystals of **I** and **II** were stored in the mother liquor in order to prevent premature dehydration. The thermal dehydrations of the studied compound were determined by employing a Perkin-Elmer TGS-1 thermobalance at a rate of $2.5^\circ\text{C min}^{-1}$ from 25 to 225°C. The thermogravimetric analyses (TGA) yielded a loss of three water molecules per formula unit for each freshly harvested compound. For each crystal system, dehydration occurred stepwise. One water molecule was lost al-

TABLE I
INFRARED FREQUENCIES FOR 1:1 (Cd/Mn) AND 1:1 (Cd/Zn)Fe(CN)₅NO · 3H₂O

Assignment	1:1 (Cd/Mn)Fe(CN) ₅ NO · 3H ₂ O Wavenumber (cm ⁻¹) ^a	1:1 (Cd/Zn)Fe(CN) ₅ NO · 3H ₂ O Wavenumber (cm ⁻¹) ^a
O—H (ν)	3660	3665
	3600	3620
O—H (ν)	3312	3316
Intermolecular H-bonding	3211	3233
C≡N (ν)	2176	2182
N=O (ν)	1949	1950
H—O—H (δ)	1604	1605
H—O—H (L)	764 br,w	760 br,w
Fe—NO (δ)	669	669
Fe—NO (ν)	651	652
Fe—CN (δ)	512	515
Fe—CN (ν)	442	441
	429	427

^a br = broad, w = weak, L = libration.

TABLE II
CRYSTAL, EXPERIMENTAL, AND STATISTICAL DATA SUMMARIES

	1:1 (Cd/Mn)Fe(CN) ₅ NO · 3H ₂ O	1:1 (Cd/Zn)Fe(CN) ₅ NO · 3H ₂ O
Lattice type	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.385(1)	7.4109(3)
<i>b</i> (Å)	14.905(3)	14.9430(9)
<i>c</i> (Å)	10.810(2)	10.8423(6)
β (°)	91.54(2)	91.570(4)
<i>V</i> (Å ³)	1189.5(4)	1200.2(1)
<i>M_r</i>	353.7	358.9
<i>Z</i>	4	4
<i>D_x</i> (Mg m ⁻³)	1.974	1.986
Crystal size (mm ³)	0.52 × 0.57 × 0.62	0.44 × 0.51 × 0.57
<i>F</i> (000) (<i>e</i> ⁻)	690	700
μ (Mo <i>K</i> α) (mm ⁻¹)	2.633	3.128
<i>g</i> (<i>e</i> ⁻²) (10 ⁻⁴)	2.9(6)	3.2(5)
$\Delta\theta$ (°)	1.5–25.0	1.5–25.0
Unique refl.	1978	2026
<i>R_{int}</i>	0.051	0.012
<i>R</i>	0.048	0.044
<i>R_w</i> (<i>R_{all}</i>)	0.069(0.050)	0.072(0.046)
<i>Gofit</i> (Σ_2)	1.82	2.23
Absorption correction		
Maximum	1.355	1.107
Minimum	0.798	0.870
Residual density (<i>e</i> ⁻ Å ⁻³)		
Maximum	1.44	1.78
Minimum	-0.76	-1.54

most immediately (monodehydration) and, as the temperature was increased, the two remaining water molecules were lost. After this observation, it was obvious that single crystals of **I** and **II** would have to be placed in glass capillaries with their mother liquor for X-ray analysis. Infrared spectroscopic analyses (pressed KBr/sample pellet) were carried out on a Mattson Fourier Transform IR instrument (range, 4000 to 400 cm⁻¹); see Table I for absorption results. Conoscopic examination of **I** and **II**, using crystal rotation between two crossed polarizers on a Zeiss photomicroscope, verified the optical quality and the biaxial nature of the systems and negated the possibility of high symmetry; i.e., cubic, tetragonal, rhombohedral, and hexagonal, but not orthorhombic which is refuted later.

An optically pure single crystal of each

mixed transition-metal nitroprusside was placed in a glass capillary and mounted on an automated X-ray diffractometer (Enraf-Nonius CAD4-F) which is equipped with a dense graphite monochromator, take-off angle 5.8° (Mo *K* α radiation, $\lambda_{\text{mean}} = 0.71073$ Å). The orientation matrices used for data collections (experimental temperature, 292 K) resulted from least-squares refinements of 25 randomly selected and accurately centered reflections in each data set. Final unit-cell parameters were obtained at high θ angles, >20°. The crystal lattice constants and other pertinent experimental and statistical data are presented in Table II. Measured intensities were collected by the ω -2 θ scan technique at a scan rate of 0.49–3.44° min⁻¹ in ω . Data for each compound were collected in the range of 3.0 < 2 θ < 50.0° at a varied scan width of 1.20 +

0.34 $\tan \theta$. All reflections having less than 75 counts above background during the fast prescan ($3.44^\circ \text{ min}^{-1}$) were assumed to be unobserved. No significant variations were observed in the intensities of the monitored standards (every 2 hr of exposure time). Hence, the reliability of the electronic hardware and crystal stability were verified. Lorentz and polarization corrections were applied to each data set as well as empirical absorption corrections. For the respective subject compounds, 2361 and 2376 reflections were collected (h ; $0 \rightarrow 8$; k ; $0 \rightarrow 17$; l ; $-12 \rightarrow 12$, for both). After averaging the data from each set, 1978 and 2026 reflections with $F > 6.0\sigma(F)$, respectively, were retained and used in the full-matrix least-squares refinements (11). Reflection conditions ($h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$) in each system were consistent with space group $P2_1/n$. In addition, an $N(Z)$ cumulative probability distribution test applied to each data set provided further evidence of centrosymmetry.

Crystallographic analyses of the reduced and averaged data employing SHELXTL-PC (11) yielded the initial location of the mixed transition metals and the octahedral framework associated with the iron centers. Difference Fourier maps of the remaining residual electron density revealed the locations of all other nonhydrogen atoms in both structures. Full-matrix least-squares method (11) was used to refine the monoclinic model for both compounds. Several cycles varying the anisotropic thermal parameters and applying secondary extinction corrections (g) yielded final reliability factors and "goodness-of-fit" values (G_{of} , Σ_2) found in Table II. The residual index factors are defined as $R = \Sigma \Delta F / \Sigma |F_0|$ and $R_w = \Sigma \sqrt{w} \Delta F / \Sigma \sqrt{w} |F_0|$, where ΔF equals $||F_0| - |F_c||$ and the weighting factor w is specified as $\sigma^{-2}(|F_0|)$. Σ_2 is expressed as $[\Sigma w(|F_0| - |F_c|)^2 / (N_0 - N_{\text{vp}})]^{1/2}$, where N_0 and N_{vp} are the number of independent observations and varied parameters, respectively. It should be mentioned that the multiplicities of the mixed transition metal atoms were

refined and that each of the refined occupancies did not deviate appreciably from the set values of one-half, see Table III. Final difference Fourier maps revealed some density in the vicinity of the mixed metal centers, elsewhere only random fluctuating background density was observed. Atomic scattering factors with related anomalous dispersion correction factors were obtained from the usual source (12). Final atomic coordinates with isotropic equivalent thermal parameters are given in Table III. Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the authors (DFM).

Discussion

Both mixed transition-metal (M) nitrosyl-pentacyanoferrate trihydrates crystallize in the monoclinic space group $P2_1/n$ (No. 14, C_{2h}^5) and are structurally isomorphic with $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$ (7). There are four molecules in the unit cell. Experimental bond and contact distances and bond angles for **I** and **II** are listed in Tables IV and V, respectively. The data were tested using the program MISSYM (13) which verified that no additional symmetry was present. This eliminated any possibility of the data fitting an orthorhombic lattice. Figure 1 is a representative view of **I** and **II**. The iron centers are coordinated octahedrally by five cyanide ligands and one nitrosyl group. The mixed metal centers are also six-coordinated by five cyanide ligands and one water molecule in an octahedral manner. The distorted octahedral metal centers, which are geometrically arranged in a staggered fashion, are linked by cyanide bridging; $\text{M}-\text{N}\equiv\text{C}-\text{Fe}$ is nonlinear. Tunnel-like channels in the crystal lattice are formed by the geometric arrangement of the coordinated water molecules and the bonded nitrosyl groups. The two uncoordinated water molecules, O(2) and O(3), are found within the formed channels and are hydrogen-bonded to the coordinated water molecules and possibly to the nitrosyl groups (see Fig. 2).

TABLE III
FRACTIONAL ATOMIC COORDINATES ($\times 10^3$) AND EQUIVALENT ISOTROPIC THERMAL
PARAMETERS ($\times 10^4$) FOR I AND II

Atoms	Occupancy	x	y	z	$U_{eq}(\text{\AA}^2)^a$
I					
Cd	0.51(1)	7552(1)	3367(1)	3172(1)	11(1)
Mn	0.50(1)	12663(2)	6724(1)	6810(1)	11(1)
Fe	1.00	7528(1)	4218(1)	7956(1)	21(1)
N(1)	1.00	10465(7)	5601(3)	7335(5)	38(1)
N(2)	1.00	4643(6)	2736(3)	8118(5)	34(1)
N(3)	1.00	10415(6)	2768(4)	8568(5)	39(1)
N(4)	1.00	4689(6)	5575(3)	6976(5)	34(1)
N(5)	1.00	7772(6)	3650(3)	5242(5)	35(1)
C(1)	1.00	9396(7)	5081(3)	7576(5)	27(1)
C(2)	1.00	5717(7)	3285(3)	8077(6)	23(1)
C(3)	1.00	9339(8)	3311(3)	8340(6)	25(1)
C(4)	1.00	5735(6)	5050(3)	7323(5)	25(1)
C(5)	1.00	7717(7)	3853(4)	6253(4)	23(1)
N	1.00	7348(6)	4579(3)	9383(5)	30(1)
O	1.00	7222(7)	4870(3)	10368(4)	55(1)
O(1)	1.00	6683(6)	3018(3)	1166(4)	48(1)
O(2)	1.00	2918(8)	3401(3)	923(6)	67(2)
O(3)	1.00	2541(8)	3709(4)	5345(7)	92(2)
II					
Cd	0.50(1)	7557(1)	3378(1)	3178(1)	6(1)
Zn	0.50(1)	12640(1)	6725(1)	6818(1)	10(1)
Fe	1.00	7527(1)	4220(1)	7963(1)	20(1)
N(1)	1.00	10465(6)	5587(3)	7339(5)	39(1)
N(2)	1.00	4660(6)	2736(3)	8115(5)	37(1)
N(3)	1.00	10402(7)	2773(4)	8595(5)	42(1)
N(4)	1.00	4702(6)	5569(4)	6954(5)	38(1)
N(5)	1.00	7776(6)	3655(4)	5249(4)	36(1)
C(1)	1.00	9359(6)	5085(3)	7591(5)	26(1)
C(2)	1.00	5707(7)	3289(3)	8069(6)	21(1)
C(3)	1.00	9349(7)	3331(3)	8340(6)	25(1)
C(4)	1.00	5764(6)	5048(3)	7316(5)	24(1)
C(5)	1.00	7724(6)	3857(4)	6256(4)	24(1)
N	1.00	7330(6)	4580(3)	9396(4)	31(1)
O	1.00	7156(7)	4860(4)	10371(4)	63(1)
O(1)	1.00	6670(7)	3025(3)	1169(4)	50(1)
O(2)	1.00	2886(8)	3406(3)	922(6)	66(1)
O(3)	1.00	2562(7)	3706(5)	5378(6)	88(1)

^a Isotropic equivalent thermal parameter (U_{eq}) is defined as one-third the trace of the orthogonalized U_{ij} tensor.

For the mixed (Cd/Mn) nitroprusside, the averaged bond distance M–N of 2.28(2) Å is quite reasonable when considering the summation of the radii of the involved atoms (in proper ratios) and the nitrogen atom found in the work of Shannon (14), 2.27 Å. The averaged M–N distance in the (Cd/Zn)

nitroprusside is 2.30(1) Å, which is also in very good agreement with that of Shannon (14), 2.30 Å. In both compounds, the averaged bond distances of Fe–C, 1.933(7) Å, and C≡N, 1.149(12) Å, as well as the bond distances of Fe–N, 1.648(6) Å, and N=O, 1.152(4) Å, are in good agreement with pub-

TABLE IV
 INTERATOMIC BOND AND CONTACT DISTANCES (Å) AND BOND ANGLES (°) FOR
 1: 1-(Cd/Mn)Fe(CN)₅NO · 3H₂O

<i>M</i> ^a —N(1)	2.306(6)	Fe—C(1)	1.938(5)
<i>M</i> —N(2)	2.268(6)	Fe—C(2)	1.937(5)
<i>M</i> —N(3)	2.257(6)	Fe—C(3)	1.939(5)
<i>M</i> —N(4)	2.282(6)	Fe—C(4)	1.926(5)
<i>M</i> —N(5)	2.290(5)	Fe—C(5)	1.929(5)
<i>M</i> —O(1)	2.283(6)	Fe—N	1.642(5)
N(1)—C(1)	1.142(7)	N—O	1.156(7)
N(2)—C(2)	1.141(7)		
N(3)—C(3)	1.156(7)	O(1)—O(2)	2.844
N(4)—C(4)	1.155(7)	O(1)—O(3)	2.801
N(5)—C(5)	1.135(7)	O(2)—ON	2.932
N(1)— <i>M</i> —N(2)	89.6(2)	C(1)—Fe—C(2)	171.0(3)
N(1)— <i>M</i> —N(3)	176.4(2)	C(1)—Fe—C(3)	91.0(2)
N(1)— <i>M</i> —N(4)	86.8(2)	C(1)—Fe—C(4)	89.1(2)
N(1)— <i>M</i> —N(5)	91.9(2)	C(1)—Fe—C(5)	85.1(2)
N(1)— <i>M</i> —O(1)	93.2(2)	C(1)—Fe—N	93.3(2)
N(2)— <i>M</i> —N(3)	89.1(2)	C(2)—Fe—C(3)	87.6(2)
N(2)— <i>M</i> —N(4)	171.9(2)	C(2)—Fe—C(4)	91.0(2)
N(2)— <i>M</i> —N(5)	96.8(2)	C(2)—Fe—C(5)	85.9(2)
N(2)— <i>M</i> —O(1)	89.4(2)	C(2)—Fe—N	95.7(2)
N(3)— <i>M</i> —N(4)	94.2(2)	C(3)—Fe—C(4)	171.3(3)
N(3)— <i>M</i> —N(5)	91.5(2)	C(3)—Fe—C(5)	86.6(3)
N(3)— <i>M</i> —O(1)	83.5(2)	C(3)—Fe—N	95.7(3)
N(4)— <i>M</i> —N(5)	88.4(2)	C(4)—Fe—C(5)	84.8(2)
N(4)— <i>M</i> —O(1)	85.3(2)	C(4)—Fe—N	92.9(2)
N(5)— <i>M</i> —O(1)	170.8(2)	C(5)—Fe—N	177.2(2)
<i>M</i> —N(1)—C(1)	178.2(4)	Fe—C(1)—N(1)	178.3(5)
<i>M</i> —N(2)—C(2)	177.2(5)	Fe—C(2)—N(2)	178.4(6)
<i>M</i> —N(3)—C(3)	157.0(5)	Fe—C(3)—N(3)	179.8(5)
<i>M</i> —N(4)—C(4)	165.2(5)	Fe—C(4)—N(4)	177.2(5)
<i>M</i> —N(5)—C(5)	171.0(4)	Fe—C(5)—N(5)	177.7(5)
O(2)—O(1)—O(3)	112.6	Fe—N—O	177.1(5)

^a *M* equals (Cd/Mn).

lished values found in BIDICS (15). Interaction of Fe 3*d* orbitals and CN π orbitals brings about strong directional bonding which is evidenced by the averaged Fe—C \equiv N angle of 178.1(7)° for both compounds. The Fe—C bond lengths are much greater than the Fe—N bond lengths (see Tables IV and V). This contributes to the distortion of the octahedral geometry about the iron atoms. Further, the greater electronegativity of the nitrosyl group with respect to the cyanide ligands gives rise to deformation away from the nitrosyl end of the octahedral arrangement (N—Fe—C > 90°, C—Fe—C < 90°); see Tables IV and V and Fig. 1. A notable point of interest associated

with the electronegativity of groups (NO > CN > H₂O), which has been calculated by Huheey (16, 17) employing the method of electronegativity equalization, is the lowering of charge coefficients that have the effect of promoting charge transfer. The view that orbital electronegativity and electronegativity equalization furnish a serviceable pathway toward understanding charge distribution in molecules is strengthened by the experimental results obtained in the crystallographic investigations of **I** and **II**. Continuing, the coordinated water molecule, O(1), that is bonded to the cationic metal atoms is less electronegative in character than the cyanide groups. This causes

TABLE V
 INTERATOMIC BOND AND CONTACT DISTANCES (Å) AND BOND ANGLES (°) FOR
 1: 1-(Cd/Zn)Fe(CN)₅NO · 3H₂O

<i>M</i> ^a —N(1)	2.318(6)	Fe—C(1)	1.926(5)
<i>M</i> —N(2)	2.281(5)	Fe—C(2)	1.943(5)
<i>M</i> —N(3)	2.294(6)	Fe—C(3)	1.931(5)
<i>M</i> —N(4)	2.304(5)	Fe—C(4)	1.918(5)
<i>M</i> —N(5)	2.304(6)	Fe—C(5)	1.938(5)
<i>M</i> —O(1)	2.287(6)	Fe—N	1.654(5)
N(1)—C(1)	1.149(7)	N—O	1.147(7)
N(2)—C(2)	1.136(7)		
N(3)—C(3)	1.170(7)	O(1)—O(2)	2.867
N(4)—C(4)	1.167(7)	O(1)—O(3)	2.809
N(5)—C(5)	1.135(6)	O(2)—ON	2.946
N(1)— <i>M</i> —N(2)	90.0(2)	C(1)—Fe—C(2)	171.0(3)
N(1)— <i>M</i> —N(3)	177.2(2)	C(1)—Fe—C(3)	90.8(2)
N(1)— <i>M</i> —N(4)	87.0(2)	C(1)—Fe—C(4)	88.1(2)
N(1)— <i>M</i> —N(5)	92.2(2)	C(1)—Fe—C(5)	85.2(2)
N(1)— <i>M</i> —O(1)	93.4(2)	C(1)—Fe—N	93.4(2)
N(2)— <i>M</i> —N(3)	89.3(2)	C(2)—Fe—C(3)	88.7(2)
N(2)— <i>M</i> —N(4)	173.6(2)	C(2)—Fe—C(4)	91.0(2)
N(2)— <i>M</i> —N(5)	97.0(2)	C(2)—Fe—C(5)	85.8(2)
N(2)— <i>M</i> —O(1)	89.8(2)	C(2)—Fe—N	95.6(2)
N(3)— <i>M</i> —N(4)	93.4(2)	C(3)—Fe—C(4)	170.8(3)
N(3)— <i>M</i> —N(5)	90.6(2)	C(3)—Fe—C(5)	86.5(3)
N(3)— <i>M</i> —O(1)	83.9(2)	C(3)—Fe—N	96.0(3)
N(4)— <i>M</i> —N(5)	87.6(2)	C(4)—Fe—C(5)	84.2(2)
N(4)— <i>M</i> —O(1)	85.4(2)	C(4)—Fe—N	93.3(2)
N(5)— <i>M</i> —O(1)	170.1(2)	C(5)—Fe—N	177.2(2)
<i>M</i> —N(1)—C(1)	176.0(4)	Fe—C(1)—N(1)	178.0(5)
<i>M</i> —N(2)—C(2)	177.0(4)	Fe—C(2)—N(2)	178.7(5)
<i>M</i> —N(3)—C(3)	155.0(5)	Fe—C(3)—N(3)	177.3(5)
<i>M</i> —N(4)—C(4)	163.8(5)	Fe—C(4)—N(4)	177.9(5)
<i>M</i> —N(5)—C(5)	171.2(4)	Fe—C(5)—N(5)	177.5(4)
O(2)—O(1)—O(3)	113.1	Fe—N—O	177.2(5)

^a *M* equals (Cd/Zn).

a deformation of the octahedral array toward the coordinated water molecule. There is, however, an anomaly related to the N(1)—*M*—O(1) angle in both compounds. This angle should be less than instead of greater than 90°, which most likely is accounted for by the distortion of the N(5)—*M*—O(1) angles from ideality, 180° (see Tables IV and V). Nevertheless, the deformation is still toward O(1) in both systems and it is the staggered deformations about the mixed cationic metals atoms and the iron centers that form the serpentine-like channels in the crystal lattice, see Fig. 2.

Contact distances between O(1)···O(2) and O(1)···O(3) in both studied compounds

are significantly different, 2.844 and 2.801 Å in **I** and 2.867 and 2.809 Å in **II**. The respective O(2)···ON contact lengths are 2.932 and 2.946 Å, see Tables IV and V. Dependence on O···O interatomic distance related to strengths of hydrogen bonds has been studied by Brown (18). His investigations on the geometry of hydrogen bonds have shown that oxygen—oxygen intermolecular distances of 2.73 Å or less can be related to strong hydrogen bonds, assuming no geometric constraints, and that as contact distances increase, hydrogen bonds become progressively weaker. Herewithin, the O(1)···O(3) lengths in **I** and **II** suggest moderately strong H-bonding, whereas the

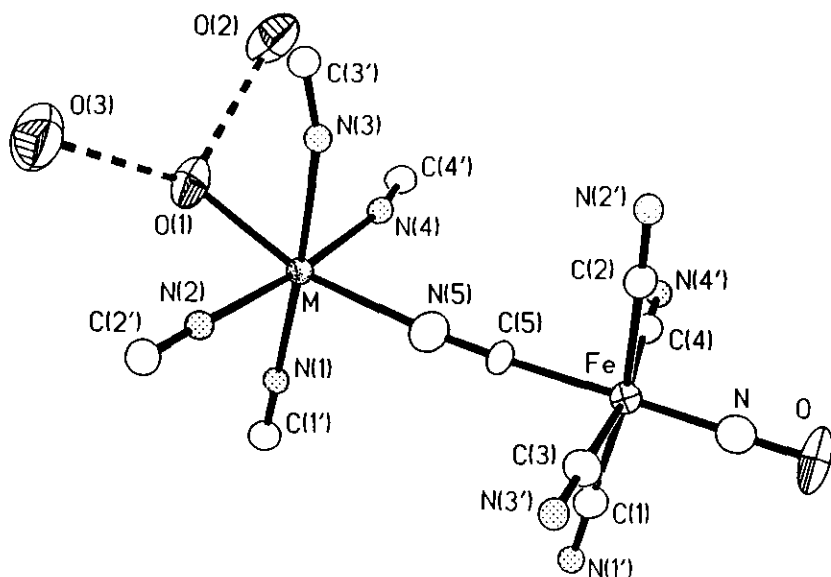


FIG. 1. A perspective view of $M[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$, where $M = (\text{Cd}/\text{Mn})$ or (Cd/Zn) , displaying the distorted octahedral arrangement about the metal centers, the cyanide bridging, and the location of the zeolitic water molecules, uncoordinated O(2) and O(3) with respect to coordinated O(1).

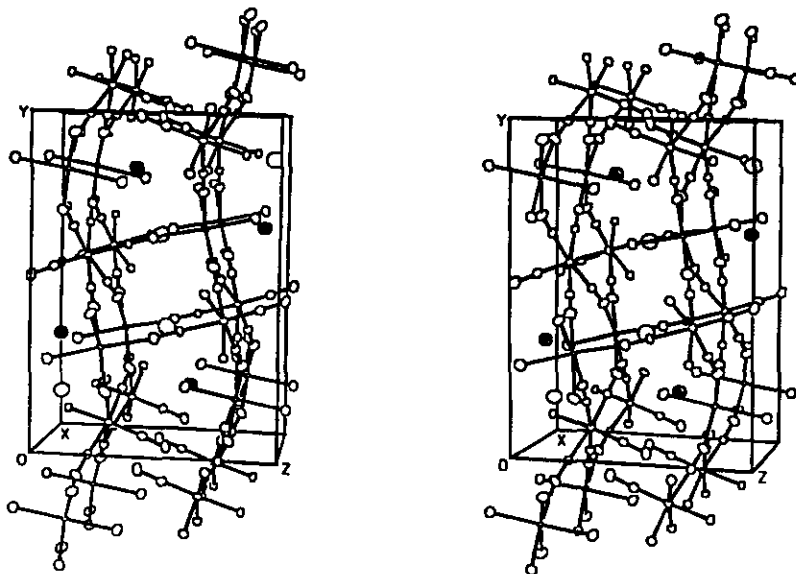


FIG. 2. A representative stereoscopic view (30% equiprobability) of the molecular packing within the unit cell revealing the extensive cyanide bridging network and the positions of O(2) as solid spheres, and O(3) as hollow spheres.

O(1)···O(2) and O(2)···ON contact lengths would represent weak H-bonding. The infrared data exhibited in Table II also suggest the existence of two different strengths of hydrogen bonds. A broad doublet-like band between 3100 and 3500 cm^{-1} is observed. Similar conclusions have been observed and verified in neutron structure analyses of $\text{In}(\text{OH})_3$ and $\text{Lu}(\text{OH})_3$ (19, 20). A neutron diffraction analysis of either I or II would help clarify any questions related to hydrogen bonding.

Finally, since the potential uses of polycyanides have found their way into nuclear chemistry as effective sorbents for radiocesium removal from primary coolants of pressurized water nuclear reactors (2) and the nitroprussides, irrespective of the metal prosthetic group, are currently being used as reversible inhibitors of a group of enzymes known as superoxide dismutases (21), further structural investigations of mixed transition metal nitrosylpentacyanide forms will be continued.

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