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Synthesis, Spectroscopic Studies and Crystal Structure Analysis of Zinc Nitrosylpentacyanoferrate Trihydrate, $ZnFe(CN)_5NO \cdot 3H_2O$

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Abstract

The crystal structure of zinc nitrosylpentacyanoferrate trihydrate has been determined from three dimensional, single-crystal X-ray diffraction data. Final full-matrix least-squares refinement yielded $R = 0.028$ and $R_w = 0.028$ for 791 unique reflections. $ZnFe(CN)_5NO \cdot 3H_2O$ contains iron and zinc atomic centers with distorted octahedral symmetries. The compound crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148, C_{3i}^2) on a hexagonal lattice, $a = 19.305(5)$ and $c = 17.627(5)$ Å, $Z = 18$, $D_m = 1.76(1)$ Mg m^{-3} and $D_x = 1.762$ Mg m^{-3}. The lattice constants were obtained from powder diffraction data, $F(30) = 38(0.011, 69)$ and $M(20) = 30.0$. The iron atom is coordinated to five cyanide ligands and one nitrosyl group, while the zinc atom is coordinated to five cyanide ligands and one water molecule. Fe–C≡N–Zn bridging links the metal atoms. Two uncoordinated water molecules, one of which is disordered, occupy channels in the crystal. Optical, infrared, X-ray fluorescence and thermal gravimetric analyses have also been carried out. Important mean bond lengths are: Zn–N = 2.110(20), Fe–C = 1.933(8) and C≡N = 1.129(6) Å. Other notable bond lengths include: Zn–O = 2.224(7), Fe–N = 1.684(9) and N=O = 1.102(9) Å.

Introduction

The first cited work related to nitrosylpentacyanoferrates was published by Playfair in 1848 [1]. For the next one hundred and twenty years, the majority of the published work in this area dealt solely with the sodium analogues. The discovery of an orthorhombic lattice (*Pnnm*) for sodium nitroprusside [2] generated interest in other metal nitroprussides and prompted a series of spectral and X-ray powder diffraction studies.

The metal prussides (hexacyanoferrates) are known to be zeolitic in nature and can take up water, ammonia and other small molecules from the air. The absorption of gases can be explained by the open channels formed between the bridging cyanide ligands in the crystal. When a nitrosyl group is substituted for a cyanide ligand, the normal and systematic arrangement of the lattice is disrupted, offering greater selectivity for separating mixtures of molecules such as CO_2 and CH_4. Subsequent, studies have reported successful separations of C6 isomers and established the precedence for predicting molecular sieving properties [3].

By 1968, many of the metal nitrosylpentacyanoferrates had been characterized by X-ray powder diffraction. Contrary to sodium nitroprusside, the heavy metal analogues adopted a primitive or face-centered cubic lattice. However, the zinc analogue (zinc nitrosylpentacyanoferrate) proved to be more difficult to characterize. Even though the reported structure [4] agreed basically with other metal nitroprussides (face-centered cubic), subsequent spectral studies raised serious doubts about the validity of earlier work on zinc nitroprusside [5].

A major discrepancy was related to the number of associated water molecules in the crystal structure. Values of two, three, four, five and six [6–8] had been reported. Since only X-ray powder diffraction studies had been carried out on zinc nitroprusside, and since X-ray powder diffraction data obtained in this laboratory revealed extraneous lines which did not relate to a cubic system, a single crystal analysis was deemed necessary.

Experimental

Synthesis and Physical Analysis

Commercially available analytical reagent grade sodium nitroprusside and zinc chloride were used as starting materials. The 'slow-diffusion-tube' method was employed to synthesize the title compound. The diffusion tubes were stored in the dark and sizeable crystals appeared in four to six months. After harvesting, the crystals were washed with distilled water and left to air-dry.

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TABLE 1. Infrared frequencies for $ZnFe(CN)_5NO \cdot 3H_2O$

Bond	Wavenumber (cm^{-1})	Transmission (%)
Fe–C (ν)	433	25.7
	445	17.9
Fe–CN (δ)	518	49.0
Fe–NO (δ)	651	51.9
	667	46.7
H–O–H (δ)	1619	28.7
N=O (ν)	1953	3.7
C≡N (ν)	2192	12.4
O–H (ν), broad		
Intermolecular H-bonding	3425 (3100–3600)	32.2
O–H (ν)	3660	39.1

Using the flotation method (1-hexene and iodomethane), the density of $ZnFe(CN)_5NO \cdot 3H_2O$ was determined, 1.76(1) Mg m^{-3}. Infrared spectroscopy was carried out using the pressed-disk method (KBr pellet). The results obtained from the absorption spectrum are presented in Table 1. A thermogravimetric analysis (TGA) employing a Perkin-Elmer TGS-1 at a rate of 2.5 ℃ min^{-1} from 25 to 245 ℃ yielded a loss of 3.1(1) water molecules per formula unit which is in accord with the work of Mohai *et al.* [7]. X-ray fluorescence data obtained on a Novascan 30 scanning electron microscope equipped with a PGT microprobe, confirmed the presence of the metal elements and yielded a molar ratio of 1:1 for the iron and zinc.

A Debye-Scherrer cylindrical camera (114.6 mm, 293 K, under vacuum using nickel filtered Cu K$\bar{\alpha}$ radiation, $\lambda_{mean} = 1.54184$ Å) was used to obtain the X-ray powder diffraction data. Zinc nitroprusside crystals were finely ground and placed into a 0.2 mm capillary. Characterization was based on 39 lines which were refined by placing measured S values into a least-squares X-ray powder diffraction data program [9]. The refined powder lattice constants are a = 19.305(5) and c = 17.627(5) Å (see Table 2) with 'figures-of-merit' values of $F(30) = 38(0.011, 69)$ [10] and $M(20) = 30.0$ [11]. Observed d-spacing values (Å) and visually estimated relative intensities based on 100 as the strongest reflection are presented in Table 3. The mean deviation between the observed and calculated d-spacing values is 0.13%.

TABLE 2. Experimental and statistical summaries of $ZnFe(CN)_5NO \cdot 3H_2O$

	Powder	Single crystal
Space group		$R\bar{3}$ (No. 148, C_{3i}^2)
Radiation	Cu K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ_{mean} (Å)	1.54184	0.71073
a (Å)	19.305(5)	19.296(6)
c (Å)	17.627(5)	17.642(6)
V ($Å^3$)	5689.2	5688.1
D_m (Mg m^{-3})	1.76(1)	1.76(1)
D_x (Mg m^{-3})	1.762	1.762
M_r		335.36
Z		18
$F(000)$ (e^-)		2988
Crystal size (mm)		0.43 × 0.35 × 0.27
μ (Mo K$\bar{\alpha}$) (mm^{-1})		3.104
$\Delta\theta$ (°)		1.5–25.0
$\Delta\omega$ (°) (ω–2θ scan)		1.25 + 0.35 tan θ
R_{int}		0.019
R		0.028
R_w		0.028
Unique reflections		791
g (e^{-2}) (×10^{-7})		1.38(8)
Shift/error ($\Delta\xi_i/\sigma(\xi_i)$) (×$10^{-5}$)		
maximum		51.5
average		1.84
Residual density (e^- $Å^{-3}$)		
maximum		0.376
minimum		−0.257
Gnft (Σ_2)		1.03

A single crystal of $ZnFe(CN)_5NO \cdot 3H_2O$, selected on the basis of optical quality, was mounted on a goniometer head. X-ray data were collected on an automated diffractometer (Enraf-Nonius CAD-4F) equipped with a dense graphite monochromator (take-off angle of 5.8°). Using Mo K$\bar{\alpha}$ radiation ($\lambda_{mean} = 0.71073$ Å), the orientation matrix and cell dimensions were obtained through the application of subroutines SEARCH and INDEX which are a part of the CAD4 operating system. After least-squares refinement of twenty-five accurately centered reflections, the hexagonal cell parameters were established, $a = 19.296(6)$ and $c = 17.642(6)$ Å. These parameters are in good agreement with the X-ray powder diffraction data, see Table 2. Data were then collected over the range of $3.0° < 2\theta < 50.0°$ utilizing the ω–2θ scan technique at a scan rate between 0.38 and 3.35° min^{-1}. No significant variations (<1.1%) were observed in the intensities of the monitored standards ($\bar{5}\ \bar{3}\ 4$ and $\bar{3}\ 1\ \bar{4}$). Of the 1058 collected reflections (h: $0 \rightarrow 19$; k: $0 \rightarrow 19$; l: $0 \rightarrow 20$), 791 reflections fitted $I_{net} > 2\sigma(I)$. Lorentz and polarization corrections were applied to the data.

Careful examination of the collected reflections revealed $-h + k + l = 3n$ which indicates a rhombohedral lattice. Additional examination of the collected reflections using an N(Z) analysis (cumulative probability distribution relative to centrosymmetry) verified a centrosymmetric symmetry. A negative pyroelectric test gave credence to the N(Z) statistical test. Further, $hki0 \neq hik0$ supports the space group assignment of $R\bar{3}$. These $hki0 \circlearrowright$ values were collected independently after the collected data set so as to distinguish $R\bar{3}$ from $R\bar{3}$m.

TABLE 3. X-ray powder diffraction data for $ZnFe(CN)_5NO \cdot 3H_2O$

$h\,k\,l$	$2\theta_{obs}$ (°)	$2\theta_{calc}$ (°)	I/I_0	d_0 (A)
1 1 0	9.17	9.16	15	9.64
0 1 2	11.35	11.35	15	7.80
2 0 2	14.62	14.61	20	6.06
3 0 0	15.90	15.90	25	5.57
1 2 2	17.28	17.27	100	5.13
2 2 0	18.40	18.38	25	4.822
1 3 1	19.80	19.80	10	4.484
1 0 4	20.85	20.85	20	4.260
3 1 2	21.68	21.66	15	4.100
0 2 4	22.82	22.81	12	3.896
0 4 2	23.58	23.56	17	3.774
4 1 0	24.40	24.40	60	3.648
2 1 4	24.63	24.63	12	3.615
2 3 2	25.35	25.35	17	3.513
0 1 5	25.83	25.83	2	3.450
3 3 0	27.72	27.72	2	3.218
1 3 4	27.95	27.93	10	3.1922
2 4 1	28.72	28.71	3	3.1078
4 2 2	30.05	30.04	5	2.9738
0 0 6	30.43	30.43	15	2.9380
1 5 2	31.50	31.48	7	2.8401
0 5 4	33.65	33.65	10	2.6634
2 4 4	34.95	34.94	80	2.5673
2 2 6	35.80	35.78	3	2.5082
6 1 2	36.73	36.70	2	2.4471
5 2 3	36.92	36.90	7	2.4344
4 2 5	38.28	38.25	5	2.3515
0 7 2	39.08	39.08	40	2.3052
6 2 1	39.20	29.19	3	2.2982
2 6 2	40.23	40.22	7	2.2419
3 3 6	41.65	41.63	3	2.1685
6 3 0	42.95	42.97	8	2.1058
7 0 4	43.07	43.08	20	2.1000
2 7 1	44.70	44.66	3	2.0273
6 3 3	45.78	45.76	2	1.9822
0 0 9	46.38	46.36	5	1.9579
6 4 2	48.60	48.59	3	1.8734
8 2 0	50.02	50.00	20	1.8233
4 2 8	50.53	50.50	5	1.8064

Average $\Delta 2\theta$ percent deviation = 0.044.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$)

Atom	x	y	z	U_{eq} ($Å^2$)
Zn	2450.1(4)	466.7(5)	8373.5(5)	16.0(2)
Fe	1812.0(6)	2254.8(6)	6654.7(6)	14.4(3)
C(1)	2037(4)	1612(4)	7342(4)	22(2)
N(1)	2159(3)	1225(3)	7746(4)	26(2)
C(2)	589(4)	4163(4)	615(4)	19(2)
N(2)	2699(3)	3382(3)	2358(4)	28(2)
C(3)	3519(4)	2736(4)	617(4)	20(2)
N(3)	2990(3)	2652(4)	954(4)	32(2)
C(4)	2157(4)	1158(4)	2655(4)	22(2)
N(4)	2092(4)	1586(3)	2262(4)	28(2)
C(5)	1665(4)	3637(4)	586(4)	22(2)
N(5)	1759(4)	3192(3)	916(4)	31(2)
N	3621(3)	5470(3)	2760(4)	25(2)
O	2357(3)	6475(4)	2400(3)	57(2)
O(1)	1257(4)	1492(4)	794(3)	58(3)
O(2)	1797(7)	314(5)	744(4)	137(5)
O(3)	2906(5)	8322(6)	2430(6)	58(4)
O(3a)	0000	0000	7200(10)	65(6)
O(3b)	0000	0000	8780(20)	97(9)

U_{eq} is the isotropic equivalent thermal parameter and is defined as one-third the trace of the orthogonalized U_{ij} tensor.

Crystallographic analysis employing MULTAN [12] revealed the initial locations of seven atoms. Difference Fourier mapping of residual electron density revealed the locations of the remaining atoms, including the positions of the oxygen atoms (water molecules) in ordered and disordered sites. Intensities greater than $2\sigma(I)$ were used in the structural refinement. A final difference Fourier map was virtually featureless, revealing only a random fluctuating background. Table 2 lists the experimental and statistical summaries for $ZnFe(CN)_5NO \cdot 3H_2O$. After applying secondary extinctions (g) and varying the anisotropic thermal parameters, the full-matrix least-squares refinement yielded final reliability factors, $R = \Sigma \Delta F / \Sigma F_o = 0.028$ and $R_w = \Sigma \sqrt{w} \Delta F / \Sigma \sqrt{w} F_o = 0.028$ where $\Delta F = ||F_o| - |F_c||$. The 'goodness-of-fit' value (Σ_2) was 1.03. Atomic scattering factors and anomalous dispersion correction factors were taken from the International Tables [13]. Final atomic coordinates and isotropic equivalent thermal parameters are presented in Table 4. See also 'Supplementary Material'.

Results and Discussion

The crystallographic data of zinc nitrosylpentacyanoferrate trihydrate best fit a rhombohedral lattice, space group $R\bar{3}$ (No. 148, C_{3i}^2), $a = 19.305(5)$ and $c = 17.627(5)$ Å, with 18 molecules per unit cell. Five cyanide ligands and one nitrosyl group form a distorted octahedral arrangement about the iron atoms. Likewise, the zinc atoms are octahedrally coordinated by five cyanide ligands and one water molecule. The metal atoms are linked by cyanide bridging, Zn–N≡C–Fe is non-linear (see Fig. 1). The coordinated water molecules bonded to the zinc atoms and the nitrosyl groups bonded to the iron atoms are geometrically arranged so that there are three tunnel-like formations in the crystal. These channels are diagonally located in the unit cell. The

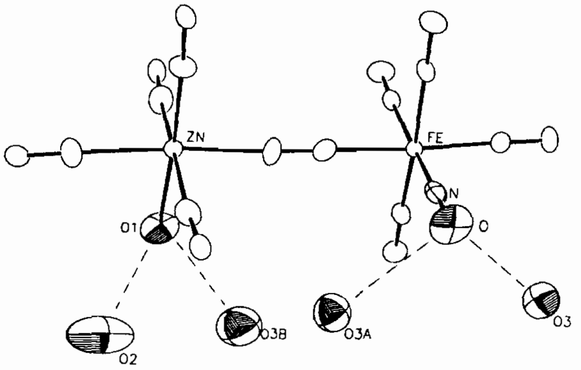

Fig. 1. A projected view of $ZnFe(CN)_5NO\cdot 3H_2O$ showing the distorted octahedral arrangements about the Zn and Fe atoms, the cyanide bridging, the location of O(2) with respect to O(1), and the locations of O(3) and O(3a) with respect to ON.

TABLE 5. Bond and contact distances for $ZnFe(CN)_5NO\cdot 3H_2O$

Bond[a]	Distance (Å)	Bond	Distance (Å)
Zn–N(1)	2.122(8)	N(1)–C(1)	1.139(12)
Zn–N(2)	2.079(8)	N(2)–C(2)	1.130(11)
Zn–N(3)	2.139(8)	N(3)–C(3)	1.121(11)
Zn–N(4)	2.104(8)	N(4)–C(4)	1.133(12)
Zn–N(5)	2.104(8)	N(5)–C(5)	1.124(11)
Zn–O(1)	2.224(7)	N–O	1.102(9)
Fe–C(1)	1.932(11)	O(2)–O(1)	2.939(15)
Fe–C(2)	1.932(10)	O(2)–O(1)	2.764(11)
Fe–C(3)	1.943(10)	O(2)–O(1)	3.025(14)
Fe–C(4)	1.919(11)	O(3)–ON	3.217(15)
Fe–C(5)	1.937(11)	O(3a)–ON	3.114(24)
Fe–N	1.684(9)	O(3b)–O(1)	2.786(12)

[a] O(1) = water molecules coordinated to the Zn atoms. O(2) = uncoordinated water molecules which are peripherally located in the diagonal channels. O(3), O(3a), O(3b) = disordered (uncoordinated) water molecules which are located within the diagonal channels at 2/3, 1/6 and 1/6 multiplicities, respectively.

TABLE 6. Bond angles (°) for $ZnFe(CN)_5NO\cdot 3H_2O$

Atoms	Angle	Atoms	Angle
N(1)–Zn–N(2)	92.2(3)	C(2)–Fe–C(3)	85.1(4)
N(1)–Zn–N(3)	175.5(4)	C(2)–Fe–C(4)	170.8(4)
N(1)–Zn–N(4)	88.4(3)	C(2)–Fe–C(5)	89.7(4)
N(1)–Zn–N(5)	89.8(3)	C(2)–Fe–N	93.1(4)
N(1)–Zn–O(1)	90.2(3)	C(3)–Fe–C(4)	85.7(4)
N(2)–Zn–N(3)	92.1(4)	C(3)–Fe–C(5)	86.5(4)
N(2)–Zn–N(4)	93.9(4)	C(3)–Fe–N	178.2(4)
N(2)–Zn–N(5)	93.1(4)	C(4)–Fe–C(5)	89.0(4)
N(2)–Zn–O(1)	177.0(8)	C(4)–Fe–N	96.1(4)
N(3)–Zn–N(4)	90.0(4)	C(5)–Fe–N	93.7(4)
N(3)–Zn–N(5)	91.3(4)	Fe–C(1)–N(1)	179.0(10)
N(3)–Zn–O(1)	85.5(3)	Zn–N(1)–C(1)	172.5(8)
N(4)–Zn–N(5)	172.8(4)	Zn–N(2)–C(2)	175.5(9)
N(4)–Zn–O(1)	88.0(3)	Fe–C(2)–N(2)	179.0(10)
N(5)–Zn–O(1)	85.0(4)	Zn–N(3)–C(3)	177.0(10)
C(1)–Fe–C(2)	91.5(4)	Fe–C(3)–N(3)	177.0(10)
C(1)–Fe–C(3)	84.9(4)	Zn–N(4)–C(4)	174.4(9)
C(1)–Fe–C(4)	88.5(4)	Fe–C(4)–N(4)	178.0(10)
C(1)–Fe–C(5)	171.1(4)	Zn–N(5)–C(5)	174.0(10)
C(1)–Fe–N	95.0(4)	Fe–C(5)–N(5)	179.0(10)
		Fe–N–O	179.0(9)

two uncoordinated water molecules are found within these channels hydrogen-bonded to the coordinated water molecules and nitrosyl groups. One of the uncoordinated water molecules is disordered and is found in three different environments, O(3), O(3a) and O(3b). The population of each was refined to multiplicities of 0.66(1), 0.16(1) and 0.17(1), respectively.

The averaged bond distances for Zn–N (2.110 Å), Fe–C (1.933 Å) and C≡N (1.129 Å) as well as the bond distances of Zn–O (2.224 Å), Fe–N (1.684 Å) and N=O (1.102 Å) are in good agreement with published values found in BIDICS [14]. There is strong directional bonding related to the interaction of the Fe 3d orbitals and the CN orbitals which is confirmed by the averaged Fe–C≡N bond angle of 178.4°. The Fe–N length is considerably shorter than the Fe–C length, see Table 5. This could readily account for the distortion of the octahedral symmetry about the Fe atom. Further, it is noted by the reported bond angles in Table 6 that the greater electronegativity of the nitrosyl ligand with respect to the cyanide ligands can also cause a deformation away from the nitrosyl end of the octahedral arrangement about the Fe atom (N–Fe–C $> 90°$, C–Fe–C $< 90°$). To the contrary, the coordinated water molecule bonded to the Zn atom is less electronegative in character than the cyanide ligands. Therefore, the octahedral arrangement about the Zn atom is distorted in the following manner, the angles O–Zn–N $< 90°$ and the angles N(2)–Zn–N $> 90°$; see Table 6.

Important intermoiety oxygen–oxygen contact distances are O(1)···O(2) (mean) = 2.909, O(1)···O(3b) = 2.786, O(3a)···ON = 3.114, and NO···O(3) = 3.217 Å. The range of these contact distances (2.764 to 3.217, see Table 5) varies significantly which can be attributed to different hydrogen bond strengths, i.e. from strong to weak to very weak. The strength of hydrogen bonds has been shown by Brown [15] to be dependent upon the O···O interatomic distances. Strong hydrogen bonds, assuming no geometric constraints, have contact distances of approximately 2.73 Å, and hydrogen bonding becomes progressively weaker as the contact distances increase. Infrared data presented in Table 1 lend credence to the X-ray diffraction analysis. The strong broad peak with a pronounced shoulder, located between 3600 and 3100 cm^{-1}, attests to hydrogen bonding. The shoulder may indicate different types of hydrogen bonding.

Since $ZnFe(CN)_5NO \cdot 3H_2O$ and related type compounds are considered to be true molecular sieves, and since many discrepancies related to the hydration content, system and space group, and structural geometry have been found in the literature, future investigations of this class of compounds are most definitely needed. This laboratory will continue chemical and structural research in this area.

Supplementary Material

Full listings of anisotropic thermal parameters and observed and calculated structure factors are available from author D.F.M.

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