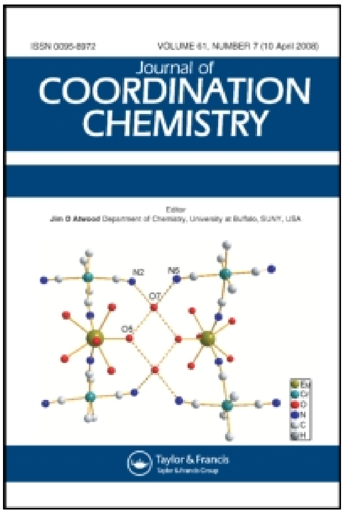

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SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY CRYSTAL STRUCTURE ANALYSIS OF COBALT NITROPRUSSIDE, $Co[Fe(CN)_5NO]\cdot 5H_2O$

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Slow diffusion of cobalt chloride with $Na_2[Fe(CN)_5NO]\cdot 5H_2O$ in aqueous solution produced crystals of $Co[Fe(CN)_5NO]\cdot 5H_2O$ suitable for analysis by three-dimensional, single-crystal X-ray diffractometry. This polynuclear transition metal cyanide crystallized in the cubic space group $Fm\bar{3}m$ (No. 225, O^5_h), $a = 10.281(2)$ Å, with three formula units per cell. $D_m = 1.67(1)$ Mg m^{-3} and $D_x = 1.673$ Mg m^{-3}. Final full-matrix least-squares refinement of 102 unique reflections converged to $R = 0.020$ and $R_w = 0.019$. The iron nucleus is octahedrally coordinated to five cyanide ligands and a nitrosyl group and the cobalt nucleus is octahedrally coordinated to five cyanide ligands and one water molecule. Cyanide bridging (Fe–C≡N–Co) links the metal centers, providing a cubic framework within which uncoordinated water molecules occupy three crystallographically distinct environments. These uncoordinated water molecules are held in position by hydrogen bonding and/or van der Waals forces. The crystal lattice of cobalt nitroprusside is characterized by unique vacancies and a high degree of disorder, which can be described as a superpositioning of various ordered unit cells. Infrared, thermogravimetric and crystallographic data have led to the formulation of a plausible model for cubic nitroprussides.

Keywords: Cobalt nitroprusside, X-ray structure, spectroscopy

INTRODUCTION

The first cited work related to the nitrosylpentacyanoferrates was published by Playfair in 1848.[1] Despite a century and a half of existence, the nitroprussides have not received the widespread interest as have the mixed valence hexacyanides (prussides). Numerous investigations of the polynuclear hexacyanides, including Prussian blue, have led to the proposal of various models,[2–4] all of which correspond to the face-centred cubic space group $Fm\bar{3}m$. The major differences in these models[2–4] are the arrangements of their uncoordinated water molecules. Initial studies of the group I and II[5–10] and transition metal[11–13] nitroprussides have shown that these systems crystallize in non-cubic space groups (orthorhombic and monoclinic) and possess no disorder or vacancies as do the hexacyanide analogues. The unique characteristics of the nitroprussides are due to the open channels formed by unbridged nitrosyl groups and coordinated water molecules,[11–13] whereas the hexacyanides attain their characteristic sieving properties from systematic $[Fe(CN)_6]^{3-}$ vacancies. Cobalt nitroprusside is the first nitroprusside verified by single-crystal X-ray diffractometry to crystallize in the same face-centred space group as the prussides, $Fm\bar{3}m$. The crystallographic data is consistent with the previous models proposed for the transition metal hexacyanides, differing only in the positioning of the uncoordinated water molecules and the presence of additional cages formed by unbridged nitrosyl groups.

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Cobalt nitroprusside exhibits the same zeolitic property as the transition metal prussides, which have been applied as molecular sieves, cation exchangers, electron scavengers and most recently as radionuclide sorbents.[14,15] The study of cobalt(II) pentacyanonitrosylferrate pentahydrate and other nitroprussides has been initiated due to interest in the structural and morphological development of semipermeable membranes and ion exchange properties.

EXPERIMENTAL

Synthesis

Commercially available analytical reagent grade $Na_2Fe(CN)_5NO{\cdot}2H_2O$ and $CoCl_2$ 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 within ten months crystals large enough for single-crystal analysis appeared in the water bridge connecting the two salt solutions.

Thermogravimetric Analysis

A TGA study was conducted using a Perkin Elmer TGS-1 thermobalance and a Sybron furnace. The thermobalance revealed a gradual loss of water molecules beginning at 40°C and continuing through 225°C at a scan rate of 2.5°/min. The exact amount of water lost could not be ascertained due to the small but continuous slope of the thermal decomposition curve. Since there was no observed plateau, an approximate value of five water molecules was concluded. However, a thermal analysis using a Sybron furnace operated at 110°C for several days clearly revealed a loss of 5.02(4) water molecules per formula unit. Higher temperatures resulted in a slow but continuous loss of cyanide and nitrosyl groups.

TABLE I
Infrared frequencies for $Co[Fe(CN)_5NO]{\cdot}5H_2O$.

Assignment	Wavenumber (cm^{-1})[a]	Transmission (%)
N=O (2v)	3868 w	72.0
O–H (v)	3656	33.9
	3651	32.8
O–H (v) intermolec.	3404 br	23.4
H-bonding	3212 sh,br	37.2
C≡N (v)	2188	13.4
N=O (v)	1948	3.4
H–O–H (δ)	1618	31.9
Fe–NO (δ)	665	40.4
Fe–N (v)	647	46.3
Fe–CN (δ)	521	45.4
Fe–CN (v)	447	20.4
	434	27.5

[a] br = broad, sh = shoulder, w = weak.

Physical Characterization

An infrared spectroscopic analysis employing a pressed KBr/sample pellet was carried out on a Mattson Fourier Transform IR spectrophotometer over a frequency range 4000–400 cm^{-1}; the results obtained from the absorption spectrum, which indicate various degrees of hydrogen bonding, are presented in Table I. Isotropic symmetry for the crystal system was confirmed by a conoscopic examination, performed by crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II. X-ray fluorescence data varied the presence of the cobalt and iron metals. Density was determined pycnometrically by flotation in a mixture of bromoform and 1-hexene. The results are in good agreement with the calculated density, Table II.

TABLE II
Experimental and statistical summaries for $Co[Fe(CN)_5NO]\cdot 5H_2O$.

Space Group	$Fm\bar{3}m$ (No. 225, O_h^5)
a(Å) -powder	10.281(2)
a(Å) -crystal	10.281(2)
V(Å^3)	1086.7
D_m (Mg m^{-3})	1.67(1)
D_x (Mg m^{-3})	1.673
M_r	364.95
Z	3
F(000)	549
μ(Mo $K_{\bar{\alpha}}$)(mm^{-1})	2.17
$\Delta\theta$ (°)	1.5–40
$\Delta\omega$ (°) (ω–2θ)	1.25–0.35 tanθ
R_{int}	0.018
R	0.020
R_w	0.019
Unique reflections ($> 3\sigma(I)$)	102
g(e^{-2})($\times 10^{-6}$) I	4.1(3)
Shift/error ($\Delta\zeta_i/\sigma(\zeta_i)$)($\times 10^{-5}$)	
Maximum	3.0
Average	0.9
Residual density (e$^-$ Å^{-3})	
Maximum	0.19(5)
Minimum	−0.34(5)
Gnft (Σ_2)	1.31

Powder Diffraction Data

A Debye-Scherrer cylindrical camera (114.6 mm, 293 K, using $CuK_{\bar{\alpha}}$ radiation, $\lambda_{mean} = 1.54184$ Å) was used to obtain the X-ray powder diffraction data. Cobalt nitroprusside crystals were finely ground and placed into a 0.2 mm capillary. Characterization was based on 17 lines which were employed to refine the lattice parameter by placing the corresponding S-values into a least-squares X-ray powder diffraction program.[16] The refined powder lattice constant is a = 10.281(2) Å, see Table II, with a 'figure-of-merit' value of F(17) = 55(0.012,25).[17] Observed d-spacings (Å) and visually estimated relative intensities based on 100 as the strongest reflection are presented in Table III. The mean deviation between the observed and calculated d-spacings is 0.05%.

TABLE III
X-ray powder diffraction data for $Co[Fe(CN)_5NO]{\cdot}5H_2O$.[a]

hkl	$2\theta_{obs}$(°)	$2\theta_{calc}$(°)	I/I_o	d_o(Å)
2 0 0	17.25	17.25	100	5.14
2 2 0	24.46	24.46	60	3.64
2 2 2	30.09	30.09	15	2.97
4 0 0	34.92	34.91	70	2.569
4 2 0	39.26	39.18	50	2.295
4 2 2	43.10	43.10	20	2.099
5 1 1	45.88	45.88	3	1.978
4 4 0	50.21	50.21	25	1.817
6 0 0	53.48	53.48	25	1.7135
6 2 0	56.63	56.62	15	1.6254
6 2 2	59.63	59.66	5	1.5506
4 4 4	62.60	62.60	10	1.4839
6 4 0	65.42	65.47	20	1.4265
6 4 2	68.25	68.27	20	1.3742
8 0 0	73.72	73.72	5	1.2851
8 2 0	76.40	76.39	10	1.2466
6 6 0	79.02	79.03	10	1.2117

[a] Average $\Delta 2\theta$ percent deviation = 0.024.

Crystallographic Data, Collection and Reduction

A single crystal of cobalt(II) pentacyanonitrosylferrate was selected after examination under a polarizing microscope for homogeneity. X-ray data were collected at 18°C on an Enraf-Nonius CAD-4F automated diffractometer, equipped with a dense graphite monochromator at a take-off angle of 5.8°. Using $MoK_{\bar{\alpha}}$ radiation, $\lambda_{mean} = 0.71073$ Å, twenty-five initial reflections were obtained from the application of subroutine SEARCH. Least-squares refinement of the twenty-five accurately centered reflections established a cubic system, $a = 10.281(2)$ Å. Data were then collected over the range $3.0° < 2\theta < 80.0°$ utilizing the ω-2θ scan technique at a scan rate between 0.38 and 3.35° min^{-1}. No significant variations (<1.8%) were observed in the intensities of the monitored standards, $0\,4\,\bar{2}$ and $4\,0\,0$. Of the 1427 reflections collected (h: $0 \rightarrow 18$, k: $0 \rightarrow 18$; l: $0 \rightarrow 18$), 506 reflections fitted $I_{net} > 3\sigma(I)$ and after averaging ($R_{int} = 0.018$), 102 were used in the final least-squares refinement. Lorentz and polarization corrections were applied to the data along with an empirical absorption correction (transmission range, 0.960–0.999). Systematic absences were consistent with space group $Fm\bar{3}m$. Additional examination of the collected reflections using an N(Z) cumulative probability distribution test provided further evidence of a centrosymmetric system.

Structural Refinement of Model

Crystallographic analysis of the reduced and averaged data employing SHELX-86[18] located the electron densities pertaining to the octahedral framework of the crystal lattice. Difference Fourier mapping of the residual electron density led to the elucidation of the nitrosyl groups, the oxygen atoms of the coordinated water molecules and the oxygen atoms associated with three distinct, uncoordinated water molecules. During the least-squares refinement, a correlation matrix which is a subroutine of the full-matrix least-squares program[19] was applied and showed high correlations between atoms sharing the same positional site. For this reason, atoms sharing the same site were alternately refined. Also, excessive deviation of the nitrosyl-associated oxygen, O, required that its thermal parameters be fixed during refinement; see Table IV. Successive alternate refinements while applying a secondary extinction (g) factor yielded final reliability factors, $R = \Sigma \Delta F / \Sigma |F_o| = 0.020$ and $R_w = \Sigma \sqrt{w} \Delta F / \Sigma \sqrt{w} |F_o| = 0.019$ where $\Delta F = ||F_o| - F_c||$ and $w = \sigma^{-2}(|F_o|)$. The "goodness-of-fit" value (Σ_2) and the value of abscission $[\Delta\zeta_i/\sigma(\zeta_i)$, where ζ_i are varied parameters] can be found in Table II. A final electron density map was virtually featureless, revealing only a random fluctuating background with a peak maximum of 0.18(5) $e^- \text{Å}^{-3}$ and a peak minimum of $-0.34(5)$ $e^- \text{Å}^{-3}$ in the vicinity of the cobalt atom. Atomic scattering factors and anomalous dispersion correction factors were taken from the International Tables.[20] Final atomic coordinates and isotropic equivalent thermal parameters are presented in Table IV.

TABLE IV
Positional and equivalent isotropic thermal parameters ($\times 10^2$) for $Co[Fe(CN)_5NO]\cdot 5H_2O$.

Atom	position	*x/a*	*y/b*	*z/c*	$U_{eq}(\text{Å}^2)^a$	Occupancy
Co	4*b*	0.5	0.5	0.5	1.56(2)	3/4
Fe	4*a*	0	0	0	4.26(4)	3/4
C	24*e*	0	0	0.1971(4)	1.61(1)	5/8
N	24*e*	0	0	0.3098(5)	5.3(2)	5/8
N(1)[b]	24*e*	0	0	0.1644(15)	1.0(4)	1/8
O[b]	24*e*	0	0	0.2756(13)	5.5[c]	1/8
O(1)	24*e*	0	0	0.2787(17)	11.3(8)	1/4
O(2)	4*a*	0	0	0	8.4(4)	1/4
O(3)	32*f*	0.2085	0.2085	0.2085(9)	16.9(4)	1/8
O(4)	32*f*	0.227	0.227	0.2269(9)	9.6(2)	1/8

[a] U_{eq} is the isotropic equivalent thermal parameter and is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] N(1) and O constitute the nitrosyl ligands. [c] The thermal parameters for O were anisotropically fixed.

DISCUSSION

The crystallographic data of cobalt nitroprusside pentahydrate best fit a face-centred cubic lattice, space group $Fm\bar{3}m$ (No. 225), $a = 10.281(2)$ Å, with three formula units per cell. The lattice is marked by random vacancies and a high degree of disorder. Both iron and cobalt atoms have 3/4 occupancy at special sites, positional number set and Wyckoff notations 4*a* and 4*b*, respectively. The iron atom is coordinated by five cyanide ligands and a nitrosyl group, and the cobalt atom is coordinated by five cyanide ligands and a coordinated water, such that Fe–C≡N–Co bridging defines the cubic lattice. The carbon and nitrogen atoms, both at positional set 24*e*, maintain 5/8 occupancy. This is due to the $Fe(CN)_5$ and $Co(NC)_5$ vacancies and to the presence of substituted nitrosyl ligands and coordinated water molecules O(1). An average of nine uncoordinated water molecules are obtained within this cell. One of the nine, O(2), is located at 0,0,0 (4*a*) having 1/4 occupancy. The eight remaining uncoordinated water molecules, O(3) and O(4), lie on symmetry site 3*m* (positional set 32*f*) and have a partial occupancy of 1/8. The positional sites and partial occupancies infer that O(3) and O(4) may be found in either the cage created by the unbridged, coordinated water molecules (cavity 1) or the cage created by the unbridged nitrosyl groups (cavity 2), see Figures 1 and 2. The O(2) atom is located unambiguously at the centre of cavity 1. For clarity, O(3) atoms are shown tetrahedrally arrayed in cavity 1, and O(4) atoms are shown tetrahedrally arrayed in cavity 2. No electron density could be found at the centre of the cage created by the nitrosyl ligands. Despite the complexity of the cobalt nitroprusside lattice, the described model is a sound and valid interpretation of the electron density within the unit cell, fully in accord with the models proposed by Herren *et al.*[3] and Beall *et al.*[4] for the transition metal prussides. Cobalt is apparently the first nitroprusside known to crystallize in the same cubic space group ($Fm\bar{3}m$) and in the same manner as the cubic prussides. The major difference is seen in the presence of a second cavity which is formed by the unbridged, octahedrally arranged nitrosyl ligands. The presence of a second cavity brings about an interesting possibility, that is to say, the potential of forming extended channels which is seen with the non-cubic nitroprussides.[11–13] Figures 1 and 2 have been deliberately constructed to show how channels might be formed, in addition to cages, by the appropriate occurrence of alternating water-bound and nitrosyl-bound cages.

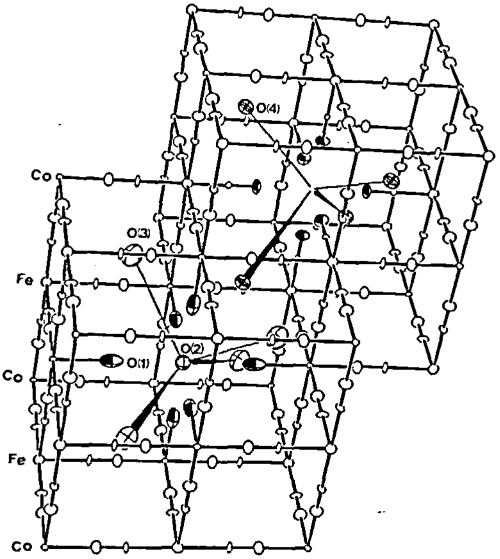

FIGURE 1 A perspective view of Co[Fe(CN)$_5$NO]·5H$_2$O showing the idealized tetrahedral arrangement of the uncoordinated water molecules, O(3) and O(4), as well as the locations of O(1) and O(2) water molecules.

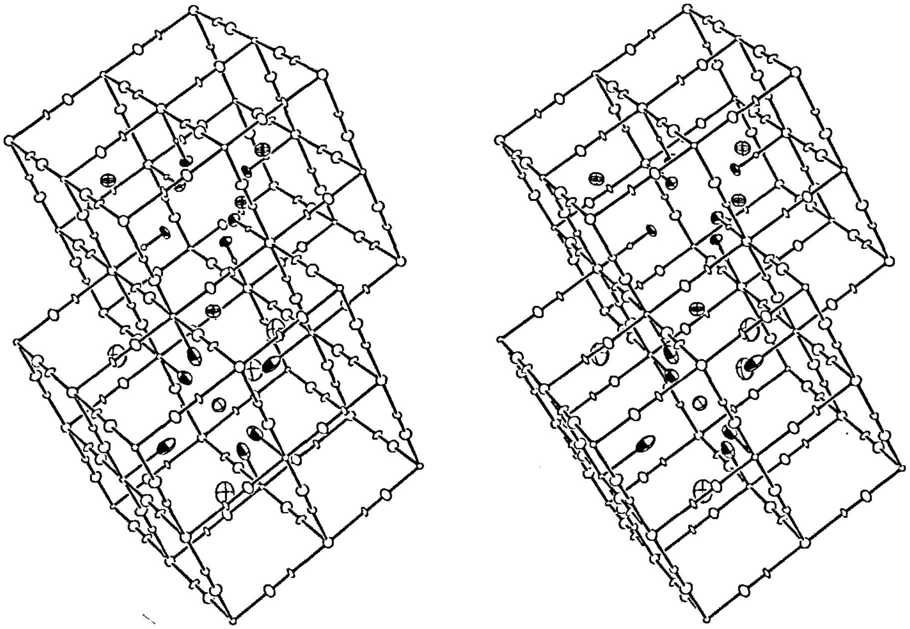

FIGURE 2 A stereoview of $Co[Fe(CN)_5NO]\cdot5H_2O$.

Spectroscopic data are also consistent with the described model. The existence of an infrared absorption band at 1617 cm^{-1} is attributed to deformation of the water molecules, while the sharp doublet at 3656 and 3651 cm^{-1} has been assigned to free OH groups. A third absorption peak at 3404 cm^{-1} (range 3600–3100 cm^{-1}) with a visible shoulder at 3200 cm^{-1} is both broad and strong and has been assigned to hydrogen bonding, *i.e.*, hydrogen bonding of O(2) and O(3). Infrared data (see Table I) is consistent with previously reported data.[21] Elucidation of the number of water molecules by thermal analysis established five water molecules *per* formula unit, as well as the zeolitic nature of cobalt nitroprusside and its potential use as a molecular sieve. Cobalt nitroprusside is able to lose all five water molecules, coordinated and uncoordinated, at 110°C and rehydrate completely in air at room temperature. The various states of hydration are accompanied by characteristic colour changes, which can be followed from a pale-pink when hydrated to a brilliant blue-green when fully dehydrated. A persistent, dark brown colour, obtained at elevated temperatures, indicates decomposition of the crystal lattice corresponding to a loss of cyanide and nitrosyl groups.

Table V lists the bond and contact distances for the title compound. The Co–N distance of 1.956 Å and the Fe–C distance of 2.026 Å agree quite well with other published structure data found in BIDICS.[22] The C≡N bond length of 1.158 Å is also in good agreement with the values found in the literature[22] as well as being in excellent agreement with the summations of the involved triple bond radii of carbon (0.603 Å) and nitrogen (0.55 Å) atoms found in the work of Pauling,[23] 1.153 Å. Other experimental bond lengths [Co–O(1) = 2.28, Fe–N(1) = 1.69 and N(1)–O = 1.14 Å] are quite reasonable and comparable to bond distances found in similar published single-crystal structural analyses, *i.e.*, Co–O = 2.28 Å;[24,25] Fe–N = 1.68,[11] 1.69[26] and 1.71 Å in $Ba[Fe(CN)_5NO]\cdot 2H_2O$,[27] which is the orthorhombic system $Pca2_1$; N–O = 1.10–1.16 Å,[11,12,27,28] Important and relevant intermoiety oxygen–oxygen contact distances are also listed in Table V. The differences in contact lengths (O(1)···O(2) and O(1)···(3) are significant, being 2.87 and 3.12 Å, respectively. The NO···O(3) contact length of 3.109 Å is also equally notable. The varied range of these contact distances can be attributed to different degrees of hydrogen bonding. The strength of a hydrogen bond has been shown by Brown[29] to be dependent upon the O···O interatomic distances. Strong hydrogen bonds, assuming no geometric constraints, have contact distances of 2.73 Å or less, and as the contact distance increases, the hydrogen bonding becomes progressively weaker. The infrared data also suggests the presence of varied degrees of intermolecular hydrogen bonding, lending credence to the X-ray diffraction analysis. The strong, broad peak located between 3600 and 3100 cm^{-1} attests to hydrogen bonding, while the shoulder at approximately 3200 cm^{-1} may indicate different types of hydrogen bonding [O(1)···O(2), O(1)···O(3) and NO···O(3)]. Based on the rather large O···O contact distances of 3.337 and 3.34 Å for NO···O(4) and O(1)···O(4), respectively, it appears that electrostatic (van der Waals) attraction is responsible for the positioning of the O(4) water molecules. If hydrogen bonding is involved, it would be 'extremely' weak. An earlier study of cobalt nitroprusside[21] suggested from infrared and electronic spectra that π electrons of the NO group might serve as an acceptor site for hydrogen bonding. It is obvious that no hydrogen bonding can occur between water molecules O(2) and O(3) or O(2) and O(4), Table V.

TABLE V

Bond lengths (Å) and contact distances (Å) for $Co[Fe(CN)_5NO]\cdot 5H_2O$.

Co–N	1.956(12)	NO–O(3)	3.109(5)
Fe–C	2.026(11)	NO–O(4)	3.337(3)
C–N	1.158(7)	O(1)–O(2)[b]	2.87(4)
Co–O(1)[a]	2.28(4)	O(1)–O(3)[b]	3.12(2)
Fe–N(1)	1.69(2)	O(1)–O(4)[b]	3.34(1)
N(1)–O	1.14(2)	O(2)–O(3)	3.71(2)
		O(2)–O(4)	4.04(3)

[a] O(1) = water molecules coordinated to the Co atoms. [b] O(2) = uncoordinated water molecules in O(1) octahedral cages. [c] O(3) and O(4) = uncoordinated water molecules tetrahedrally arrayed about the cages.

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SUPPLEMENTARY MATERIAL

A listing of anisotropic thermal parameters (1 page) and tables of observed and calculated structure factor amplitude (3 pages) are available from D.F.M.

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