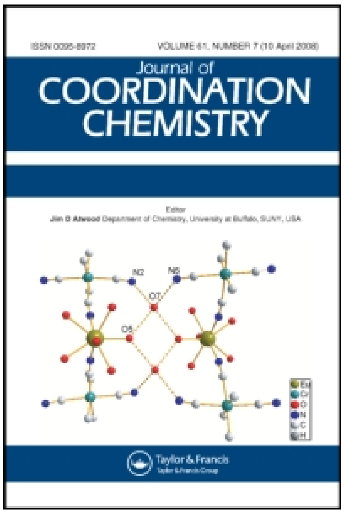

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The Jahn-Teller Effect in the Molecular Structure of Copper Nitroprusside, $Cu[Fe(CN)_5NO]\cdot 2H_2O$

D. F. Mullica[a]; D. B. Tippin[a]; E. L. Sappenfield[a]
[a] Department of Chemistry, Baylor University, Waco, Texas, USA

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NOTE

THE JAHN–TELLER EFFECT IN THE MOLECULAR STRUCTURE OF COPPER NITROPRUSSIDE, $Cu[Fe(CN)_5NO]\cdot 2H_2O$

D. F. MULLICA,* D. B. TIPPIN and E. L. SAPPENFIELD

Department of Chemistry, Baylor University, Waco, Texas 76798, USA.

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The nitrosylcyanide crystallizes in space group *Pnma* with $a = 13.4911(9)$, $b = 7.1698(6)$, $c = 10.8623(7)$ Å, $Z = 4$, $D_m = 2.01(2)$ Mg m^{-3} and $D_x = 1.99$ Mg m^{-3}. Full-matrix least-squares refinement of 1232 unique reflections yielded final reliability factors, $R = 0.048$ and $R_w = 0.052$, and a "goodness-of-fit" value of 1.04. The iron atoms are coordinated by five cyanide ligands and a nitrosyl group and the copper atoms are coordinated by five cyanide ligands and a water molecule. The distorted octahedral metal centres, which are geometrically arranged in a staggered fashion, are linked by cyanide bridging (Fe–C≡N–Cu). The copper centre displays a characteristic Jahn–Teller distortion typical of octahedral copper complexes, and accounts for bond distance deviation in lattice symmetry from octahedral ideality, $Cu-N_{(equatorial, mean)} = 1.981(5)$ Å and $Cu-N_{(axial)} = 2.160(7)$ Å. Conoscopic, infrared, thermal gravimetric, and X-ray fluorescence analyses are reported.

Keywords: Copper(II), nitroprusside, copper complex, X-ray structure

INTRODUCTION

Research related to the nitroprussides was first published by Playfair in 1848,[1] whose work dealt solely with the sodium analogue. In 1963, the crystal structure of sodium nitroprusside (orthorhombic, *Pnnm*) was resolved at Brookhaven National Laboratory by Manoharan and Hamilton.[2] Subsequent studies of groups I and II nitroprussides,[3–8] *via* single-crystal analysis, have shown that these compounds are monoclinic or orthorhombic. Recent single-crystal investigations of the transition metal nitroprussides have thus far established that many of the previously reported face-centred cubic nitroprussides actually crystallize in space groups of lower symmetry,[9–11] cobalt nitroprusside being a notable exception.[12]

The prussides (hexacyanides) have been the most widely studied of the polycyanides. These hexacyanides have been employed as molecular sieves, cation exchangers, electron scavengers and most recently as radionuclide sorbents.[13,14] Within the transition hexacyanoferrates, channels are formed by systematic $[Fe(CN)_6]^{3-}$ vacancies in the structural array and give rise to pore sizes of *ca* 5.6 × 8.6 Å.[15] In the case of most nitrosylpentacyanides, the cyanide complexes generally possess no vacancies, and channels formed are the result of unbridged nitrosyl groups; cobalt nitrosylpentacyanide is an exception.[12] These channels are significantly smaller than their hexacyanide counterparts, offering greater selectivity in the separation of smaller molecules.

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* Author for correspondence.

EXPERIMENTAL

The "slow-diffusion-tube" method was employed for the synthesis, whereby separately prepared solutions of $Na_2Fe(CN)_5NO{\cdot}2H_2O$ and $CuCl_2$ are joined by a U-tube water bridge. After eight months storage in the dark, green crystals large enough for single-crystal analysis appeared in the water bridge. Contrary to the monoclinic nitroprussides,[10,11] $Cu[Fe(CN)_5NO]{\cdot}2H_2O$ retains its water of hydration at room temperature, and for this reason, special storage and mounting precautions were unnecessary. Using the flotation method (bromoform and 1-hexene), the density of the titled compound was determined (Table I). An infrared spectrum obtained over the frequency range 4000–400 cm^{-1} (KBr pellet) on a Mattson Fourier Transform IR analyzer, yielded the results presented in Table II. X-ray fluorescence results obtained using a Norelco Wide Range Goniometer, equipped with an X-ray spectrograph and scintillation counter, verified the presence of the copper and iron metals. A conoscopic analysis using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II, provided evidence that the studied system was biaxial in nature. This then eliminates the possibility of $CuFe(CN)_5NO{\cdot}2H_2O$ belonging in a high symmetry system. Thermal dehydration of copper nitroprusside was conducted on a Perkin-Elmer TGS-1 thermobalance up to 225°C at a temperature increase of 2.5°/minute. Higher temperatures resulted in a slow continuous loss of cyanide and nitrosyl groups (decomposition). The thermogravimetric analysis (TGA) unambiguously revealed the loss of two water molecules per formula unit. Dehydration of the uncoordinated and coordinated water molecules occurred gradually, without any division between loss of channel and bound water molecules. The dehydrated copper nitroprusside lattice is stable up to 180° and is able to rehydrate at room temperature.

TABLE I

Experimental and statistical summaries for $Cu[Fe(CN)_5NO]{\cdot}2H_2O$

Space Group	*Pnma*
a(Å)	13.4911(9)
b(Å)	7.1698(6)
c(Å)	10.8623(7)
V(Å^3)	1052.7(2)
D_m(Mg m^{-3})	2.01(2)
D_x(Mg m^{-3})	1.99
M_r	315.52
Z	4
F(000) (e^-)	620
μ (Mo $K_{\bar{\alpha}}$) (mm^{-1})	3.41
$\Delta\theta$ (°)	1.5–30.0
$\Delta\omega$ (°) (ω–2θ scan)	1.25 + 0.35 tanθ
R_{int}	0.013
R	0.048
R_w	0.052
Unique reflections ($>3\sigma(I)$)	1232
g (e^{-2}) ($\times 10^{-4}$)	1(3)
shift/error ($\Delta\zeta i/\sigma(\zeta i)$) ($10^{-4}$) Maximum	1.39
Minimum	0.15
Gnft (Σ_2)	1.04

TABLE II
Infrared frequencies for $Cu[Fe(CN)_5NO]\cdot 2H_2O$.

Assignment	Wavenumber (cm^{-1})	Transmission (%)
N=O (2v)	3881 w	25.0
O–H (v)	3653	2.6
O–H (v) intermolec. H-bonding	3458 br	12.0
C≡N (v)	2202	0.6
	2200	0.6
	2159 sh	28.6
	2152 sh	27.2
N=O (v)	1957	0.3
H–O–H (δ)	1607	13.7
	1594	14.1
Fe–NO (δ)	663	25.5
Fe–N (v)	641	16.5
Fe–CN (δ)	531	3.4
Fe–CN (v)	464	0.5
	418	11.0

w = weak, br = broad, sh = shoulder.

The single crystal (0.10 × 0.12 × 0.12 mm) used in the structural analysis was selected on the basis of optical homogeneity and was mounted on an Enraf-Nonius CAD-4F diffractometer, equipped with a dense graphite monochromator (take-off angle = 5.8°). Twenty-five centred reflections, obtained from a rotation photograph, produced the orientation matrix for data collection. The intensities were measured using the ω-2θ scan technique at a varied scan rate (0.38 to $3.35° min^{-1}$) determined by a fast pre-scan of $3.35° min^{-1}$. Data were then collected in the range of $3.0° < 2\theta < 60.0°$ using Mo K_α, $\lambda = 0.71073$ Å (294K). Two check reflections ($\bar{3}$ 0 2 and 0 4 1) were monitored for crystal stability and electronic hardware reliability. The deviations of the averaged standard values were less than 0.3%. Final unit cell parameter values were obtained at high θ angles, $>20°$. Of the 2481 measured reflections (h: $-9 \rightarrow 18$; k: $0 \rightarrow 10$; l: $-7 \rightarrow 15$), 1643 were independent ($R_{int} = 0.013$) of which 1232 fitted $I_{net} > 3\sigma(I)$. Lorentz, polarization and an empirical absorption correction[16] (transmission factors: max., 0.999; min., 0.945) were applied to the data. Systematic absences ($0kl$: $k + l = 2n + 1$, $hk0$: $h = 2n + 1$) were consistent with space group *Pnma* (No. 62). An N(Z) cumulative probability distribution test lends credence to a centrosymmetric lattice. A crystallographic analysis of the reduced and averaged data employing SHELXTL-PC-89[17] revealed the locations of the copper and iron centres. Difference Fourier mapping of the residual electron density located the remaining non-hydrogen atoms. Excessive deviations in thermal motion of the oxygen atoms associated with the water molecules required the thermal parameters to be fixed during the final stages of refinement, see Table III (for both, $U_{iso} = 0.15$). After applying a secondary extinction correction (g) and varying the anisotropic thermal parameters of all other non-hydrogen atoms, a full-matrix least-squares refinement[16] yielded final reliability factors of $R = \Sigma\Delta F/\Sigma|F_o| = 0.048$ and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}|F_o| = 0.052$ where $\Delta F = |\,|F_o| - |F_c|\,|$ and $w = \sigma^{-2}(|F_o|)$. A final difference Fourier map revealed some density ($< 1.5\ e^-Å^{-3}$) in the vicinity of the metal atoms and a minimal amount (0.95 e$^-$Å^{-3}) near the water molecules. Elsewhere, the map was featureless, revealing only a random fluctuating background. Atomic scattering factors and associated anomalous dispersion correction factors were taken from International Tables.[18] Final atomic coordinates and isotropic equivalent thermal parameters are presented in Table III.

TABLE III
Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (× 10^2) for $Cu[Fe(CN)_5NO]{\cdot}2H_2O$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)[a]
Cu	3217(1)	2500	3405(1)	1.2(1)
Fe	4391(1)	2500	7990(1)	1.0(1)
N(1)	3586(5)	2500	5340(7)	2.9(2)
N(2)	5828(3)	5566(7)	7117(5)	2.3(1)
N(3)	2831(3)	5554(6)	8422(4)	2.2(1)
C(1)	3892(6)	2500	6326(7)	1.9(2)
C(2)	5289(3)	4401(7)	7429(5)	1.7(1)
C(3)	3400(3)	4403(8)	8271(4)	1.6(1)
N	4825(5)	2500	9417(6)	2.1(2)
O	5113(8)	2500	10389(8)	5.9(3)
O(1)	2630(11)	2500	1145(5)	15.0[b]
O(2)	751(10)	2500	350(20)	15.0[b]

[a] U_{eq} is the isotropic thermal parameter and is defined as one-third the trace of the orthogonalized U_{ij} tensor. [b] Thermal parameters were isotropically fixed (U_{iso}).

DISCUSSION

The crystallographic data obtained from the single-crystal analysis of copper nitroprusside dihydrate best fit an orthorhombic lattice, space group *Pnma*, with lattice parameters $a = 13.4911(9)$, $b = 7.1698(6)$ and $c = 10.8623(7)$ Å. There are four formula units per unit cell such that there are no vacancies or disorder. The data were tested using the program MISSYM,[19] which verified no additional symmetry. The structure contains distorted octahedral metal centres which are joined by cyanide bridging in a staggered manner. Five cyanide groups and one water molecule, O(1), are bonded to the copper atoms while the iron atoms are coordinated by five cyanide ligands and one unbridged nitrosyl group. Channels permeate the orthorhombic crystal lattice in which uncoordinated water molecules, O(2), are found (see Figures 1 and 2).

The averaged bond distances for Cu–N$_{(equatorial)}$ (1.981 Å), Fe–C (1.929 Å) and C≡N (1.149 Å) as well as the bond distances for Cu–N$_{(axial)}$ (2.160 Å), Cu–O(1) (2.580 Å), Fe–NO (1.658 Å) and N=O (1.124 Å) are in accord with published values found in BIDICS,[20] see Table IV. As with previously studied nitroprussides,[9-12] there is strong directional bonding related to the interaction of Fe 3d orbitals and CN

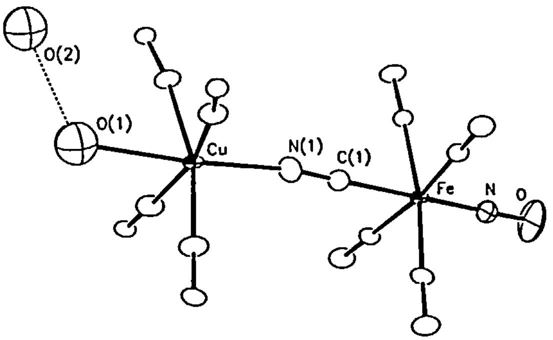

FIGURE 1 A projected view of Cu[Fe(CN)$_5$NO]·2H$_2$O showing the distorted octahedral cyanide bridging and the location of the zeolitic water molecule, O(2), with respect to the coordinated water molecule, O(1).

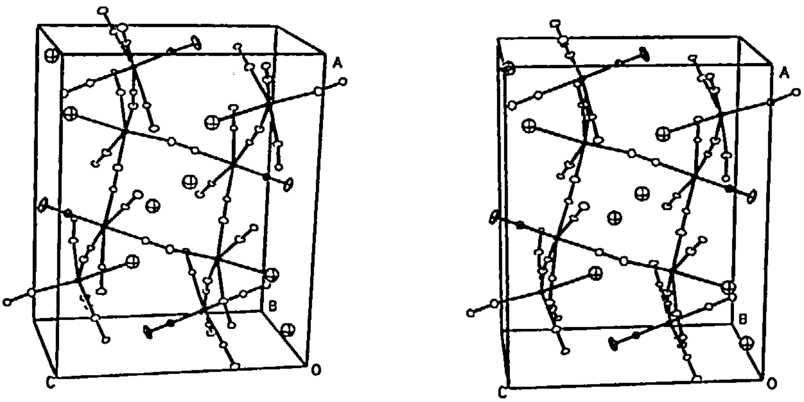

FIGURE 2 A stereoview of Cu[Fe(CN)$_5$NO]·2H$_2$O revealing the extensive cyanide bridging and the positions of the zeolitic water molecule O(2) within the open channels.

TABLE IV

Selected bond and contact distances for Cu[Fe(CN)$_5$NO]·2H$_2$O.

Bond[a]	Distance (Å)	Bond	Distance (Å)
Cu-N(1)	2.160(7)	Fe-C(1)	1.928(8)
Cu-N(2)	1.976(5)	Fe-C(2)	1.923(5)
Cu-N(3)	1.986(5)	Fe-C(3)	1.935(5)
Cu-O(1)	2.580(7)	Fe-NO	1.658(7)
N(1)-C(1)	1.148(11)	N=O	1.124(11)
N(2)-C(2)	1.159(7)		
N(3)-C(3)	1.139(7)	O(1)-O(2)	2.679(20)

[a] O(1) is the coordinated water molecule. O(2) is the uncoordinated water molecule.

π orbitals which is evidenced by the averaged Fe–C≡N bond angle of 178.7(5)°. There is also deformation about the iron metal centres. It is noted from the reported bond angles in Table V that the greater electronegativity of the nitrosyl group with respect to the cyanide ligands causes deformation away from the nitrosyl end of the octahedral coordination, C(2,3)–Fe–NO $>$ 90° while C(1)–Fe–C(2,3) $<$ 90°. The copper centres show a similar but more severe distortion of their octahedral array towards the coordinated water molecule, N(2,3)–Cu–O(1) $<$ 90° while N(1)–Cu–N(2,3) $>$ 90°. Such deformations are in agreement with the electronegativity calculations of Huheey[21,22] (NO $>$ CN $>$ H_2O) and strengthen the argument that the lowering of charge coefficients has the effect of promoting charge transfer. The octahedral array about the copper atoms also displays axial elongation of the N(1) and O(1) ligands due to the d^9 configuration of the Cu(II) ion. It is well known that Cu(II) in an octahedral environment is subject to Jahn–Teller distortion and that the distortion can bring about a tetragonally elongated octahedron.[23] Such is the case in this crystallographic investigation. Considering that the analogous nitroprussides (iron, manganese and cadmium)[10,11] possess two uncoordinated water molecules and crystallize in monoclinic space groups, it is perceivable that the Jahn–Teller effect, through axial extension of the coordinated water molecule, directly or indirectly accounts for one less water molecule per formula unit for copper nitroprusside. This condition would reduce lattice strain and allow the lattice to assume an orthorhombic configuration. Iron ($a = 7.205$, $b = 14.641$, $c = 10.680$ Å and $\beta = 91.14°$), manganese ($a = 7.302$, $b = 14.783$, $c = 10.751$ Å and $\beta = 91.47°$), cadmium ($a = 7.425$, $b = 14.963$, $c = 10.848$ Å and $\beta = 91.64°$) and copper ($b = 7.170$, $a = 13.491$ and $c = 10.862$ Å) nitroprussides have unit axes that differ proportionally with cation radii and have β angles that differ by less than 1.64°. An increase in stability of copper nitroprusside is also evidenced by its increased thermal stability over those of the monoclinic nitroprussides. It is recalled that copper nitroprusside is stable up to 180°C and is able to rehydrate at room temperature, while the monoclinic nitroprussides spontaneously mono-dehydrate at room temperature (followed by breakdown of the crystal lattice). Moreover, dehydration studies conducted on the alkaline and alkaline-earth nitroprussides have established a tendency to change from a monoclinic to an orthorhombic lattice upon the loss of zeolitic (uncoordinated) water molecules.[5,8]

Spectroscopic data are consistent with the model obtained from the single-crystal analysis. The existence of an infrared doublet at 1594 and 1607 cm^{-1} has been assigned to the deformation of water molecules which may be attributed to the unique symmetry of the copper octahedron (Jahn–Teller effect). The sharp intense single peak at 3653 cm^{-1} is attributed to free OH groups, while the strong and broad absorption band at 3460 cm^{-1} has been assigned to hydrogen bonding, *i.e.*, O(2) and O(1) water molecules. The infrared data are consistent with a previously reported spectroscopic study on some bivalent transition metal nitroprussides.[14] The inter-moiety oxygen–oxygen contact distance of 2.679 Å relates to strong hydrogen bonding, *i.e.*, the involved oxygen–hydrogen–oxygen angles would be idealized with an angle extremely close to or equal to 180°. Studies by Brown[25] on the geometry of hydrogen bonds have demonstrated that $O \cdots O$ intermolecular distances of approximately 2.73 Å or less are considered to be strong hydrogen bonds, assuming no geometric constraints. The atomic position of the uncoordinated water molecule, O(2), in the channel yields a Cu–O(1)$\cdots$O(2) angle of 126.7(6)° which is extremely close to an ideal angle (126–127°) when considering strong head-on O(1)–H$\cdots$O(2) hydrogen bonding in crystalline hydrates.[26] Neutron diffraction studies should clarify the exact orientations of the coordinated and uncoordinated water molecules and shed light on the semi-permeable membrane properties of this unique nitroprusside.

TABLE V

Selected bond angles for $Cu[Fe(CN)_5NO]\cdot 2H_2O$.

Atoms	Angle (°)	Atoms	Angle (°)
N(1)-Cu-N(2)	97.4(2)	C(1)-Fe-C(2)	85.6(2)
N(1)-Cu-N(3)	98.9(2)	C(1)-Fe-C(3)	84.7(2)
N(1)-Cu-O(1)	175.5(4)	C(1)-Fe-NO	179.7(5)
N(2)-Cu-N(3)	88.5(2)	C(2)-Fe-C(3)	89.2(2)
N(2)-Cu-N(2)'	89.2(3)	C(2)-Fe-C(2)'	90.3(3)
N(2)-Cu-N(3)'	163.7(2)	C(2)-Fe-C(3)'	170.2(2)
N(2)-Cu-O(1)	85.8(3)	C(2)-Fe-NO	94.2(2)
N(3)-Cu-O(1)	77.9(3)	C(3)-Fe-NO	95.5(2)
N(3)-Cu-N(3)'	89.3(3)	C(3)-Fe-C(3)'	89.7(3)
Cu-N(1)-C(1)	172.3(7)	Fe-C(1)-N(1)	179.4(8)
Cu-N(2)-C(2)	178.2(4)	Fe-C(2)-N(2)	178.4(5)
Cu-N(3)-C(3)	170.8(5)	Fe-C(3)-N(3)	178.3(5)
Cu-O(1)-O(2)	126.7(6)	Fe-N-O	179.5(8)

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SUPPLEMENTARY MATERIAL

A listing of anisotropic thermal parameters and tables of observed and calculated structure factor amplitudes are available from the authors.

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