DTA-TGA, crystal and molecular structure determination and vibrational studies of potassium nitroprusside sesquiquarterhydrate, $K_2[Fe(CN)_5NO] \cdot 1.25H_2O$

J. I. AMALVY,[1] E. L. VARETTI,[2] and P. J. AYMONINO[2]*

Programa QUINOR, Departamento de Química
Facultad de Ciencias Exactas
Universidad Nacional de La Plata
47 esquina 115, C.C.962
1900 La Plata, República Argentina

E. E. CASTELLANO

Instituto de Física e Química de Sao Paulo
Universidade de Sao Paulo
Caixa Postal 369
13.560, Sao Carlos, S.P., Brasil

and

O. E. PIRO[2] and G. PUNTE[2]

Departamento de Física, Facultad de Ciencias Exactas
Universidad Nacional de La Plata
49 esquina 115, C.C.67
1900 La Plata, República Argentina

Abstract

The crystal structure of the title compound has been determined from diffractometer data and refined with isotropic thermal parameters to final R_w factors

of $R = 0.058$ and $R_w = 0.056$. It crystallizes in the orthorhombic space group $p2_12_12_1$ (No. 19), with $a = 9.706(7)$, $b = 18.826(6)$, and $c = 25.258(6)$ Å. The asymmetric unit contains four nitroprusside ions, eight potassium ions, and five water molecules, one of which shows disorder. The infrared spectra of the polycrystalline compound, both normal and with different degrees of deuteration at temperatures ranging from liquid nitrogen to room temperature, were obtained. The vibrational spectra present an unusual number of fundamental and first overtone NO stretching bands and a rich structure in the water bending region, in accordance with the existence of inequivalent nitroprusside ions and water molecules.

Introduction

The present work is part of a research program on the crystallographic and vibrational properties of hydrated alkaline and alkaline-earth nitroprusside salts (see Rigotti *et al.*, 1984 and references therein). When the program was initiated, sodium nitroprusside dihydrate was the only nitroprusside studied spectroscopically by the isotopic dilution technique with deuterium (Holzbecher *et al.*, 1971).

It is to be noted that the water content reported for alkaline nitroprussides is not always the same, especially for lithium and potassium salts (Tosi, 1973; Chamberlain and Green, 1963; Garg and Goel, 1971; Long *et al.*, 1978; Gentil, 1973). In the last case differences are due to the existence, not always recognized, of various hydrates. Therefore, it is mandatory to work with well-defined crystalline samples in controlled experimental conditions to avoid the risk of mistaking the species. In the case of potassium nitroprusside the growth of crystals proved to be very difficult, and for some time only aggregates of microcrystals were obtained. After many trials, however, crystals of $K_2[Fe(CN)_5NO] \cdot 1.25H_2O$ (PNP) were finally obtained by slow evaporation from saturated water solutions of potassium nitroprusside under special conditions (see below). An X-ray crystallographic study was then undertaken and the vibrational properties at different temperatures and degrees of deuteration were investigated.

Experimental

PNP was prepared by reaction of silver nitroprusside [obtained as a pink solid by mixing solutions of sodium nitroprusside and $AgNO_3$ (Garg and Goel, 1971)] and a solution of the corresponding chloride (in an amount slightly less than stoichiometric) and by filtering out the silver chloride. Bright orange crystals were obtained from the mother solution by slow evaporation in a desiccator

containing a saturated solution of NH$_4$Cl and KNO$_3$ and an excess of the solids to assure an approximately constant water vapor pressure (about 13 torr at room temperature). Deuterated samples were obtained by the same technique in a smaller jar to spare heavy water.

Thermograms were obtained under flowing nitrogen at 2.7 liter h^{-1} and a heating rate of 6°C min^{-1} in a Mettler Model 1 belonging to the Atomic Energy Commission, Buenos Aires, R. Argentina.

The density was measured pycnometrically in benzene at 20°C.

A prismatic 0.2 × 0.5 × 0.6 mm crystal was used for data collection on an Enraf-Nonius CAD-4 diffractometer. As PNP is hygroscopic, the crystal was coated with Nujol and mounted in a sealed Lindemann capillary tube. The cell parameters and the orientation matrix for data collection were refined by least-squares methods employing 15 carefully centered high-angle reflections. Intensities were measured by the ω–2θ scan technique at speeds between 2.85 and 20.0° min^{-1} after a fast prescan at 20.0° min^{-1}. Reflections were collected in the range $0 < \theta < 22°$ using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The intensities of three standard reflections were essentially constant during the experiment. From 4558 measured intensities, 1869 independent reflections with $I > 3\sigma(I)$ were used. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. The atomic scattering factors of Cromer and Waber (1974) and the coefficients for anomalous dispersion corrections of Cromer and Ibers (1974) were employed in the calculations. Most of these were performed on a VAX computer with MULTAN-80 (Main *et al.*, 1980) and SHELX systems of programs (Sheldrick, 1976).

The IR absorption spectra of Nujol mulls of PNP between CsI plates and of KBr pellets were recorded on a Perkin-Elmer 580B spectrophotometer provided with an Infrared Data Station Model 3500. The deuterated samples prepared in KBr pellets sandwiched between layers of KBr proved to be very stable as no changes in the water bands could be detected after several months. The spectrophotometer was routinely calibrated using water, carbon monoxide, ammonia (Tables of Wavenumbers for the Calibration of Infrared Spectrometers, 1961), and sodium nitroprusside dihydrate (Della Védova *et al.*, 1981) absorption bands. Calibration of the OD stretching region was made by recording DCl and HCl spectra (Tables of Wavenumbers for the Calibration of Infrared Spectrometers, 1961). The accuracy of wave numbers reported below for sharp bands is ± 1 cm^{-1} and ± 2 cm^{-1} for broad bands. An RIIC VLT-2 cell was used to obtain spectra at the boiling temperature of nitrogen (referred to below as low-temperature spectra).

Polarized single crystal spectra of very thin plates (almost invisible to the naked eye) mounted between CsI plates were attempted for the crystallographic planes (100), (010), and (001). Unfortunately, strong absorbance severely limited the usefulness of these spectra.

PNP is orthorhombic, space group $P2_12_12_1$ (No. 19), with $a = 9.706(7)$, $b = 18.826(6)$, $c = 25.258(6)$ Å, Mw $= 316.67$, $V = 4615(1)$ Å^3, $D_m = 1.80$, $D_c = 1.82$ g cm^{-3}, μ(Mo $K\alpha$) $= 1.92$ mm^{-1}, $F(000) = 2472$.

Three iron and two potassium atoms were readily found by direct methods. All other nonhydrogen atoms were then located from alternate difference Fourier and isotropic least-squares refinement cycles. The model was refined with isotropic thermal parameters to $R_w = 0.068$ [weighting scheme: $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ estimated from counting statistics]. At this stage a difference map was essentially flat except for a peak of about 3 electrons Å^{-3}. This peak was interpreted as another water oxygen, and after four additional cycles in which only the positional and isotropic parameters of this atom were refined, R_w dropped to 0.061. Further refinement of all atoms gave final values of $R = 0.058$ and $R_w = 0.056$. Refinement using anisotropic temperature parameters was not performed due to the small number of reflections per independent parameter. Final positional parameters and temperature factors are given in Table 1. Bond distances and angles for the four nitroprusside anions are given in Table 2. Lists of observed and calculated structure factors are available on request.

Table 1. Final positional coordinates and isotropic thermal parameters

Atom	x/a	y/b	z/c	B_{ISO} (Å^2)
Fe(1)	0.2885(3)	0.3905(1)	0.2641(1)	1.82(6)
N(1)	0.288(2)	0.4303(9)	0.3209(7)	3.7(4)
O(1)	0.294(2)	0.4631(8)	0.3598(6)	4.2(4)
C(11)	0.463(2)	0.435(1)	0.2467(8)	2.4(5)
N(11)	0.564(2)	0.461(1)	0.2369(8)	4.3(5)
C(12)	0.119(2)	0.345(1)	0.2757(8)	2.4(5)
N(12)	0.012(2)	0.3202(9)	0.2848(7)	3.2(4)
C(13)	0.297(2)	0.3444(9)	0.1958(7)	1.2(3)
N(13)	0.301(2)	0.3180(9)	0.1546(7)	3.6(4)
C(14)	0.384(2)	0.306(1)	0.2847(8)	2.7(5)
N(14)	0.443(2)	0.2540(9)	0.2970(6)	2.8(4)
C(15)	0.193(2)	0.463(1)	0.2256(8)	2.2(4)
N(15)	0.134(2)	0.506(1)	0.2011(7)	3.6(4)
Fe(2)	0.2149(3)	0.0886(1)	0.9353(1)	1.72(6)
N(2)	0.208(2)	0.0490(9)	0.9926(7)	2.8(4)
O(2)	0.199(2)	0.0178(7)	1.0307(6)	3.6(3)
C(21)	0.142(2)	0.180(1)	0.9565(7)	1.5(4)
N(21)	0.097(2)	0.2347(9)	0.9676(7)	2.9(4)
C(22)	0.294(2)	0.012(1)	0.8988(7)	2.0(4)
N(22)	0.344(2)	−0.0360(9)	0.8775(7)	2.9(4)
C(23)	0.215(3)	0.135(1)	0.8687(9)	3.3(5)
N(23)	0.223(2)	0.1608(8)	0.8267(7)	2.9(4)
C(24)	0.400(2)	0.122(1)	0.9444(8)	2.1(4)
N(24)	0.515(2)	0.1332(9)	0.9485(7)	2.8(4)
C(25)	0.028(2)	0.059(1)	0.9179(8)	2.2(4)

Table 1. Continued

Atom	x/a	y/b	z/c	B_{ISO} (Å^2)
N(25)	−0.084(2)	0.0406(9)	0.9137(7)	2.9(4)
Fe(3)	0.0098(3)	0.1513(1)	0.1530(1)	1.76(6)
N(3)	0.004(2)	0.2355(8)	0.1561(6)	1.5(3)
O(3)	0.005(1)	0.2967(7)	0.1597(5)	2.1(3)
C(31)	0.121(2)	0.142(1)	0.2173(7)	1.2(4)
N(31)	0.178(2)	0.1337(8)	0.2545(7)	2.7(4)
C(32)	−0.095(2)	0.138(1)	0.0895(8)	1.7(4)
N(32)	−0.158(2)	0.1271(9)	0.0520(7)	3.0(4)
C(33)	0.024(2)	0.049(1)	0.1513(7)	1.8(4)
N(33)	0.037(2)	−0.0106(9)	0.1525(6)	2.7(4)
C(34)	−0.155(2)	0.137(1)	0.1925(8)	2.2(4)
N(34)	−0.257(2)	0.1324(9)	0.2172(7)	3.1(4)
C(35)	0.171(2)	0.151(1)	0.1113(7)	1.7(4)
N(35)	0.272(2)	0.1537(8)	0.0845(6)	2.1(3)
Fe(4)	0.4450(3)	−0.1778(2)	1.0332(1)	1.82(6)
N(4)	0.405(2)	−0.2604(9)	1.0411(6)	2.3(4)
O(4)	0.374(2)	−0.3187(8)	1.0480(6)	4.0(4)
C(41)	0.518(2)	−0.192(1)	0.9632(8)	2.3(4)
N(41)	0.555(2)	−0.1985(9)	0.9207(7)	3.2(4)
C(42)	0.371(2)	−0.150(1)	1.0994(8)	2.1(4)
N(42)	0.321(2)	−0.1301(9)	1.1385(7)	3.0(4)
C(43)	0.492(2)	−0.078(1)	1.0226(8)	3.1(5)
N(43)	0.529(2)	−0.023(1)	1.0203(7)	4.2(5)
C(44)	0.276(2)	−0.152(1)	1.0027(8)	2.3(4)
N(44)	0.166(2)	−0.1377(9)	0.9850(7)	3.0(4)
C(45)	0.628(2)	−0.185(1)	1.0620(8)	2.2(4)
N(45)	0.737(2)	−0.1905(8)	1.0804(6)	2.5(4)
K(1)	0.7949(5)	0.2001(2)	0.9566(2)	2.6(1)
K(2)	0.2262(5)	0.2267(3)	0.7247(2)	3.2(1)
K(3)	0.4674(5)	0.1134(2)	0.2384(2)	2.9(1)
K(4)	−0.0166(6)	0.3630(3)	0.4060(2)	3.4(1)
K(5)	0.0510(5)	0.3817(3)	0.9310(2)	2.9(1)
K(6)	0.2519(5)	−0.1753(3)	0.8641(2)	3.0(1)
K(7)	0.3526(5)	0.0265(3)	0.7652(2)	3.5(1)
K(8)	0.3607(6)	0.4940(3)	0.5883(2)	4.4(1)
OW(1)	0.273(2)	0.3516(8)	0.6595(6)	5.4(4)
OW(2)	0.495(2)	0.1016(7)	0.3481(6)	4.1(4)
OW(3)	0.016(2)	0.2881(7)	0.8448(6)	4.0(4)
OW(4)	0.398(2)	0.0307(8)	0.1475(6)	3.5(3)
OW(5)	0.116(2)	0.459(1)	0.4759(8)	8.0(6)

Results and discussion

TGA-DTA experiments

Figure 1 reproduces a thermogram showing three distinct decomposition stages. The first, at 114°C, corresponds to the dehydration of the sample, the second, at 308°C, involves the loss of NO and CN groups, and the third, an exothermic first-order transition. The residue was apparently a mixture of

Table 2. Bond distances (Å) and angles (deg) in the four nitroprusside anions

Bond distances

	$i = 1$	$i = 2$	$i = 3$	$i = 4$
Fe(i)–N(i)	1.62(2)	1.63(2)	1.59(2)	1.62(2)
Fe(i)–C(i1)	1.93(2)	1.93(2)	1.96(2)	1.92(2)
Fe(i)–C(i2)	1.88(2)	1.88(2)	1.91(2)	1.89(2)
Fe(i)–C(i3)	1.93(2)	1.89(2)	1.93(2)	1.94(2)
Fe(i)–C(i4)	1.92(2)	1.91(2)	1.90(2)	1.88(2)
Fe(i)–C(i5)	1.91(2)	1.95(2)	1.89(2)	1.93(2)
N(i)–O(i)	1.16(2)	1.13(2)	1.16(2)	1.15(2)
C(i1)–N(i1)	1.13(3)	1.15(3)	1.10(2)	1.14(3)
C(i2)–N(i2)	1.16(3)	1.15(3)	1.14(3)	1.16(3)
C(i3)–N(i3)	1.15(2)	1.17(3)	1.13(3)	1.11(3)
C(i4)–N(i4)	1.17(3)	1.15(3)	1.17(3)	1.19(3)
C(i5)–N(i5)	1.18(3)	1.15(3)	1.19(3)	1.16(3)

Bond angles

	$i = 1$	$i = 2$	$i = 3$	$i = 4$
N(i)–Fe(i)–N(i1)	90.3(9)	98.5(8)	93.8(8)	94.1(8)
N(i)–Fe(i)–C(i2)	94.0(9)	95.7(8)	98.5(8)	93.8(8)
N(i)–Fe(i)–C(i3)	177.5(9)	178(1)	177.6(8)	179.1(9)
N(i)–Fe(i)–C(i4)	98.4(9)	94.6(9)	94.6(8)	95.1(8)
N(i)–Fe(i)–C(i5)	97.0(9)	91.9(9)	93.5(8)	96.0(8)
C(i1)–Fe(i)–C(i2)	175.7(9)	165.7(8)	167.7(8)	171.7(8)
C(i1)–Fe(i)–C(i3)	87.3(8)	80.6(8)	83.9(8)	85.3(9)
C(i1)–Fe(i)–C(i4)	89.7(9)	91.1(8)	90.9(8)	88.7(9)
C(i1)–Fe(i)–C(i5)	90.2(9)	88.6(8)	90.3(8)	90.0(8)
C(i2)–Fe(i)–C(i3)	88.4(8)	85.3(9)	83.8(8)	86.8(9)
C(i2)–Fe(i)–C(i4)	90.1(9)	85.9(9)	88.6(8)	87.8(9)
C(i2)–Fe(i)–C(i5)	88.9(9)	92.8(9)	88.4(8)	91.2(8)
C(i3)–Fe(i)–C(i4)	81.2(8)	87(1)	86.1(8)	84.3(9)
C(i3)–Fe(i)–C(i5)	83.4(8)	86.1(9)	85.9(8)	84.6(9)
C(i4)–Fe(i)–C(i5)	164.6(9)	173.4(8)	171.7(8)	168.9(9)
Fe(i)–N(i)–O(i)	174(2)	175(2)	177(2)	178(2)
Fe(i)–C(i1)–N(i1)	179(2)	178(2)	175(2)	177(2)
Fe(i)–C(i2)–N(i2)	176(2)	178(2)	177(2)	176(2)
Fe(i)–C(i3)–N(i3)	179(2)	175(2)	176(2)	173(2)
Fe(i)–C(i4)–N(i4)	180(1)	171(2)	177(2)	177(2)
Fe(i)–C(i5)–N(i5)	179(2)	172(2)	177(2)	178(2)

iron(II) hexacyanoferrate(II), potassium hexacyanoferrate(II), and potassium cyanide (Gentil *et al.*, 1975). The expected weight change for the dehydration step was 7.1%, while the observed loss was 7.4%, in agreement with the value obtained after heating a sample for 6 h at 100°C under high vacuum. For the second step calculated and observed values were 17.7% and 17.9%, respectively.
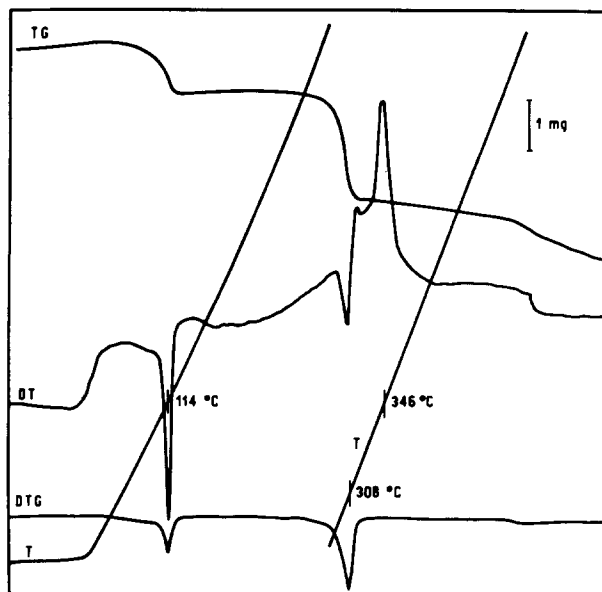
Fig. 1. TGA-DTA of K$_2$ [Fe(CN)$_5$NO] · 1.25H$_2$O.

Crystal structure and its determination

Figure 2 is a stereoscopic projection of one asymmetric unit of the structure, and it includes the labeling of the atoms. The nitroprusside ions present the usual distorted octahedral configuration. The Fe–N and Fe–C distances range within the intervals 1.59(2)–1.63(2) Å and 1.88(2)–1.96(2) Å, respectively, and the angles found among the iron atom and the nitrosyl and equatorial cyanide groups range from 90.3(9) to 98.5(8)°. These are in agreement with
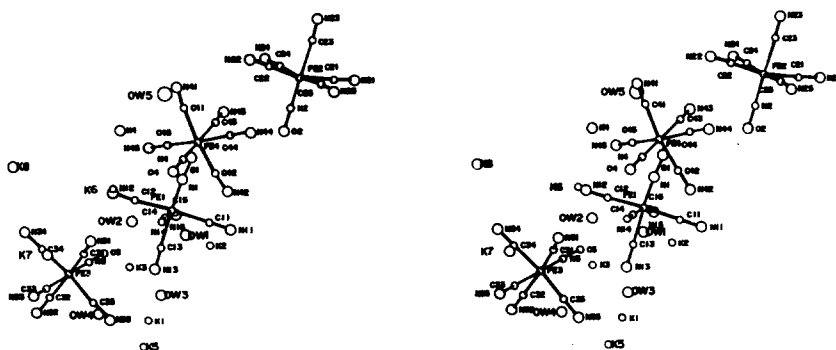

Fig. 2. Stereoscopic view of one asymmetric unit of K$_2$ [Fe(CN)$_5$NO] · 1.25H$_2$O. Projection direction was chosen so as to minimize overlap.

previous determinations (Punte *et al.*, 1980, and references therein). The water oxygen OW(5) shows a relatively high thermal parameter possibly due to a positional disorder. An occupational number less than unity for this water molecule was discarded because the weight change observed in the TG analysis is slightly larger than the expected value (see above).

Table 3 includes bond angles and distances for the coordination polyhedra assumed for the water molecules. Though proton positions cannot be determined from the present results, water coordination and possible hydrogen bond-

Table 3. Coordination distances (Å) and angles (deg) around the oxygen atoms of the water molecules

W1			
$OW(1^i)-N(15^i)$	3.02	$N(15^i)-OW(1^i)-N(41^v)$	112
$OW(1^i)-N(41^v)$	2.79	$N(15^i)-OW(1^i)-K(2^{vi})$	125
$OW(1^i)-K(2^{vi})$	2.91	$N(15^i)-OW(1^i)-OW(2^{vii})$	92
$OW(1^i)-OW(2^{vii})$	2.85	$N(41^v)-OW(1^i)-K(2^{vi})$	103
		$N(41^v)-OW(1^i)-OW(2^{vii})$	129
		$K(2^{vi})-OW(1^i)-OW(2^{vii})$	98
W2			
$OW(2^i)-N(25^{iii})$	3.27	$N(25^{iii})-OW(2^i)-K(3^{vii})$	126
$OW(2^i)-K(3^{vii})$	2.79	$N(25^{iii})-OW(2^i)-K(6^{iii})$	124
$OW(2^i)-K(6^{iii})$	2.79	$N(25^{iii})-OW(2^i)-OW(1^i)$	92
$OW(2^i)-OW(1^i)$	2.85	$K(3^{vii})-OW(2^i)-K(6^{iii})$	91
		$K(3^{vii})-OW(2^i)-OW(1^i)$	90
		$K(6^{iii})-OW(2^i)-OW(1^i)$	132
W3			
$OW(3^i)-N(13^v)$	2.89	$N(13^v)-OW(3^i)-N(23^i)$	86
$OW(3^i)-N(23^i)$	3.16	$N(13^v)-OW(3^i)-K(3^v)$	109
$OW(3^i)-K(3^v)$	2.84	$N(13^v)-OW(3^i)-K(5^i)$	121
$OW(3^i)-K(5^i)$	2.82	$N(23^i)-OW(3^i)-K(3^i)$	120
		$N(23^i)-OW(3^i)-K(5^i)$	121
		$K(3^v)-OW(3^i)-K(5^i)$	100
W4			
$OW(4^i)-N(35^i)$	3.06	$N(35^i)-OW(4^i)-N(42^{iv})$	127
$OW(4^i)-N(42^{iv})$	3.12	$N(35^i)-O(4^i)-K(3^i)$	96
$OW(4^i)-K(3^i)$	2.85	$N(35^i)-OW(4^i)-K(5^{iii})$	56
$OW(4^i)-K(5^{ii})$	2.98	$N(42^{iv})-OW(4^i)-K(3^i)$	130
		$N(42^{iv})-OW(4^i)-K(5^{ii})$	127
		$K(3^i)-OW(4^i)-K(5^{iii})$	97
W5			
$OW(5^i)-N(25^{iv})$	3.20	$N(25^{iv})-OW(5^i)-N(32^i)$	75
$OW(5^i)-N(32^i)$	3.27	$N(25^{iv})-OW(5^i)-O(4^{viii})$	85
$OW(5^i)-O(4^{viii})$	3.20	$N(25^{iv})-OW(5^i)-K(4^{ix})$	144
$OW(5^i)-K(4^{ix})$	2.83	$N(32^i)-OW(5^i)-O(4^{viii})$	156
		$N(32^i)-OW(5^i)-K(4^{ix})$	123
		$O(4^{viii})-OW(5^i)-K(4^{ix})$	81

Symmetry code: (i) x, y, z; (ii) $0.5 - x, -y, 0.5 + z$; (iii) $0.5 + x, 0.5 - y, 1 - z$; (iv) $x, y, z - 1$; (v) $-0.5 + x, 0.5 - y, 1 - z$; (vi) $0.5 - x, 1 - y, -0.5 + z$; (vii) $1 - x, 0.5 + y, 0.5 - z$; (viii) $-0.5 + x, -0.5 - y, 1 - z$; (ix) $-x, -0.5 + y, 0.5 - z$.

ing schemes can be deduced by looking for the most probably proton- and electron-acceptor atoms. Estimated standard deviations in the coordination distances are 0.03 Å. The estimated error in the coordination angles smaller than 90° is 1°, while accuracy for those angles with values close to 180° is 2°.

For OW(1), the most probable proton acceptors are N(15) at 3.02 Å and N(41) at 2.79 Å, with an angle N(15)–OW(1)–N(41) of 112°. The lone pairs of this oxygen could be accepted by one potassium ion at 2.91 Å [K(2)] and one hydrogen atom of W(2) whose oxygen is at 2.85 Å from OW(1). The three heavy atoms make an angle OW(2)–OW(1)–K(2) of 98°.

Friedman and Lewis (1976) proposed a parameter, the angle θ, which measures the deviation from planarity of the system formed by the water oxygen, a cation, and the two proton acceptors. Its value is zero for planar coordination and 31.5° for ideal tetrahedral geometry. For the calculations they use the proton acceptor–oxygen–proton acceptor angle instead of the HOH angle and conclude that for θ values of 15° or more the coordination is tetrahedral. For OW(1), $\theta = 20°$, and therefore it could be concluded that this water molecule has approximately tetrahedral geometry, with little distortion.

The water molecule W(2) has probably OW(1) as the acceptor of one of its protons, as discussed above. The other acceptor could be N(25) at 3.27 Å from OW(2). This gives an angle OW(1)–OW(2)–N(25) of 92°. The electron-pair acceptors should be K(3) and K(6) at 2.79 and 2.80 Å, respectively [angle K(6)–OW(2)–K(3) = 91°]. The θ values obtained from K(3) and K(6) are, respectively, 52 and 12°. If the HOH angle is closer to 109° than to 92°, as found for the OW(1)–OW(2)–N(25) angle, the θ values would be definitely smaller by approximately 17° than the previous values. It is then concluded that the coordination polyhedron for OW(2) is a little distorted tetrahedron.

For the W(3) water molecule the situation seems to be different because the two proton acceptors are now nitrogen atoms of cyanide groups [N(13) at 2.89 Å, N(23) at 3.16 Å, angle N(13)–OW(3)–N(23) = 86°] and the lone-pair acceptors are potassium ions [K(3) at 2.84 Å and K(5) at 2.82 Å with the angle K(3)–OW(3)–K(5) = 100°]. The values of the θ parameters are in this case 45 and 32° using K(3) and K(5), respectively, for the calculations. This indicates that the coordination polyhedron is close to a tetrahedron.

For the OW(4) oxygen atom the proton acceptors could be N(35) and N(42) at 3.06 and 3.12 Å, respectively [angle N(35)–OW(4)–N(42) = 127°]. Potassium ions K(3) at 2.86 and K(5) at 2.98 Å seem to be the electron acceptors, forming a K(5)–OW(4)–K(3) angle of 97°. The values of θ are in this case 7° [K(3)] and 50° [K(5)].

There is only one electron pair-acceptor ion near to OW(5) [K(4) at 2.83 Å] and neighboring proton acceptors are positioned in not very suitable orientations for hydrogen bonding. Nevertheless, N(32) is at 3.27 Å from OW(5) and it could be the acceptor for one of the W(5) protons. The other hydrogen

atom could form a bifurcated hydrogen bond with N(25) at 3.20 Å and O(4) at 3.21 Å, in a trigonal coordination, in agreement with the zero θ value. This loose bonding is perhaps responsible for the relative high thermal parameter exhibited by OW(5).

IR spectra

A typical room temperature Nujol mull spectrum is shown in Fig. 3. Tables 4 and 5 present wavenumbers and tentative assignments for the absorption features. Owing to the large distance between species related by screw axes in the unit cell (for NO groups, between 6.55 and 10.46 Å, and for water molecules, between 10.27 and 11.42 Å), the coupling of like vibrations is expected to be very weak. We shall therefore assume that the observed IR bands originate exclusively in the asymmetric unit composed of four independent nitroprusside anions and five independent water molecules. The assignment of bands due to the nitroprusside anions is as follows:

(a) CN stretching bands. Five bands at 2163 cm^{-1} (weak), 2155 cm^{-1} (medium), 2149 cm^{-1} (strong), 2140 and 2137 cm^{-1} (both very strong) are seen in the CN stretching region when the spectrum of PNP is run with Nujol mulls at room temperature (Fig. 3). In the low-temperature spectra the same number of bands are seen. Owing to the low sensitivity of the CN stretching wavenumber to the characteristics of the crystal, the observed bands can be interpreted as a nonresolved superposition of corresponding bands of the four different anions. Thus, the two most intense bands at 2140 and 2137 cm^{-1} could be attributed to the equatorial E modes of ideal C_{4v} anions split by the low symmetry of the C_1 sites, the strong band at 2140 cm^{-1} to the axial groups, and the less intense bands at 2163 and 2155 cm^{-1} to the equatorial modes
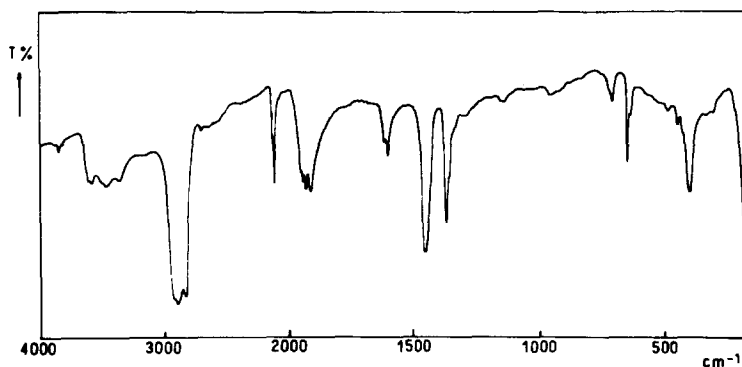

Fig. 3. Room temperature IR mull spectra of potassium nitroprusside sesquiquarterhydrate.

Table 4. Assignments for the IR absorption bands of the [Fe(CN)$_5$NO]$^{2-}$ ions in
K$_2$ [Fe(CN)$_5$NO] · 1.25H$_2$O^a

Mode^b	Room temperature	Low temperature (liquid-nitrogen temperature)	Description
	3905 (sh)	3922 (vvw)	
	3893 (vvw)	3906 (vvw)	$2\nu_{NO}$
	3854 (vvw)	3866 (vvw)	
	3828 (vvw)	3836 (vvw)	
A_1	2163 (w)	2168 (w)	ν_{CN} axial
A_1	2155 (m)	2162 (m)	
B_1	2149 (s)	2154 (s)	
E	2140 (vs)	2142 (vs)	ν_{CN} equatorial
	2137 (vs)	2138 (vs)	
	2115 (vvw)	2119 (vvw)	
	2109 (vvw)	2114 (vvw)	$\nu^{12}C^{15}N + \nu^{13}C^{14}N$
	2098 (vvw)	2102 (vvw)	
	2093 (sh)	2098 (vvw)	
	1964 (vs)	1968 (vs)	
A_1	1955 (vs)	1956 (vs)	ν_{NO}
	1942 (vs)	1947 (vs)	
	1924 (vs)	1928 (vs)	
E	664 (s)	668 (s)	δ_{FeNO}
		665 (sh)	
A_1	650 (w)	656 (sh)	ν_{FeN}
		652 (w)	
A_1, E	503 (w)	ca. 500 (w)	δ_{FeCN}
	463 (w)	465 (w)	
	442 (m)	447 (m)	
	419 (s)	420 (s)	c
	412 (s)	414 (s)	
	327 (vw)	ca. 330 (vw)	

^{a}Data in cm^{-1}; vvw, very very weak; vw, very weak; w, weak; m, medium; s, strong; vs, very strong; vvs, very very strong; sh, shoulder.
^{b}For C_{4v} symmetry.
^{c}FeC stretchings and FeCN deformations (cf. Varetti and Aymonino, 1973).

[otherwise inactive (B_1) or weakly active (A_1) under C_{4v} symmetry (cf. Varetti and Aymonino, 1973)].

(b) NO and FeN stretching and FeNO deformation bands. Four well-defined features are seen in the powder spectra in the NO fundamental stretching region at 1964, 1955, 1942, and 1924 cm^{-1} (Fig. 3). In the first overtone region there is a shoulder at 3905 cm^{-1} and there are three bands at 3893, 3854, and 3828 cm^{-1}. These features are consequences of the existence in the asymmetric unit of four different NO groups, which are more sensitive to the surroundings than the CN groups (Gans *et al.*, 1966). The sharpness of the bands suggests that the NO groups are vibrationally isolated from each other, a situation differing from that found in other nitroprussides where strong interaction between NO groups is observed (González *et al.*, 1984). The splitting of the NO stretch-

Table 5. Bands due to hydration water in K_2 [Fe(CN)$_5$NO] · 1.25 ($H_2O + D_2O$)[a]

Vibration	Room temperature	Low temperature (liquid-nitrogen temperature)	Assignment[b]
Stretchings	3640 (sh)	3642	H_2O (W5)
	3622	3623	H_2O
		3608	HOD (W5)
	3595	3596	H_2O
		3580	HOD (W5)
		3554	H_2O
		3552	HOD (W2)
		3544	HOD (W3)
	ca. 3524	3531	H_2O
			HOD (W4)[c]
		3497	H_2O
		3490 (sh)	HOD (W1)
		3485 (sh)	HOD (W4)
	3482	3480	H_2O
			HOD (W3)[c]
		3460	H_2O
		3431 (sh)	HOD (W2)
		3424 (sh)	H_2O
	3383	3375 (sh)	HOD (W1)
		3360	H_2O (W1)
	2692	2702	D_2O (W5)
		2688	D_2O
	2657	2658	HOD (W5)
	2655	2657	D_2O
		2644	D_2O
	2643	2638	HOD (W5)
		2630	D_2O
	2620 (sh)	2619	HOD (W2)
	2611	2615	HOD (W3)
		2596	D_2O
	2584	2591	HOD (W4)
	2579	2576	HOD (W1)
	2573	2557	HOD (W4)
		2556	D_2O
	2542	2547 (sh)	HOD (W3)
		2544 (sh)	D_2O
	2540 (sh)	2530	HOD (W2)
		2529 (sh)	D_2O
	2520	2499	HOD (W1)
	ca. 2500	2486	D_2O (W1)
Bendings		1647	HOH (W1)
	1628	1632	HOH (W2)
	1616	1625	HOH (W3)
		1613 (sh)	HOH (W4)
		1610	HOH (W5)
		1467	
		1450	
	1426 (br)	1422 (sh)	HOD[c]
		1433 (sh)	
		1429	
		1412	

Table 5. Continued

Vibration	Room temperature	Low temperature (liquid-nitrogen temperature)	Assignment[b]
		1213	DOD (W1)
	1201	1203	DOD (W2)
	1193	1195	DOD (W3)
		1190 (sh)	DOD (W4)
		1188	DOD (W5)
Librations[c]		699	H_2O (W1)
	590 (sh)	599	H_2O
		595	(HOD, D_2O)
	550 (sh)	558	H_2O
		530	(HOD, D_2O)
		514	(HOD, D_2O)
	504	495	(HOD, D_2O)
		ca. 490	H_2O
		437 (sh)	(HOD, D_2O)
		432	H_2O (W5)
		401 (sh)	(HOD, D_2O)
		390	H_2O (W1)
	355	362	H_2O
	329	331	H_2O
	325	330	(HOD, D_2O)
		318	H_2O
		311	(HOD, D_2O)
	ca. 305	299	H_2O (W5)
	278	279	(HOD, D_2O)
	267	263	(HOD, D_2O)

[a] Data in cm^{-1}; br, broad; sh, shoulder.
[b] HOD in the stretchings represent OH or OD isolated stretchings, as the case may be.
[c] See text.

ings must be due, therefore, to differences in the crystal sites occupied by the anions and not to dynamic coupling in the lattice which is unfavored by the large distances existing between equivalent anions.

The bands at 664 cm^{-1} and 650 cm^{-1} in the room temperature spectrum (Fig. 3) are due to the FeNO deformation modes and to the FeN stretchings, respectively (Sabatini, 1967; Khanna et al., 1969; Paliani et al., 1971). These modes are also not sensitive enough to the surroundings (Gans et al., 1966) to give rise to any band splitting at room temperature. Anyway, in the low-temperature spectrum two bands are seen at 668 and 652 cm^{-1}, and two shoulders at 665 and 656 cm^{-1}.

(c) FeC stretchings and FeCN deformations. Bands at 503, 463, 442, 419, 412, and 327 cm^{-1} in the room-temperature IR spectra and at ca. 500, 465, 447, 420, 414 and ca. 330 cm^{-1} in the low-temperature spectra which are due

to anions by comparison with the spectra of the anhydrous sample and other nitroprussides (Varetti and Aymonino, 1973) should be assigned to these modes. According to Swanson and Jones (1974) the band of higher wavenumber should be assigned to deformation and the others to deformations and stretchings, although no clear-cut distinction can be made between the two groups.

(d) CFeC and CFeN deformations. These bands appear below 250 cm^{-1} (Bates and Khanna, 1970), a spectral region where the quality of the spectra does not allow a clear recognition of expected bands.

Bands assigned to water vibrations display features expected from several crystallographically different molecules. Figure 4 shows the IR absorption bands obtained for the compound with different degrees of deuteration, whereas the corresponding wavenumbers and assignments are presented in Table 5. The assignment of bands due to water is as follows:

(a) Stretching regions. Ten features are observed in the OD stretching zone at 2658, 2638, 2619, 2615, 2591, 2576, 2557, 2547 (sh), 2530, and 2499 cm^{-1} in the low-temperature spectra of samples with a small degree of deuteration (Fig. 4), in agreement with that expected from five inequivalent and asymmetric water molecules. As the deuterium content increases, new bands due to the antisymmetric and symmetric D_2O stretchings appear at 2702, 2688, 2657, 2644, 2630, 2596, 2556, 2544 (sh), 2529 (sh), and 2486 cm^{-1}. Again the number of D_2O stretching bands is in accordance with expectation for the five types of water molecules present in the crystal. In the OH stretching region (Table 5 and Fig. 4) deuteration causes bands due to OH stretchings of HOD species at 3608, 3580, 3552, 3544, 3490 (sh), 3485 (sh), 3431 (sh), and 3375 cm^{-1}. The one-to-one correspondence between these features and those observed in the OD region, also for isolated stretchings, are suggested by the following quotients: $3608/2658 = 1.357$, $3580/2638 = 1.357$, $3552/2619 =$
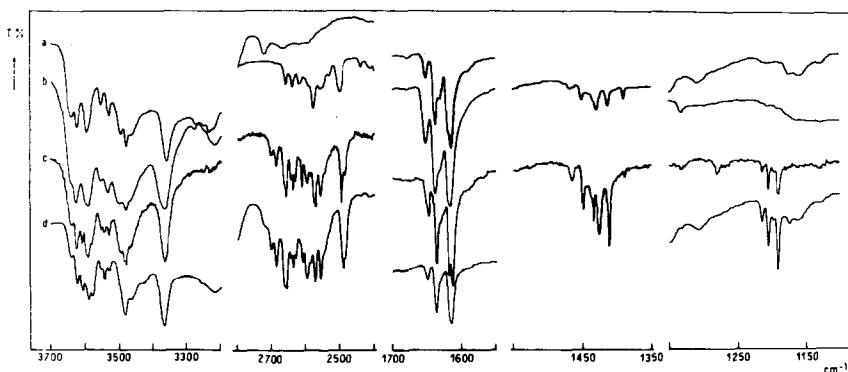

Fig. 4. IR water bands (due to internal vibrations) in partially deuterated samples of K_2 [Fe(CN)$_5$NO] · 1.25H$_2$O at liquid-nitrogen temperature: (a) 0%; (b) 5%; (c) 24%; (d) 50% D.

1.356, 3544/2615 = 1.355, 3490/2576 = 1.355, 3485/2557 = 1.363, 3431/ 2530 = 1.356, and 3375/2499 = 1.351. These ratios are the expected ones for the isotopic substitution shifts, increasing with the OH (OD) stretching wavenumber (Berglund *et al.*, 1978a).

The OH stretching bands related to OD bands at 2591 and 2547 cm^{-1} should be located at about 3510 and 3460 cm^{-1}, respectively, where they are hidden by stronger bands.

(b) The bending region. The bands due to the bending modes of H$_2$O and D$_2$O are doublets at room temperature. In the low-temperature spectra with different degrees of deuteration five features are seen in each bending region (Fig. 4). For the H$_2$O bendings they are at 1647, 1632, 1625, 1613 (sh), and 1610 cm^{-1} in the undeuterated sample. In the D$_2$O region, features were found at 1213, 1203, 1195, 1190 (sh), and 1188 cm^{-1}. The five features found in each region should correspond therefore to the five inequivalent water molecules present in the lattice. It seems that between the five water molecules there are two pairs whose components do not differ too much in bending behavior. In the HOD region, a broad band is seen at 1426 cm^{-1} in the spectrum with 5% of deuterium content at room temperature. In the low-temperature spectra six features are seen at 1467, 1450, 1442 (sh), 1433 (sh), 1429 (sh), and 1412 cm^{-1}. In fact, one should expect ten bands arising from the five kinds of asymmetrical water molecules, but again differences between the components of pairs of water molecules seem to be not too great.

(c) The librational region. The following bands can be assigned by taking advantage of the increase in intensity experienced by librational bands upon cooling and by comparison with the spectrum of the anhydrous substance: 699, 599, 558, ca. 490, 432, 390, 362, 331, 318, and 299 cm^{-1} (wavenumbers from low-temperature spectra). In the spectra of deuterated samples (Fig. 5) new bands appear at 595, 530, 514, 495, 437 (sh), 401 (sh), 330, 311, 279, and 263 cm^{-1}. As the HOD content in the samples is higher than the D$_2$O content, most of these bands must correspond to the former species. The number of bands observed is again explained by the existence of different water molecules.

A tentative detailed assignment of water bands

To facilitate the assignment of the corresponding IR absorption bands we can characterize the five water molecules by classifying them into three different coordination groups: (1) W(5) is nearly free, with trigonal coordination; (2) W(1) and W(2) can be treated as a dimer; (3) W(3) and W(4) have tetrahedral crystal environments.

Bands belonging to W(5) are the easiest to assign because of its nearly free H(D)–O bonds and the minor polarization effect due to neighboring cations, since it is coordinated to only one of them. As the distance between OW(5) and the nearest proton acceptor [N(32)] is the largest found in the crystal between
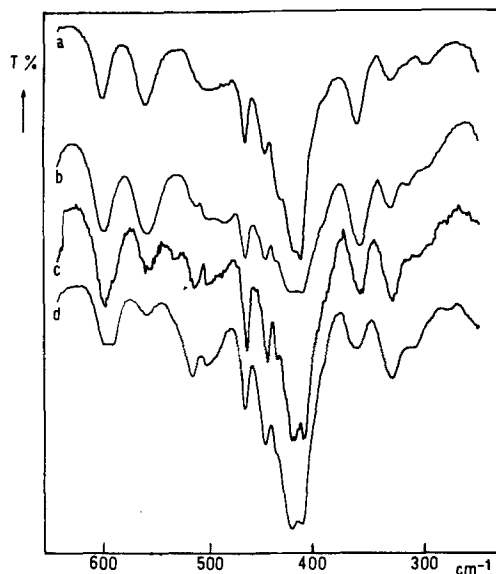
Fig. 5. Low-frequency IR spectra (liquid-nitrogen temperature) for partially deuterated
K$_2$[Fe(CN)$_5$NO] $\cdot$ 1.25H$_2$O: (a) 0%; (b) 5%; (c) 24%; (d) 50% D.

proton donors and acceptors, the stretching wavenumber for the corresponding
OH (OD) group should be the highest. This behavior could also be expected
from the smaller polarization perturbation on W(5) due to a single cation as
compared with the other water molecules which are bonded to two cations. [An
explanation for the behavior of the stretching band of the OD group in the
presence of cations will be discussed elsewhere (Amalvy and Aymonino, 1986).]
Thus, the two OD bands of highest wavenumber (2658 and 2638 cm^{-1}) could
be assigned to this loosely bound water molecule. The assignment of each band
to a particular bond can be made on the basis of the dependence of the OH
stretching wavenumber on the temperature and the hydrogen-bonding type. For
straight H-bonds the stretching wavenumber decreases with decreasing temper-
ature while a negative correlation with temperature is characteristic of highly
bent or bifurcated bonds (Knop *et al.*, 1980). The band at 2658 cm^{-1} has a
negative temperature coefficient (-0.005 cm^{-1} K^{-1}) and the band at 2638 cm^{-1}
a positive one ($+0.002$ cm^{-1} K^{-1}). This latter band should correspond to the
OD bond located between OW(5) and N(32). The wavenumber of the band
assigned to the stretching of the least bonded OD group of W(5) is higher than
the wavenumbers reported for such stretching in other nitroprussides where the
water molecules are affected only by the cation (Varetti and Aymonino, 1982).

The W(1) $\cdots$ W(2) dimer can be considered as nearly isolated because of
the intrinsic weakness of the CN $\cdots$ H bonds (Holzbecher *et al.*, 1971) (see

below). Therefore, the pair of OH(OD) stretching bands associated with the asymmetric water molecule that donates one of its protons to form a strong hydrogen bond [W(2) in this case] should be well separated from each other and the band corresponding to the bonded hydrogen should have the lowest wavenumber. The other molecule should be almost unchanged by the bonding. This fact and the relationship between oxygen–acceptor distances and ν(OH) [ν(OD)] stretching wavenumbers (Berglund *et al.*, 1978b) (in the following referred to as the d(O · · · O) vs ν relationship) sustains the assignment of the 2619 and 2530 cm^{-1} bands to the W(2) water, the former to the OH bond pointing to N(25) and the latter to the other bond which points to OW(1). Though the water molecule W(1) should not be much affected by the proton of W(2), it could be perturbed by the neighboring N(41) nitrogen atom which is at the shortest O–N distance found in this compound [d(OW(1)–N(41)) = 2.79 Å]; therefore the band of lower wave number (2499 cm^{-1}) can be assigned to the corresponding OD bond while the band at 2576 cm^{-1} to the other OH(OD) group on the basis of the d(O · · · O) vs ν relationship. The N(41)–OW(1)–N(15) angle of 112° points to a nearly linear H bond and therefore to a positive temperature coefficient for these bands (observed values: +0.105 cm^{-1} K^{-1} and +0.015 cm^{-1} K^{-1}, respectively).

Assuming again that the shorter bond distance corresponds to the lower wavenumber, the shoulders at 2615 and 2547 cm^{-1} can be assigned to W(1). The other two bands at 2591 and 2557 cm^{-1} should be assigned therefore to the W(4) water molecule. The new bands which appear when the deuterium content increases and which are due to the D$_2$O molecules, are more difficult to assign.

In the bending region the band of high wavenumber (1647 cm^{-1}) can be assigned to W(1) because of the strength of the hydrogen bond and the small effect of the cation on this water (Falk, 1984). W(5), which is the loosely held water molecule, should have the lower bending wavenumber and therefore the band at 1610 cm^{-1} is assigned to it (Falk, 1984). As the cation effect should be approximately the same for the other water molecules, the corresponding assignments can be made using the fact that a strong hydrogen bond gives rise to a high bending frequency (Falk, 1984). In this way, the bands at 1632, 1625, and 1613 cm^{-1} can be assigned, respectively, to W(2), W(3), and W(4). The same pattern of assignments can be proposed for the D$_2$O bending region (Table 5).

In the HOD bending region the situation is not so clear because only six bands appear instead of the ten bands expected for five asymmetric water molecules. It is to be taken into account, however, that the separation between bending bands for the two conformations X · · · HOD · · · Y and X · · · DOH · · · Y is smaller than for the OH (OD) stretching bands (Brink and Falk, 1970). As the half-width of the HOD bending bands is about 10 cm^{-1} at

low temperature, the splitting could not be detected. Anyway, the existence of different kinds of water molecules is spectroscopically confirmed, although their number is not determined from the features seen in this region of the spectrum.

Although the assignment of librational bands to definite water molecules is difficult, the bands at 699 and 390 cm^{-1} can be assigned straightforwardly to the W(1) water molecule in correspondence with the low stretching frequencies found for this molecule. The bands at 432 and 299 cm^{-1} could be due to the least hydrogen-bonded water, W(5).

Acknowledgment

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