Structures of the Potassium Nitroprusside 2·5 and 0·8 Hydrates

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Abstract. Potassium pentacyanonitrosylferrate hydrate (1/2·5), $K_2[Fe(CN)_5NO].2·5H_2O$, $M_r = 339·18$, monoclinic, $P2_1/n$ (No. 14), $a = 10·054$ (4), $b = 24·510$ (5), $c = 11·018$ (6) Å, $\beta = 109·60$ (4)°, $V = 2558$ (3) Å^3, $Z = 8$, $D_m = 1·75$, $D_x = 1·762$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, $\mu(Mo\ K\alpha) = 18$ cm^{-1}, $F(000) = 1352$. Potassium pentacyanonitrosylferrate hydrate (1/0·8), $K_2[Fe(CN)_5NO].0·8H_2O$, $M_r = 311·98$, orthorhombic, $Pna2_1$ (No. 33), $a = 30·000$ (8), $b = 11·272$ (3), $c = 16·053$ (4) Å, $V = 5428$ (2) Å^3, $Z = 20$, $D_x = 1·909$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, $\mu(Mo\ K\alpha) = 21$ cm^{-1}, $F(000) = 3108$. Both structures were solved by the heavy-atom technique and refined anisotropically to R factors 0·040 and 0·059, from 2805 and 3436 $I \geq 3\sigma(I)$ independent reflections, respectively. In both structures the water molecules are not involved in strong hydrogen bonds. The low specificity of these interactions is probably responsible for the occurrence of the three different hydrates reported [Amalvy, Varetti, Aymonino, Castellano, Piro & Punte (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 537–555].

Experimental. $K_2[Fe(CN)_5NO].0·8H_2O$ was obtained from an aqueous solution of commercial potassium nitroprusside, after several recrystallizations had been carried out to remove impurities. $K_2[Fe(CN)_5NO].2·5H_2O$ was prepared as described by Amalvy, Varetti & Aymonino (1985). Density was measured by flotation. In both cases, single crystals, appropriate for X-ray structure determination, were grown from a saturated aqueous solution by slow evaporation at room temperature. We point out the interesting fact that the same hygrostatic system stabilized both hydrates, as well as the previously reported $K_2[Fe(CN)_5NO].1·25H_2O$ (Amalvy, Varetti, Aymonino, Castellano, Piro & Punte, 1986).

Table 2. *Fractional atomic coordinates and isotropic temperature factors* (Å^2) *in the* 2·5 *hydrate*

	x	y	z	B_{iso}
Fe(1)	1·0578 (1)	0·0736 (0)	0·6963 (1)	2·45 (2)
N(1)	1·1408 (4)	0·0726 (2)	0·5892 (4)	2·7 (1)
O(1)	1·1910 (4)	0·0744 (2)	0·5121 (4)	4·3 (1)
C(11)	0·8741 (5)	0·0578 (2)	0·5725 (5)	3·1 (1)
N(11)	0·7644 (5)	0·0505 (2)	0·4988 (5)	4·6 (2)
C(12)	1·0145 (5)	0·1505 (2)	0·6661 (5)	2·9 (1)
N(12)	0·9855 (5)	0·1951 (2)	0·6410 (5)	4·1 (2)
C(13)	1·2221 (6)	0·0880 (2)	0·8459 (5)	3·3 (2)
N(13)	1·3188 (6)	0·0935 (2)	0·9390 (5)	5·5 (2)
C(14)	1·0810 (5)	−0·0030 (2)	0·7414 (5)	2·8 (1)
N(14)	1·0941 (5)	−0·0475 (2)	0·7726 (4)	4·0 (1)
C(15)	0·9574 (5)	0·0772 (2)	0·8192 (5)	3·0 (1)
N(15)	0·8969 (5)	0·0783 (2)	0·8903 (5)	4·4 (2)
Fe(2)	0·8063 (1)	0·2517 (0)	−0·1015 (1)	2·38 (2)
N(2)	0·7517 (4)	0·2124 (2)	−0·2318 (4)	2·7 (1)
O(2)	0·7089 (4)	0·1844 (2)	−0·3164 (4)	4·3 (1)
C(21)	0·9959 (5)	0·2224 (2)	−0·0321 (4)	2·6 (1)
N(21)	1·1107 (4)	0·2077 (2)	0·0105 (4)	3·5 (1)
C(22)	0·7365 (4)	0·1983 (2)	−0·0071 (5)	2·6 (1)
N(22)	0·6919 (4)	0·1664 (2)	0·0434 (4)	3·7 (1)
C(23)	0·6318 (5)	0·2925 (2)	−0·1442 (5)	3·0 (1)
N(23)	0·5310 (4)	0·3185 (2)	−0·1714 (5)	4·0 (1)
C(24)	0·8877 (5)	0·3095 (2)	−0·1760 (5)	3·0 (1)
N(24)	0·9367 (5)	0·3430 (2)	−0·2194 (5)	4·4 (2)
C(25)	0·8579 (5)	0·2942 (2)	0·0547 (5)	3·2 (1)
N(25)	0·8887 (5)	0·3203 (2)	0·1474 (5)	4·5 (2)
K(1)	0·0953 (1)	0·1107 (1)	0·1391 (1)	4·46 (4)
K(2)	0·7615 (1)	0·1358 (1)	0·3101 (1)	4·02 (4)
K(3)	0·6611 (2)	0·0487 (1)	0·9715 (1)	5·60 (5)
K(4)	0·4046 (1)	0·2033 (1)	0·0209 (1)	3·85 (3)
O(W1)	1·2443 (5)	0·2542 (2)	−0·1969 (4)	5·5 (1)
O(W2)	0·5586 (4)	0·0431 (2)	0·1701 (4)	5·6 (1)
O(W3)	1·2720 (5)	0·0261 (2)	0·2330 (5)	6·8 (2)
O(W4)	0·4895 (6)	0·0685 (2)	−0·2728 (5)	7·8 (2)
O(W5)	0·4791 (5)	0·0608 (2)	0·4657 (6)	8·2 (2)

Table 1. *X-ray data collection parameters*

Hydrate	2·5	0·8
Crystal shape	Prismatic, rectangular basis	Prismatic, rectangular basis
Crystal size (mm)	0·15 × 0·35 × 0·55	0·18 × 0·36 × 0·50
Scan technique	ω–2θ	ω–2θ
Scanning speed range (° min^{-1})	6·7–20	6·7–20
No. of centered reflections	25	25
θ range of centered reflections (°)	8–24	14–26
θ range for data collection (°)	0–24	0–25
hkl ranges	$-11 \leq h \leq 10$	$0 \leq h \leq 35$
	$0 \leq k \leq 28$	$0 \leq k \leq 13$
	$0 \leq l \leq 12$	$0 \leq l \leq 19$
No. of independent reflections	4009	5078
No. of reflections above $3\sigma(I)$	2805	3436
Minimization function	$\sum w(|F_o| - |F_c|)^2$	$\sum w(|F_o| - |F_c|)^2$
Weighting scheme	$w = [\sigma^2(F_o) + 0·04F_o^2]^{-1}$	$w = [\sigma^2(F_o) + 0·15F_o^2]^{-1}$
R	0·040	0·059
wR	0·046	0·066
No. of refined parameters	202	393
S	1·23	1·40
R_{sym} and No. of equivalent reflections	0·061, 433	0·022, 471
Extinction correction	$F_{corr} = F_c[1 - 1·1 \times 10^{-7} \times F_c^2(\sin\theta)]$	$F_{corr} = F_c[1 - 1·1 \times 10^{-7} \times F_c^2(\sin\theta)]$

Table 3. *Fractional atomic coordinates and isotropic temperature factors (Å^2) in the 0·8 hydrate*

	x	y	z	B_{iso}
Fe(1)	0·1161 (1)	0·0170 (1)	0·0162 (1)	1·26 (5)
N(1)	0·1382 (3)	0·1185 (9)	−0·0400 (6)	2·4 (2)
O(1)	0·1562 (3)	0·1840 (9)	−0·0827 (6)	4·2 (2)
C(11)	0·0846 (3)	0·1211 (8)	0·0936 (5)	0·3 (2)
N(11)	0·0640 (3)	0·1659 (9)	0·1430 (6)	2·9 (2)
C(12)	0·0639 (4)	0·005 (1)	−0·0449 (7)	1·8 (2)
N(12)	0·0320 (4)	0·000 (1)	−0·0865 (8)	4·9 (3)
C(13)	0·1404 (4)	−0·105 (1)	−0·0472 (7)	2·1 (2)
N(13)	0·1569 (3)	−0·1647 (9)	−0·1022 (6)	3·2 (2)
C(14)	0·1650 (4)	0·022 (1)	0·1002 (7)	1·8 (2)
N(14)	0·1901 (3)	0·0245 (8)	0·1486 (6)	1·9 (2)
C(15)	0·0883 (4)	−0·109 (1)	0·0769 (7)	2·2 (2)
N(15)	0·0715 (3)	−0·1794 (9)	0·1174 (7)	3·2 (2)
Fe(2)	0·1182 (1)	0·5114 (1)	−0·0014 (1)	1·31 (5)
N(2)	0·1448 (3)	0·6092 (7)	0·0548 (5)	1·1 (1)
O(2)	0·1611 (3)	0·6881 (7)	0·0864 (5)	2·8 (2)
C(21)	0·0714 (4)	0·4946 (9)	0·0798 (7)	1·9 (2)
N(21)	0·0381 (3)	0·4892 (9)	0·1237 (7)	3·2 (2)
C(22)	0·1511 (3)	0·395 (1)	0·0555 (7)	1·6 (2)
N(22)	0·1664 (3)	0·3159 (8)	0·0878 (5)	1·7 (2)
C(23)	0·1609 (3)	0·5072 (9)	−0·0882 (7)	1·3 (2)
N(23)	0·1905 (4)	0·526 (1)	−0·1364 (8)	3·8 (2)
C(24)	0·0823 (3)	0·6121 (9)	−0·0674 (6)	1·3 (2)
N(24)	0·0594 (3)	0·6758 (8)	−0·1089 (6)	1·9 (2)
C(25)	0·0874 (3)	0·3907 (9)	−0·0647 (6)	1·3 (2)
N(25)	0·0690 (3)	0·3167 (7)	−0·1019 (5)	1·5 (2)
Fe(3)	0·1169 (1)	0·0182 (1)	0·4843 (1)	1·51 (5)
N(3)	0·1420 (3)	0·1186 (7)	0·5435 (5)	1·0 (1)
O(3)	0·1593 (3)	0·1797 (7)	0·5864 (5)	2·4 (2)
C(31)	0·1642 (3)	0·0092 (9)	0·4073 (7)	1·2 (2)
N(31)	0·1954 (3)	0·0188 (9)	0·3594 (7)	3·1 (2)
C(32)	0·0827 (4)	0·111 (1)	0·4072 (8)	3·0 (3)
N(32)	0·0632 (3)	0·1710 (8)	0·3603 (6)	1·8 (2)
C(33)	0·0640 (3)	0·0113 (8)	0·5614 (6)	0·9 (2)
N(33)	0·0327 (3)	0·0082 (7)	0·6016 (6)	1·4 (2)
C(34)	0·1468 (3)	−0·1024 (9)	0·5540 (6)	1·3 (2)
N(34)	0·1608 (3)	−0·1779 (8)	0·5879 (6)	1·9 (2)
C(35)	0·0906 (4)	−0·102 (1)	0·4189 (1)	1·6 (2)
N(35)	0·0728 (3)	−0·1729 (9)	0·3815 (7)	2·9 (2)
Fe(4)	0·1181 (1)	0·5116 (1)	0·5031 (1)	1·40 (5)
N(4)	0·1422 (3)	0·6179 (8)	0·4525 (6)	1·9 (2)
O(4)	0·1626 (3)	0·6784 (7)	0·4108 (5)	2·8 (2)
C(41)	0·0686 (4)	0·487 (1)	0·4258 (8)	2·3 (2)
N(41)	0·0465 (3)	0·4691 (8)	0·3685 (7)	2·8 (2)
C(42)	0·0795 (4)	0·619 (1)	0·5642 (8)	2·3 (2)
N(42)	0·0580 (4)	0·670 (1)	0·6009 (7)	4·1 (2)
C(43)	0·1624 (3)	0·5212 (9)	0·5944 (7)	1·3 (2)
N(43)	0·1857 (3)	0·5227 (7)	0·6479 (5)	0·9 (1)
C(44)	0·1491 (3)	0·3809 (9)	0·4505 (6)	1·1 (2)
N(44)	0·1709 (4)	0·308 (1)	0·4171 (7)	3·5 (2)
C(45)	0·0893 (4)	0·391 (1)	0·5656 (8)	2·7 (2)
N(45)	0·0702 (4)	0·330 (1)	0·6606 (8)	4·4 (2)
Fe(5)	0·2435 (0)	0·0215 (1)	0·7518 (2)	1·66 (4)
N(5)	0·1879 (3)	0·0227 (6)	0·748 (1)	2·3 (2)
O(5)	0·1495 (3)	0·0249 (6)	0·748 (1)	4·4 (2)
C(51)	0·2470 (3)	0·1885 (9)	0·754 (2)	2·5 (2)
N(51)	0·2494 (3)	0·2888 (8)	0·752 (2)	3·5 (2)
C(52)	0·2491 (5)	0·029 (2)	0·874 (1)	1·3 (3)
N(52)	0·2499 (6)	0·039 (1)	0·943 (1)	3·3 (3)
C(53)	0·2480 (3)	−0·1453 (8)	0·753 (2)	2·0 (2)
N(53)	0·2486 (2)	−0·2462 (7)	0·755 (1)	2·3 (2)
C(54)	0·2474 (6)	0·022 (2)	0·635 (1)	2·1 (3)
N(54)	0·2497 (6)	0·030 (1)	0·562 (1)	3·0 (3)
C(55)	0·3088 (3)	0·0217 (7)	0·748 (1)	1·5 (2)
N(55)	0·3459 (3)	0·0254 (7)	0·749 (1)	3·1 (2)
O(W1)	0·2498 (2)	0·8264 (6)	0·0610 (5)	1·6 (1)
O(W2)	0·0603 (2)	−0·1379 (6)	−0·250 (1)	4·0 (2)
O(W3)	0·0713 (4)	−0·4916 (8)	−0·243 (1)	7·8 (3)
O(W4)	−0·0196 (3)	−0·2363 (6)	0·250 (1)	4·3 (2)
K(1)	0·2532 (2)	0·2105 (5)	0·4292 (4)	4·3 (2)
K(2)	0·0024 (1)	0·3289 (2)	0·2513 (3)	2·76 (7)
K(3)	0·2460 (1)	0·7044 (4)	0·5727 (3)	2·4 (1)
K(4)	0·0230 (1)	0·9780 (2)	0·2525 (3)	3·12 (8)
K(5)	0·1350 (1)	0·6994 (2)	−0·2485 (3)	3·82 (9)
K(6)	0·1474 (1)	0·2409 (2)	0·2506 (4)	3·49 (8)
K(7)	0·0686 (1)	0·6510 (2)	0·2505 (4)	3·06 (8)
K(8)	0·0006 (2)	0·2263 (4)	0·5046 (3)	3·3 (2)
K(9)	0·2523 (1)	−0·0023 (3)	0·2520 (4)	6·0 (1)
K(10)	0·4974 (2)	0·7277 (4)	0·5013 (3)	3·7 (2)

Table 4. *Interatomic bond distances (Å) and intramolecular bond angles (°) in the 2·5 hydrate*

Fe(1)–N(1)	1·658 (4)	Fe(2)–N(2)	1·662 (4)
Fe(1)–C(13)	1·935 (6)	Fe(2)–C(21)	1·938 (5)
Fe(1)–C(11)	1·932 (5)	Fe(2)–C(22)	1·943 (5)
Fe(1)–C(14)	1·936 (5)	Fe(2)–C(23)	1·935 (5)
Fe(1)–C(12)	1·938 (5)	Fe(2)–C(24)	1·950 (5)
Fe(1)–C(15)	1·944 (5)	Fe(2)–C(25)	1·928 (6)
N(1)–O(1)	1·125 (6)	N(2)–O(2)	1·121 (6)
C(13)–N(13)	1·160 (8)	C(21)–N(21)	1·148 (7)
C(11)–N(11)	1·143 (7)	C(22)–N(22)	1·136 (7)
C(14)–N(14)	1·138 (7)	C(23)–N(23)	1·149 (7)
C(12)–N(12)	1·141 (7)	C(24)–N(24)	1·142 (7)
C(15)–N(15)	1·142 (7)	C(25)–N(25)	1·156 (8)
N(1)–Fe(1)–C(13)	96·9 (2)	N(2)–Fe(2)–C(21)	97·0 (2)
N(1)–Fe(1)–C(11)	94·9 (2)	N(2)–Fe(2)–C(22)	89·9 (2)
N(1)–Fe(1)–C(14)	97·0 (2)	N(2)–Fe(2)–C(23)	94·6 (2)
N(1)–Fe(1)–C(12)	91·7 (2)	N(2)–Fe(2)–C(24)	97·0 (2)
N(1)–Fe(1)–C(15)	178·0 (2)	N(2)–Fe(2)–C(25)	175·1 (2)
C(13)–Fe(1)–C(11)	168·2 (2)	C(21)–Fe(2)–C(22)	91·3 (2)
C(13)–Fe(1)–C(14)	87·9 (2)	C(21)–Fe(2)–C(23)	168·2 (2)
C(13)–Fe(1)–C(12)	92·7 (2)	C(21)–Fe(2)–C(24)	86·5 (2)
C(13)–Fe(1)–C(15)	83·8 (2)	C(21)–Fe(2)–C(25)	85·0 (2)
C(11)–Fe(1)–C(14)	89·5 (2)	C(22)–Fe(2)–C(23)	91·0 (2)
C(11)–Fe(1)–C(12)	88·1 (2)	C(22)–Fe(2)–C(24)	173·0 (2)
C(11)–Fe(1)–C(15)	84·5 (2)	C(22)–Fe(2)–C(25)	85·6 (2)
C(14)–Fe(1)–C(12)	171·1 (2)	C(23)–Fe(2)–C(24)	89·8 (2)
C(14)–Fe(1)–C(15)	84·9 (2)	C(23)–Fe(2)–C(25)	83·6 (2)
C(12)–Fe(1)–C(15)	86·3 (2)	C(24)–Fe(2)–C(25)	87·6 (2)
Fe(1)–N(1)–O(1)	175·5 (4)	Fe(2)–N(2)–O(2)	175·5 (4)
Fe(1)–C(13)–N(13)	175·6 (5)	Fe(2)–C(21)–N(21)	176·5 (4)
Fe(1)–C(11)–N(11)	177·4 (5)	Fe(2)–C(22)–N(22)	177·2 (4)
Fe(1)–C(14)–N(14)	177·2 (5)	Fe(2)–C(23)–N(23)	177·1 (5)
Fe(1)–C(12)–N(12)	176·1 (5)	Fe(2)–C(24)–N(24)	179·2 (5)
Fe(1)–C(15)–N(15)	178·5 (5)	Fe(2)–C(25)–N(25)	179·1 (5)

Table 5. *Interatomic bond distances (Å) and intramolecular bond angles (°) in the 0·8 hydrate*

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$
Fe(i)–N(i)	1·62 (1)	1·653 (9)	1·679 (8)	1·64 (1)	1·669 (8)
Fe(i)–C(i1)	1·953 (9)	1·93 (1)	1·88 (1)	1·96 (1)	1·88 (1)
Fe(i)–C(i2)	1·85 (1)	1·90 (1)	1·93 (1)	1·96 (1)	1·97 (2)
Fe(i)–C(i3)	1·86 (1)	1·89 (1)	2·01 (1)	1·98 (1)	1·88 (1)
Fe(i)–C(i4)	1·99 (1)	1·91 (1)	2·00 (1)	1·94 (1)	1·88 (2)
Fe(i)–C(i5)	1·91 (1)	1·93 (1)	1·91 (1)	1·92 (1)	1·960 (9)
N(i)–O(i)	1·16 (1)	1·15 (1)	1·12 (1)	1·15 (1)	1·15 (1)
C(i1)–N(i1)	1·13 (1)	1·22 (2)	1·22 (2)	1·15 (2)	1·16 (1)
C(i2)–N(i2)	1·17 (2)	1·15 (1)	1·18 (1)	1·05 (2)	1·11 (2)
C(i3)–N(i3)	1·23 (2)	1·20 (2)	1·14 (1)	1·11 (1)	1·14 (1)
C(i4)–N(i4)	1·08 (1)	1·21 (1)	1·11 (1)	1·19 (2)	1·18 (3)
C(i5)–N(i5)	1·16 (2)	1·18 (1)	1·15 (1)	1·07 (2)	1·11 (1)
N(i)–Fe(i)–C(i1)	96·0 (4)	93·0 (4)	94·1 (4)	97·4 (5)	92·7 (7)
N(i)–Fe(i)–C(i2)	96·0 (5)	88·4 (4)	103·9 (5)	93·4 (5)	97·0 (7)
N(i)–Fe(i)–C(i3)	93·3 (5)	95·3 (4)	91·9 (4)	91·6 (4)	94·5 (6)
N(i)–Fe(i)–C(i4)	93·1 (5)	99·1 (4)	88·0 (4)	97·5 (4)	91·5 (7)
N(i)–Fe(i)–C(i5)	176·3 (5)	177·7 (4)	177·0 (4)	177·9 (5)	176·1 (6)
C(i1)–Fe(i)–C(i2)	88·5 (4)	89·0 (5)	90·6 (5)	87·8 (5)	86·2 (7)
C(i1)–Fe(i)–C(i3)	169·2 (4)	171·4 (5)	173·7 (4)	170·6 (5)	172·7 (7)
C(i1)–Fe(i)–C(i4)	84·8 (4)	91·5 (5)	89·5 (4)	88·6 (5)	90·7 (7)
C(i1)–Fe(i)–C(i5)	86·4 (4)	86·3 (5)	84·9 (5)	83·4 (5)	86·9 (6)
C(i2)–Fe(i)–C(i3)	89·1 (5)	89·1 (5)	89·8 (5)	89·5 (5)	91·6 (7)
C(i2)–Fe(i)–C(i4)	169·2 (5)	172·5 (5)	169·5 (5)	168·9 (5)	171·1 (8)
C(i2)–Fe(i)–C(i5)	81·2 (5)	89·4 (5)	80·4 (5)	86·2 (5)	86·9 (6)
C(i3)–Fe(i)–C(i4)	85·9 (5)	89·4 (4)	89·0 (4)	92·5 (4)	90·5 (7)
C(i3)–Fe(i)–C(i5)	84·3 (5)	85·4 (4)	89·1 (4)	87·5 (5)	86·1 (6)
C(i4)–Fe(i)–C(i5)	89·9 (5)	81·7 (4)	89·1 (4)	83·0 (5)	84·6 (7)
Fe(i)–N(i)–O(i)	174 (1)	170·7 (8)	175·5 (8)	169·1 (9)	178 (1)
Fe(i)–C(i1)–N(i1)	169·6 (8)	172 (1)	171·4 (9)	166 (1)	177 (1)
Fe(i)–C(i2)–N(i2)	177 (1)	171 (1)	177 (1)	174 (1)	175 (1)
Fe(i)–C(i3)–N(i3)	165 (1)	166 (1)	176·5 (9)	176·2 (9)	177 (1)
Fe(i)–C(i4)–N(i4)	177 (1)	179·7 (9)	172 (1)	174·3 (9)	176 (1)
Fe(i)–C(i5)–N(i5)	176 (1)	179·0 (9)	177 (1)	174 (1)	177 (1)

An Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation was employed. In both cases data were corrected for Lorentz, polarization, absorption (max. and min. transmission factors of 0·763–0·372 and 0·685–0·350 for the 2·5 and 0·8 hydrates, respectively) and extinction effects.

Table 6. *Distances* (Å) *up to* 3 Å *around* K *ions in the* 2·5 *hydrate*

	N(14^i)	N(15^{ii})	N(21^{iii})	N(23^{iv})	O(W3^{iii})	
K(1)	2·866 (6)	2·908 (5)	2·798 (5)	2·949 (6)	2·701 (5)	
	N(11)	N(22)	N(23^v)	O(W1^v)		
K(2)	2·942 (6)	2·882 (5)	2·875 (5)	2·701 (6)		
	N(15)	N(22^{vi})	O(W2^{vi})	O(W4^{vi})		
K(3)	2·893 (6)	2·980 (5)	2·717 (5)	2·710 (5)		
	N(12^{vii})	N(13^{ii})	N(21^{iii})	N(22)	N(24^{iv})	O(W1^{iii})
K(4)	2·809 (5)	2·877 (5)	2·920 (4)	2·957 (4)	2·993 (6)	2·705 (4)

Symmetry code: (i) $1-x$, $-y$, $1-z$; (ii) $x-1$, y, $z-1$; (iii) $x-1$, y, z; (iv) $-0·5+x$, $0·5-y$, $0·5+z$; (v) $0·5+x$, $0·5-y$, $0·5+z$; (vi) x, y, $1+z$; (vii) $-0·5+x$, $0·5-y$, $-0·5+z$.

Table 7. *Distances* (Å) *up to* 3 Å *around* K *ions in the* 0·8 *hydrate*

	N(23^i)	N(31)	N(44)	N(53^{ii})	N(54)	O(W1^i)
K(1)	2·88 (1)	2·99 (1)	2·71 (1)	2·84 (2)	2·95 (2)	2·49 (1)
	N(21)	N(24^{iii})	N(41)	O(W2^i)	O(W3^{iv})	
K(2)	2·93 (1)	2·91 (1)	2·79 (1)	2·859 (7)	2·87 (1)	
	N(22^v)	N(34^{vi})	N(43)	N(52^{ii})	N(53^{vi})	
K(3)	2·92 (1)	2·89 (1)	2·987 (9)	2·80 (1)	2·98 (2)	
	N(33^{vii})	O(W4^{vi})				
K(4)	2·95 (1)	2·733 (8)				
	N(13^{vi})	O(W2^{vi})	O(W3^{vi})			
K(5)	2·88 (1)	2·896 (7)	2·88 (1)			
	N(22)	N(44)				
K(6)	2·81 (1)	2·87 (1)				
	N(15^{vi})	N(21)	N(35^{vi})	N(41)	N(55^{ii})	O(W4^{vi})
K(7)	2·87 (1)	2·88 (1)	2·89 (1)	2·87 (1)	2·930 (9)	2·935 (9)
	N(15^{iv})	N(24^{iii})	N(45)			
K(8)	2·87 (1)	2·79 (1)	2·85 (1)			
	N(14)	N(23^i)	N(31)	N(43^{viii})	N(51^{viii})	N(53^{ii})
K(9)	2·52 (1)	2·50 (1)	2·44 (1)	2·52 (1)	2·36 (1)	2·887 (9)
	N(25^v)	N(42^{ix})				
K(10)	2·78 (1)	2·68 (1)				

Symmetry code: (i) $0·5-x$, $-0·5+y$, $0·5+z$; (ii) $0·5-x$, $0·5+y$, $-0·5+z$; (iii) $-x$, $1-y$, $0·5+z$; (iv) $-x$, $-y$, $0·5+z$; (v) $0·5-x$, $0·5+y$, $0·5+z$; (vi) x, $1+y$, z; (vii) $-x$, $1-y$, $-0·5+z$; (viii) $0·5-x$, $-0·5+y$, $-0·5+z$; (ix) $0·5+x$, $1·5-y$, z.

The intensities of three standard reflections in the 2·5 hydrate and of two in the 0·8 hydrate were essentially constant over the duration of the experiments.

In both cases the positions of the Fe atoms were readily found by Patterson methods and the rest of the non-H atoms were located by alternate cycles of difference Fourier maps and isotropic least-squares refinement. Anisotropic refinement was then carried out until the shifts were less than 0·1 of their corresponding standard deviations. In the 0·8 hydrate structure, only Fe and K atoms were treated anisotropically. H atoms were not included in the model. Final difference maps showed maximum and minimum fluctuations of $-0·51$, $0·55$ and $-2·02$, $1·42$ e Å^{-3} for the 2·5 and 0·8 hydrate structures, respectively. Final R factors and relevant parameters are given in Table 1. Most calculations were performed on a VAX computer using the *SHELX*76 system of programs (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Atomic scattering factors as incorporated in *SHELX*76.

The final positional parameters and equivalent isotropic temperature factors, calculated following Hamilton (1959), are given in Tables 2 and 3.* Interatomic bond distances and intramolecular bond angles are both given in Tables 4 and 5. Distances, up to 3 Å, around K atoms are given in Tables 6 and 7. Figs. 1 and 2 are stereoscopic projections showing the packing arrangements.

Related literature. Several structural studies on various nitroprusside salts, including TGA-DTA and infrared spectroscopic data can be found in the paper by Amalvy, Varetti, Aymonino, Castellano, Piro & Punte (1986) and references therein.
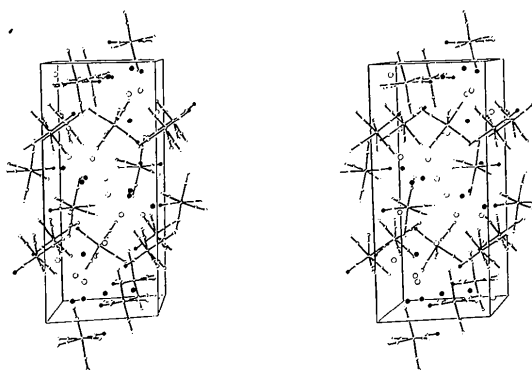
Fig. 1. Stereoscopic projection of K$_2$[Fe(CN)$_5$NO].2·5H$_2$O. Nitrosyl and water O atoms are depicted as full circles. Atom sizes on arbitrary scale.
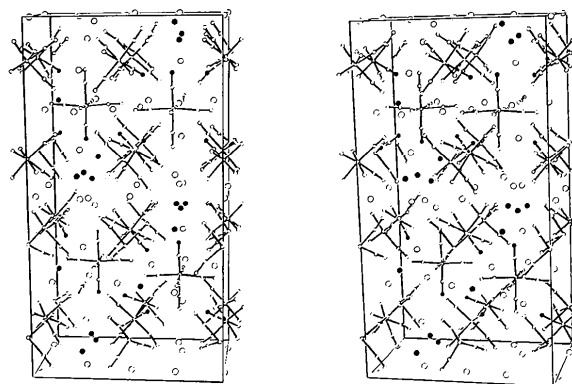

Fig. 2. Stereoscopic projection of K$_2$[Fe(CN)$_5$NO].0·8H$_2$O. Nitrosyl and water O atoms are depicted as full circles. Atoms sizes on arbitrary scale.

Infrared optical properties and vibrational studies of barium nitroprusside trihydrate are reported by Piro, González, Aymonino & Castellano (1987) and similar studies of sodium nitroprusside dihydrate by Piro, Castellano, Guida & Aymonino (1989). The attenuated total reflectance infrared spectrum of the latter compound is reported by Guida, Piro, Castellano & Aymonino (1989).

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Structure of CsVP₂O₇

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Abstract. Caesium vanadium pyrophosphate, $M_r = 357{\cdot}790$, monoclinic, $P2_1/c$, $a = 7{\cdot}701$ (3), $b = 9{\cdot}997$ (2), $c = 8{\cdot}341$ (4) Å, $\beta = 104{\cdot}82$ (4)°, $V = 620{\cdot}8$ (2) Å³, $Z = 4$, $D_x = 3{\cdot}828$ g cm⁻³, Mo $K\bar\alpha$, $\lambda = 0{\cdot}7093$ Å, $\mu = 77{\cdot}9$ cm⁻¹, $F(000) = 656$, $T = 296$ K, $R = 0{\cdot}029$, $wR = 0{\cdot}038$ for 1241 reflections with $I > 2{\cdot}5\sigma(I)$. The title compound is isostructural with CsMoP₂O₇ [Lii & Haushalter (1987). *Acta Cryst.* C**43**, 2036–2038]. The Cs⁺ ions are located in tunnels formed by pyrophosphate groups and V³⁺O₆ octahedra and are each coordinated by ten O atoms.

Experimental. Yellow crystals of CsVP₂O₇ crystallized as a minor product in an attempt to prepare 'CsV₃P₄O₁₇' by heating a mixture of Cs₄V₂O₇, V, V₂O₅ and P₂O₅ at 1423 K in a sealed silica tube. Enraf–Nonius CAD-4 diffractometer, graphite-mono-chromated Mo $K\bar\alpha$ radiation; $\theta/2\theta$ scan technique. Cell parameters on crystal $0{\cdot}08 \times 0{\cdot}11 \times 0{\cdot}16$ mm from least-squares procedure on 25 reflections ($21 < 2\theta < 30°$). Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. Max./min. transmission factors: 1·000/0·870. Systematic absences: $0k0$, $k = 2n$; $h0l$, $l = 2n$. Total of 1413 reflections measured with $(\sin\theta/\lambda)_{max} = 0{\cdot}595$ Å⁻¹ ($-9 \le h \le 9$, $0 \le k \le 12$, $0 \le l \le 10$). No significant variation in intensities of three standards monitored

every 300 reflections. Scan width of $(0{\cdot}70 + 0{\cdot}35\tan\theta)°$ and scan speed $5{\cdot}5°$ min⁻¹. 1241 unique structure amplitudes with $I > 2{\cdot}5\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares based on F values. All of the atoms were refined anisotropically. At convergence $R = 0{\cdot}029$, $wR = 0{\cdot}038$, $w = 1/\sigma^2(F)$, $\sigma^2(F)$ based on counting statistics, $(\Delta/\sigma)_{max} = 0{\cdot}001$, $S = 0{\cdot}779$, $(\Delta\rho)_{max} = 1{\cdot}15$, $(\Delta\rho)_{min} = -1{\cdot}34$ e Å⁻³. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX 11/780 computer system using the *NRC VAX* program (Larson, Lee, Le Page & Gabe, 1986). Atomic parameters are given in Table 1, bond distances and

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{eq} = (\tfrac{4}{3})\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
Cs	0·80211 (6)	0·20510 (5)	0·96096 (6)	1·112 (17)
V	0·75946 (14)	−0·39878 (11)	0·74130 (13)	0·28 (4)
P(1)	0·86838 (21)	−0·09430 (18)	0·66697 (20)	0·33 (6)
P(2)	0·57426 (22)	−0·37300 (17)	0·31783 (20)	0·31 (6)
O(1)	0·9052 (6)	−0·2372 (5)	0·7296 (6)	0·59 (17)
O(2)	0·6777 (7)	−0·3974 (6)	0·4931 (6)	1·05 (19)
O(3)	0·6119 (6)	−0·5660 (5)	0·7280 (6)	0·62 (18)
O(4)	0·8423 (7)	−0·4163 (5)	0·9841 (6)	0·84 (19)
O(5)	0·5639 (6)	−0·2725 (5)	0·7673 (6)	0·67 (18)
O(6)	0·9882 (6)	−0·5031 (5)	0·7336 (6)	0·55 (16)
O(7)	0·6817 (6)	−0·4513 (5)	0·2033 (6)	0·54 (17)