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The Crystal Structure of Disodium Pentacyanoammineferrate(III) Dihydrate, $Na_2[Fe(CN)_5NH_3].2H_2O$

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The crystal structure of disodium pentacyanoammineferrate(III) dihydrate, $Na_2[Fe(CN)_5NH_3].2H_2O$, has been determined by single crystal X-ray diffraction methods. The crystals are orthorhombic space group *Pnnm* with $a = 6.111 \pm 1$ Å, $b = 11.899 \pm 2$ Å, $c = 15.623 \pm 3$ Å, and $Z = 4$. An R-value of 0.091 has been obtained

The structure consists of double chains of distorted sodium ion coordination octahedra, held together in three dimensions by octahedral $[Fe(CN)_5NH_3]^{2-}$ ions. Each sodium ion is thus surrounded by four nitrogen atoms of cyanide groups and two water oxygen atoms all at distances of approximately 2.5 Å.

Each $[Fe(CN)_5NH_3]^{2-}$ ion is octahedral with almost linear Fe − C − N groups. The C − N bond distances are 1.17, 1.14, and 1.14 Å, the Fe − NH_3 distance is 2.01 Å and the Fe − C distances are 1.89, 1.93, and 1.94 Å.

There seems to be no hydrogen bonding between the complex ions and the water molecules.

In a systematic investigation of pentacyanidomonoligandferrates the crystal structure of $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ has been determined since the NH_3 ligand can be regarded as only σ-bonded in contrast to the strongly π-bonded NO^+ ligand.

EXPERIMENTAL

Preparation of $Na_2[Fe(CN)_5NH_3].2H_2O$. Crystals of $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ were prepared according to a method described by Brauer.[1] $Na_3[Fe(CN)_5NH_3]$ was first prepared by passing ammonia through an aqueous solution of $Na_2[Fe(CN)_5NO]$ at 10 °C. $Na_3[Fe(CN)_5NH_3]$ was then treated at 0 °C with a solution of sodium nitrate and acetic acid. From this solution it is easy to get a pure but microcrystalline precipitate of $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ by adding ethanol and ether. To obtain crystals suitable for X-ray diffraction work, however, the original mother liquid was allowed to stand. Single crystals of $Na_2[Fe(CN)_5NH_3].2H_2O$ form in the solution after some time. They are needle-shaped, yellow in colour and decompose slightly in air. The infra-red absorption spectrum from a selection of crystals was recorded. It showed bands characteristic of both $Na_2[Fe(CN)_5NH_3]$ [2] and $Na_2[Fe(CN)_5NO]$.[2] Crystals of the latter may have formed in the solution. They are redder than those of the ammine compound. To prove that the crystals prepared were not of the hypothetical compound, $Na_2[Fe(CN)_4NH_3NO]$, a crystal sample (several mg) was analysed for

Table 1. X-Ray powder diffraction data for $Na_2Fe(CN)_5NH_3\cdot 2H_2O$. Guinier camera. Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å).

h	k	l	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	d (calc) Å	I_{calc}	I_{obs}
0	0	2	974	972	7.811	385	s
0	2	0	1679	1676	5.950	31	vvw
1	0	1	1830	1832	5.691	427	s
1	1	0	2005	2008	5.436	38	vvw
0	1	3	2607	2607	4.771	45	vw
0	2	2	2641	2648	4.733	632	vs
1	1	2	2978	2980	4.462	148	m
1	2	1	3508	3508	4.113	666	vs
1	0	3	3778	3776	3.964	118	m
0	0	4	3888	3889	3.906	47	w
1	3	0	5358	5360	3.327	27	vvw
1	2	3	5449	5452	3.299	76	w
0	2	4	5565	5565	3.265	99	w
0	3	3	5960	5959	3.155	22	vvw
2	1	0	6776	6774	2.960	34	vvw
2	1	1	7015	7017	2.908	23	vvw
1	2	4	7152	7154	2.880	470	vs
2	0	2	7325	7327	2.846	30	vvw
2	2	1	8270	8274	2.678	112	m
2	2	2	9004	9003	2.567	128	m
1	3	4	9250	9249	2.533	346	s

Table 2. Observed and calculated structure factors for $Na_2[Fe(CN)_5NH_3].2H_2O$.

0 K 0			11 43 -43			0 K 24			1 K 6			20 12 -11			2 K 0		
2	42	-40	13	23	27	2	15	-16	1	27	30				2	19	-19
4	64	-51				4	17	17	2	9	-9		1 K 12		3	35	-36
6	28	25		0 K 10					3	8	-9	1	20	-17	4	166	182
8	87	87					1 K 0		4	38	34	2	11	-8	5	31	30
10	42	43	0	56	56	2	22	32	5	96	90	3	57	-54	6	23	22
12	15	-18	2	97	-94	3	50	-47	6	10	-9	4	11	-12	8	22	23
14	27	26	4	28	27	4	15	14	7	48	-48	5	7	-6	10	26	26
18	13	13	6	12	-9	5	20	25	8	15	-16	7	49	-49	14	31	29
20	13	-18	8	13	-11	7	42	-42	9	46	46	14	12	-2	16	17	-17
22	11	17	12	22	-21	9	51	59	10	7	8	16	10	4	18	16	23
			14	11	11	10	12	-12	11	11	-10	20	10	-3			
0 K 1			16	14	-11	11	48	-54	13	24	24					2 K 1	
3	34	-30	20	14	-14	13	22	23	15	9	-12		1 K 13		2	90	83
5	6	1				15	10	-8	17	8	8	0	62	58	3	51	-55
7	74	-75		0 K 11		16	15	8				1	8	10	4	26	-24
9	45	48	1	26	26	18	12	-3		1 K 7		2	41	-38	5	61	61
11	55	-58	3	34	-35	20	12	-5	0	51	50	3	8	7	6	23	-24
13	30	34	5	17	15	21	9	-7	1	15	-12	4	42	41	7	64	-66
15	9	-9	9	56	56	22	9	1	2	76	-71	6	9	-8	9	29	29
17	9	-11	11	53	-60				3	22	-21	7	9	-6	10	11	13
			13	17	18		1 K 1		4	43	39	8	7	5	11	34	-36
0 K 2						2	117	-132	5	38	35	10	8	7	13	13	14
4	35	34		0 K 12		3	17	21	6	47	-43	12	9	-9	14	11	-10
6	38	-36	0	94	91	4	34	33	7	22	23	14	17	16	15	15	-16
8	24	-25	2	66	-62	5	8	6	8	8	8	16	13	-12	16	17	1
10	8	-4	4	16	16	6	37	-35	9	37	-39	18	11	11	18	15	7
12	26	-23	8	14	13	7	6	-5	11	8	-10	20	10	-10			
14	12	9	12	19	-19	8	11	-10	12	19	-19					2 K 2	
16	16	-18	14	15	13	12	21	-22	13	20	22		1 K 15		2	95	-94
18	12	13	16	11	11	14	15	17	14	19	19	0	31	33	3	26	20
20	14	-16	18	13	-14	16	16	-17	15	10	1	2	30	-34	4	17	17
						18	14	12	16	21	-21	4	26	28	5	14	-16
0 K 4				0 K 15		20	13	-14	18	15	16	5	11	12	6	57	-62
0	90	73	3	29	-28				20	10	-10	6	19	-22	7	18	-19
2	96	-91	5	15	15		1 K 2					7	13	11	9	11	16
4	53	54	7	41	-42	5	79	77		1 K 8		8	9	7	10	10	-3
6	17	-17	9	25	26	6	8	-8	1	16	15	9	16	-18	12	25	-28
8	25	28	11	22	-20	7	28	-32	2	21	-17	13	10	11	13	17	-11
12	24	-26	13	14	12	9	62	67	3	41	-39	14	10	13	14	19	17
14	17	16				11	27	-29	4	25	21	16	15	-14	16	23	-24
16	13	-13		0 K 16		13	26	32	5	44	41	18	12	14	17	18	2
18	20	23	18	18	18				6	12	11				18	14	13
20	12	-14					1 K 3		7	47	-46		1 K 16				
				0 K 17		2	61	-56	8	14	-14	2	20	-19		2 K 3	
0 K 5			3	18	-19	3	37	-33	9	37	38	3	25	-23	1	31	31
1	8	7	5	31	32	4	103	101	11	29	-31	4	13	13	2	16	-17
3	7	7	7	32	-33	5	16	-14	13	17	17	5	30	29	5	74	74
5	104	106	9	16	17	6	17	-17	14	11	9	7	32	-33	6	9	11
7	53	-56	11	17	-16	7	15	16	15	9	-12	8	8	-8	7	66	-68
9	50	50	13	9	9	8	10	11	18	12	-7	9	21	21	8	9	-7
11	16	-14				10	15	15				11	17	-15	9	40	40
13	24	22		0 K 18		14	23	24		1 K 9		15	9	-10	11	11	-8
15	12	-14	0	12	12	15	16	-9	0	28	27				13	24	29
17	12	7	2	37	-36	16	14	-20	1	25	22		1 K 17		15	14	-16
			4	26	25	18	15	17	2	88	-84	2	36	-36	18	14	-2
0 K 6			6	14	-15				3	13	11	4	26	28			
0	50	46	12	14	-12		1 K 4		4	42	40	6	24	-27		2 K 4	
2	94	-89	14	10	9	1	18	-17	5	13	-14	16	16	-19	22	5	7
4	18	18	16	13	-14	2	154	-160	6	38	-35	18	11	12			
6	73	-74				3	134	-134	8	16	-16					2 K 5	
8	8	-8		0 K 19		5	12	-11	12	15	-15		1 K 18		1	53	49
12	24	-20	3	14	-15	6	58	58	14	13	14	1	19	19	3	27	-26
14	14	10	5	19	20	7	86	-86	16	20	-20	2	29	-29	4	20	20
16	25	-27	7	20	-20	9	26	28	18	12	11	3	7	-9	5	71	71
18	16	17	9	21	23	10	12	-11	20	11	-10	5	32	32	6	11	-11
20	13	-13	11	17	-19	11	50	-50				6	12	14	7	40	-37
			13	9	10	12	7	-8		1 K 10		7	17	-18	8	11	-12
0 K 7						14	11	10	1	47	43	9	28	27	9	42	43
3	49	-49		0 K 20		15	17	-19	2	25	-22	11	9	-9	11	16	-19
5	27	25	0	40	41	17	8	3	3	8	-8	13	12	13	13	27	26
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9	34	33	4	15	14	22	9	2	5	48	45		1 K 19				
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13	20	21					1 K 5		7	15	-14	2	22	-21	0	16	17
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0 K 8			7	14	-13	3	23	-17	21	11	-4				5	11	9
0	194	202	9	22	23	4	111	108					1 K 20		6	49	-47
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4	41	41	13	15	20	6	29	-28	0	86	83	3	19	-21	9	18	-19
8	52	49				7	15	14	1	8	-6	5	8	9	10	10	-11
10	36	35		0 K 22		8	12	9	2	48	-46	7	29	-28	12	27	-30
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14	25	22	2	31	-32	10	14	13	4	48	44	11	18	-20	18	12	11
16	9	-9	6	12	-10	12	7	-5	5	8	-7	13	10	10			
18	18	18	12	10	-12	13	9	10	6	7	-2					2 K 7	
						14	24	24	8	8	8		1 K 24		1	28	-26
0 K 9				0 K 23		15	11	-12	9	11	13	3	11	-11	2	9	-8
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7	53	-52	11	21	-26	22	10	4	16	9	-11	11	13	-17	7	52	-49
9	32	30	13	11	12				18	11	11				8	21	-9

Table 2. Continued.

9 23 22	2 K 17	4 12 -10
10 11 7	3 23 -23	5 61 58
11 34 -35	5 17 20	7 36 -34
13 18 13	7 31 -29	9 36 37
14 14 3	9 18 18	13 22 18
15 14 -12	11 14 -14	15 14 -9
16 16 -3	18 12 -4	
18 15 -3		3 K 11
	3 K 0	0 43 37
2 K 8	5 62 60	2 28 -26
0 64 62		3 20 20
1 17 -16	3 K 2	4 52 50
2 15 -16	3 22 -20	6 17 -20
3 27 -27	4 13 -16	7 25 -25
4 106 106	5 60 61	10 12 12
5 15 14	6 10 12	14 13 13
6 11 11	7 28 -26	16 12 -17
7 15 18	9 54 57	
8 28 28	11 17 -21	3 K 12
10 17 17	12 10 4	1 26 -26
13 12 4	13 19 21	2 18 19
14 27 29		3 43 -39
16 13 -15	3 K 3	4 11 -11
18 20 18	2 48 -46	5 22 22
	3 31 28	7 54 -54
2 K 10	4 46 46	9 11 9
0 50 48	6 14 -13	11 24 -24
1 12 9	7 20 -24	15 18 -15
2 57 -56	8 24 24	17 12 1
3 14 13	10 12 12	
4 17 18	12 14 -15	3 K 13
5 10 -9	14 15 20	0 45 43
6 46 -47	16 11 -14	2 30 -28
7 15 -17		4 35 34
9 12 16	3 K 4	6 15 -16
12 17 -17	1 72 -65	7 11 -12
13 19 -11	2 25 23	8 11 9
14 13 13	3 55 -53	13 15 -10
16 20 -21	4 8 8	14 15 12
20 12 -10	5 21 23	16 15 -15
	7 79 -79	17 13 -1
2 K 11	11 44 -46	18 11 15
2 13 10	13 12 19	
4 15 -16	15 15 -15	3 K 24
5 45 45		4 16 -4
7 54 -56	3 K 5	7 19 -19
9 26 26	0 140 129	
11 12 -6	1 24 23	4 K 1
12 11 0	2 55 -51	3 49 -50
13 23 22	3 10 8	5 15 16
	4 23 23	6 16 19
2 K 12	8 25 29	7 50 -53
0 45 43	12 15 -21	9 34 36
2 35 -35	14 19 21	11 26 -24
4 42 41		13 11 11
6 27 -27	3 K 6	15 16 -12
7 12 -11	1 63 58	
9 11 12	2 19 -16	4 K 2
13 12 -9	3 35 -35	2 68 -74
14 13 17	4 10 -4	3 27 -28
15 11 7	5 30 29	4 20 20
16 16 -17	6 10 9	5 23 25
18 16 14	7 9 -4	6 35 -33
	9 53 59	7 8 9
2 K 13	11 36 -40	8 10 -4
2 32 31	13 19 22	9 10 -13
3 10 -11		12 20 -19
5 46 47	3 K 7	16 17 -18
7 22 -22	0 43 41	18 13 13
9 33 32	1 10 11	20 14 -12
11 15 -17	2 70 -66	
13 18 17	3 10 -8	4 K 3
	4 45 43	1 12 12
2 K 14	5 10 -11	2 22 22
2 53 -54	6 23 -25	3 12 -12
4 30 29	12 11 -11	4 7 -6
5 12 8	14 14 16	5 44 44
6 25 -25	16 17 -17	6 10 -10
10 11 -6		7 21 -22
14 14 12	3 K 8	9 43 44
16 16 -18	1 11 11	10 12 11
	2 11 -6	11 33 -35
2 K 15	3 32 -30	13 18 19
2 11 -7	4 16 -17	14 11 -3
3 25 -25	5 32 30	19 12 5
4 14 6	7 38 -39	
5 31 32	9 38 35	4 K 4
7 32 -31	11 32 -30	0 67 66
9 16 16	13 15 15	1 7 8
11 20 -22		2 67 -66
16 15 -3	3 K 9	3 8 -8
	0 56 51	4 37 38
2 K 16	2 66 -60	12 15 -15
0 48 48	4 10 6	14 18 13
2 16 -14	6 35 -36	18 12 12
4 39 39	7 11 -15	
7 12 9	11 10 6	4 K 5
8 21 21	12 19 -22	1 28 29
14 21 21		3 10 -10
16 13 -12	3 K 10	5 24 23
18 16 11	1 21 20	7 11 -11
	2 23 24	9 52 55
11 39 -42	12 19 -4	12 11 -10
13 21 22	13 14 15	18 11 9
19 13 5		
	5 K 5	5 K 16
4 K 6	0 58 58	1 11 -4
0 68 67	2 36 -36	4 12 -4
1 9 8	3 10 -11	5 16 15
2 78 -77	4 38 40	7 19 -21
3 9 -10	16 13 -10	9 16 18
6 23 -23	20 11 -10	11 19 -19
8 11 -12		13 12 12
12 19 -17	5 K 6	16 12 3
14 11 7	3 13 13	
16 12 -11	5 40 41	5 K 17
	7 31 -31	0 15 18
4 K 7	9 29 32	2 27 -30
1 14 15	11 15 -17	3 12 -6
2 9 7	13 23 24	4 15 16
3 35 -34		6 11 -11
7 36 -36	5 K 7	
9 41 42	0 54 53	5 K 18
11 40 -38	1 22 23	5 16 16
13 17 17	2 46 -46	7 14 -13
	3 13 12	9 20 23
4 K 8	4 14 14	11 14 -13
0 92 91	6 13 -15	13 14 12
1 14 14	7 12 -9	
2 16 -17	12 12 -15	5 K 19
4 52 53	18 17 11	0 20 27
8 14 14	20 11 -11	
10 15 18		5 K 20
14 22 19	5 K 8	3 11 -13
18 12 12	3 14 -13	7 23 -23
	4 8 4	
4 K 9	5 28 29	5 K 19
2 9 -5	7 33 -32	2 13 -17
3 31 -32	8 12 -11	4 14 15
5 18 16	9 21 21	
7 34 -35	11 22 -23	5 K 20
9 29 32	13 15 15	9 13 9
11 28 -28	15 11 -8	
15 12 -7		5 K 21
16 12 -1	5 K 9	0 18 17
	0 18 20	2 13 -14
4 K 10	2 40 -42	3 13 -3
0 18 20	3 13 -14	4 13 13
1 14 -14	4 22 21	6 12 -9
2 50 -49	5 9 9	
3 17 -18	6 23 -24	5 K 22
4 24 24	7 11 10	5 18 19
5 18 18	9 16 -9	6 11 5
6 22 -23	12 12 -12	
12 17 -16	16 14 -15	5 K 23
14 13 10		2 14 -12
16 16 -15	5 K 10	3 14 -6
18 16 14	1 18 19	4 12 13
	2 13 -16	8 12 6
4 K 12	3 11 -11	
0 27 26	5 38 41	5 K 24
1 11 -7	7 18 -18	3 12 -10
2 32 -31	9 22 25	5 12 12
3 11 -11	10 10 7	
4 34 34	13 14 17	6 K 0
5 11 12		2 11 -12
6 11 -14	5 K 11	3 9 -10
14 13 12	0 36 36	4 34 36
16 15 -14	2 18 -20	8 33 34
	3 18 -20	10 11 6
4 K 14	4 26 26	12 12 -15
0 30 30	6 13 -15	14 22 25
2 41 -41	8 14 15	18 12 11
4 14 11	10 10 4	
6 23 -22	14 15 17	6 K 2
16 14 -15	15 12 -4	4 28 28
18 10 7	16 13 -14	6 26 -28
		8 9 -5
4 K 22	5 K 12	12 11 -11
2 20 -18	1 10 -8	14 11 15
5 12 5	2 14 -15	16 20 -19
6 16 -17	3 34 -34	
	5 13 14	6 K 3
4 K 23	7 36 -37	1 25 25
5 15 13	8 12 -8	3 22 -22
6 13 4	11 17 -18	4 6 -5
7 16 -19	13 11 7	5 22 22
11 12 -8	14 12 5	7 22 -23
	15 11 -11	9 28 30
4 K 24		11 11 -14
0 15 17	5 K 13	13 15 11
2 13 -11	0 29 30	
4 13 18	2 21 -21	6 K 4
	4 23 25	0 30 28
5 K 0	6 14 -13	1 6 8
2 14 -14	13 11 5	2 27 -26
3 27 -29	14 16 14	4 34 34
4 16 16	16 12 -12	6 21 -22
5 40 44		7 10 -9
6 8 9	5 K 15	10 10 10
7 36 -37	0 31 32	14 11 13
8 16 -20	2 28 -27	16 15 -16
9 17 18	4 16 16	20 10 -6
11 15 -20	5 10 -1	

Table 2. Continued.

6 K 5			6 K 11			4 17 17			7 K 5			2 21 -20			8 K 3		
1 8 10			1 23 23			6 11 -14			0 25 25			4 12 13			5 20 19		
2 12 13			2 10 -7						2 21 -20			6 10 -4			7 15 -15		
4 11 -11			3 27 -29			6 K 19			4 25 26			14 15 12			9 18 18		
5 32 32			5 14 14			7 18 -17			6 9 -10						11 14 -16		
7 28 -30			7 15 -14			9 14 13			7 12 -12			7 K 12			13 12 11		
9 24 26			8 11 -7						14 13 11			3 19 -21					
13 13 13			9 23 22			6 K 20						7 17 -18			8 K 4		
			11 16 -15			0 15 15			7 K 6			9 12 13			0 23 23		
6 K 6						2 15 -14			1 9 8			11 23 -21			2 21 -20		
2 42 -41			6 K 12			4 14 15			2 16 16						4 16 16		
4 29 29			0 25 25						4 12 -13			7 K 13					
6 21 -23			1 11 11			7 K 0			5 28 29			0 27 27			8 K 5		
7 12 -13			2 19 -19			3 17 -19			7 20 -21			2 20 -18			3 10 -10		
8 13 -11			3 10 -3			4 7 -6			9 21 21			4 14 12			5 19 21		
12 12 -9			4 20 20			5 12 12			11 12 -7						9 14 17		
14 14 7			6 14 -14			6 7 -5			13 13 12			7 K 14					
16 17 -16			12 12 -9			7 16 -18			16 12 -5			3 10 -8			8 K 6		
18 13 12			14 16 18			9 22 22						5 15 16			0 19 18		
			16 12 -12			10 12 10			7 K 7			7 14 -13			2 24 -23		
6 K 7			18 10 6			11 22 -22			0 24 24			9 18 18			6 17 -15		
1 8 -9									1 12 -11			11 14 -10					
2 8 8			6 K 13			7 K 1			2 25 -24			15 11 -3			8 K 8		
3 17 -17			1 14 8			2 30 -33			3 10 -13						0 34 31		
4 9 -9			3 10 -9			3 8 -10			4 15 15			7 K 15			2 11 -11		
5 27 27			5 29 29			4 7 7			5 12 13			0 19 19			4 21 21		
7 31 -30			7 16 -16			6 11 -14			6 14 -15			1 11 -5			14 14 9		
9 17 17			9 14 16			12 14 -14			12 11 -8			2 17 -16					
11 18 -17			11 13 -10			13 11 -4						5 10 7			8 K 10		
15 11 -10									7 K 8			6 14 -11			0 25 24		
			6 K 14			7 K 2			2 9 7						2 27 -26		
6 K 8			0 11 10			2 13 15			3 13 -14			7 K 16					
0 40 39			2 28 -28			3 8 -8			4 9 -10			5 13 13			8 K 11		
2 14 -13			4 13 13			5 22 24			5 15 16			7 16 -19			5 12 11		
4 39 40			6 14 -16			7 11 -14			7 23 -22			9 11 13			9 16 17		
8 15 16			12 13 -14			9 25 26			9 17 18			15 10 -6					
10 11 11						10 10 9			11 15 -14						8 K 12		
14 15 15			6 K 15			11 15 -15			13 12 9			7 K 18			0 28 26		
16 12 -10			1 10 -3			13 15 14						5 14 16			2 18 -19		
18 12 13			3 13 -13						7 K 9			9 15 14					
			5 18 18			7 K 3			0 23 25						8 K 13		
6 K 9			7 17 -20			2 21 -22			1 9 8			7 K 19			9 17 18		
3 23 -23			9 12 14			4 21 23			2 28 -28			0 16 15					
5 23 22			11 15 -13			8 10 8			4 10 10			2 12 -13			8 K 16		
7 24 -25						12 11 -8			6 13 -13			4 13 13			0 21 20		
9 14 15			6 K 16			14 14 13			12 12 -10						4 13 13		
10 10 7			0 21 18			16 13 -9			16 13 -10			8 K 0					
11 13 -16			2 14 -11									2 14 -15			9 K 8		
13 14 11			4 29 31			7 K 4			7 K 10			4 25 25			3 10 -10		
16 15 -1			16 10 -9			1 7 -9			1 13 14			10 17 14			7 14 -13		
						2 6 7			5 18 18								
6 K 10			6 K 17			3 24 -26			7 12 -9			8 K 1			9 K 0		
0 13 14			2 10 8			4 7 -7			9 22 23			3 10 -9			5 10 9		
1 10 13			5 12 13			5 9 10			11 15 -15			7 17 -18			7 17 -17		
2 28 -28			7 19 -22			6 10 12			13 14 13			9 18 21					
4 21 19			9 15 15			7 32 -34			14 11 3			11 17 -21					
6 23 -22						9 12 13											
14 13 15			6 K 18			11 18 -19			7 K 11			8 K 2					
16 20 -17			0 11 11			12 10 4			0 33 33			2 29 -30					
			2 19 -18			15 12 -10			1 10 11			6 10 -10					

Table 3. Atomic coordinates, expressed as fractions of the cell edges, and their standard deviations.

Atom	x	y	z
Fe	0.4952(3)	0.2780(1)	0.5
Na(1)	0.5	0	0.2472(3)
Na(2)	0	0	0.3785(4)
C(1)	0.2519(19)	0.1794(8)	0.5
C(2)	0.6140(14)	0.1830(6)	0.5897(5)
C(3)	0.3448(14)	0.3641(6)	0.4113(5)
N(1)	0.0997(23)	0.1200(12)	0.5
N(2)	0.6725(18)	0.1247(8)	0.6433(6)
N(3)	0.2439(17)	0.4118(8)	0.3610(6)
N(4)	0.7683(21)	0.3733(11)	0.5
O	0.1750(17)	0.1249(7)	0.2690(5)

carbon. The result was 20.4 % carbon; calculated for $[Na_2Fe(CN_5NH_3].2H_2O$ is 21.1 %. This shows beyond reasonable doubt that the complex ions contain five carbon atoms. Further confirmation has subsequently been obtained from the results of the X-ray investigation.

Crystallographic investigation. X-Ray diffraction patterns of crystals of disodium pentacyanoammineferrate(III) dihydrate show the following systematic absences:

$0\,k\,l$ $\quad k+l=2n+1$

$h\,0\,l$ $\quad h+l=2n+1$

These are constant with space groups No. 34, *Pnn*2 and No. 58, *Pnnm*.[3]

The unit cell dimensions were determined from Guinier powder photographs (Cu$K\alpha_1$ radiation, $\lambda = 1.54050$ Å), lead nitrate ($a = 7.8404$ Å, 21 °C)[4] being used as an internal standard. Refinement of the cell dimensions based on the measured Bragg angles of 21 indexed reflexions was made with the program POWDER,[5] and yielded the following values:

$a = 6.110 \pm 0.0006$ Å, $b = 11.8990 \pm 0.0023$ Å,

$c = 15.6228 \pm 0.0028$ Å and $V = 1136$ Å^3.

Table 4. Anisotropic thermal parameters and their standard deviations. The temperature coefficient is expressed as exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.076(3)	0.0023(1)	0.0009(0)	0.0002(4)	0.0000	0.0000
Na(1)	0.0122(11)	0.0043(3)	0.0015(2)	−0.0029(14)	0.0000	0.0000
Na(2)	0.0162(15)	0.0059(4)	0.0023(2)	0.0033(18)	0.0000	0.0000
C(1)	0.0084(22)	0.0016(4)	0.0020(4)	0.0014(18)	0.0000	0.0000
C(2)	0.0105(17)	0.0028(4)	0.0012(2)	0.0023(14)	0.0012(10)	0.0008(5)
C(3)	0.0116(19)	0.0025(3)	0.0009(2)	0.0032(14)	0.0010(10)	0.0016(5)
N(1)	0.0132(34)	0.0052(8)	0.0034(6)	−0.0058(28)	0.0000	0.0000
N(2)	0.0199(26)	0.0058(6)	0.0026(4)	0.0030(24)	−0.0004(16)	0.0030(8)
N(3)	0.0227(26)	0.0046(5)	0.0021(3)	0.0030(23)	−0.0038(15)	0.0015(7)
N(4)	0.0141(29)	0.0051(8)	0.0017(4)	0.0013(27)	0.0000	0.0000
O	0.0246(25)	0.0050(5)	0.0035(4)	0.0027(21)	−0.0001(16)	0.0017(7)

Table 5. Geometry of the $Fe(CN)_5NH_3^{3-}$ octahedron. Interatomic distances (in Å) and angles, with their standard deviations in parentheses.

Distance		Angle	
Fe−C(1)	1.891(11)	Fe−C(1)−N(1)	179.0(11)
Fe−C(2)	1.932(8)	Fe−C(2)−N(2)	176.1(9)
Fe−C(3)	1.945(8)	Fe−C(3)−N(3)	175.6(8)
Fe−N(4) (NH_3)	2.015(13)	C(1)−Fe−C(2)	86.1(3)
C(1)−N(1)	1.168(18)	C(1)−Fe−C(3)	87.5(3)
C(2)−N(2)	1.141(12)	C(1)−Fe−N(4)	175.9(5)
C(3)−N(3)	1.144(12)	C(2)−Fe−C(3)	88.7(3)
		C(2)−Fe−N(4)	91.1(4)
		C(2)−Fe−C(2)	92.0(5)
		C(3)−Fe−C(3)	90.0(5)
		C(3)−Fe−N(4)	95.4(4)

Table 6. Geometry of the sodium ion coordination octahedra. Interatomic distances (Å) and angles, their standard deviations in parenthesis.

Coordination of Na (1)

Atom	x	y	z
Na(1)	0.5	0	0.2472
N(2)	0.3275	−0.1247	0.3567
N(2)′	0.6725	0.1247	0.3567
N(3)	0.7439	0.0882	0.1390
N(3)′	0.2561	−0.0882	0.1390
O	0.1750	0.1249	0.2690
O′	0.8250	−0.1249	0.2690

Distance

Na(1)−N(2)	2.488(10)
Na(1)−N(3)	2.475(10)
Na(1)−O	2.501(10)
Mean	2.488

Angle

N(2)−Na(1)−N(3)	165.8(3)
N(2)−Na(1)−N(3)′	87.4(3)
N(2)−Na(1)−O	85.8(3)
N(2)−Na(1)−O′	83.6(3)
N(3)−Na(1)−N(3)′	94.7(5)
N(3)−Na(1)−O	108.4(3)
N(3)−Na(1)−O′	82.4(3)
O−Na(1)−O′	164.4(4)

Coordination of Na (2)

Atom	x	y	z
Na(2)	0	0	0.3785
N(1)	0.0997	0.1200	0.5
N(1)′	−0.0997	−0.1200	0.5
N(2)	0.3275	−0.1247	0.3567
N(2)″	−0.3275	0.1247	0.3567
O	0.1750	0.1249	0.2690
O″	−0.1750	−0.1249	0.2690

Distance

Na(2)−N(1)	2.441(10)
Na(2)−N(2)	2.511(11)
Na(2)−O	2.495(10)
Mean	2.482

Angle

N(1)−Na(2)−N(1)′	79.0(5)
N(1)−Na(2)−N(2)	104.5(4)
N(1)−Na(2)−N(2)″	87.5(4)
N(1)−Na(2)−O	94.0(3)
N(1)−Na(2)−O″	168.4(4)
N(2)−Na(2)−N(2)″	164.6(5)
N(2)−Na(2)−O	85.4(3)
N(2)−Na(2)−O″	84.1(3)

Observed and calculated $\sin^2\theta$ values are listed in Table 1. The cell dimensions and the experimental density (1.69 g cm^{-3} as determined by the flotation method) indicate that the unit cell contains four formula units. The corresponding calculated density is 1.66 g cm^{-3}.

STRUCTURE DETERMINATION

The crystal structure was solved and determined using standard methods.

Observed and calculated structure amplitudes are listed in Table 2. Final atomic parameters are given in Tables 3 and 4. Interatomic distances and angles were calculated with the program DISTAN.[6] The results are listed in Tables 5 and 6.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The complex ion $[Fe(CN)_5NH_3]^{2-}$ (Fig. 1) lies in a mirror plane and has approximately C_{4v} symmetry if the three hydrogen atoms are not taken into consideration. The distances and angles within it are listed in Table 5. The Fe – C – N groups are almost linear. The cyanide ligand *trans* to the ammonia molecule appears to be more firmly bonded than the other ligands, presumably due to additional π-bonding.

Comparison of the $Fe-N(NH_3)$ distance of 2.02 Å with the short Fe – N(NO) distance of 1.63 Å in $Na_2[Fe(CN)_5NO].2H_2O$ [7] illustrates the importance of the π-bond contribution to the latter bond. The Fe – C distances in the plane perpendicular to the $Fe-N(NH_3)$ bond are

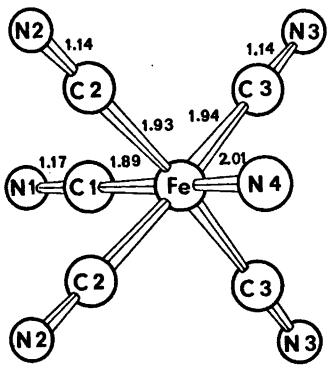

Fig. 1. The complex ion $[Fe(CN)_5NH_3]^{2-}$.

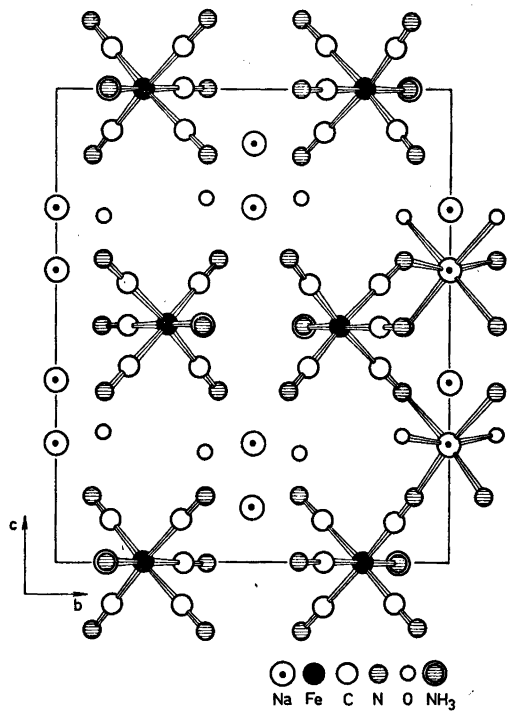

Fig. 2. Projection of the structure of $Na_2[Fe(CN)_5NH_3].2H_2O$ along the *a*-axis. Full lines indicate one unit cell. Two nitrogen atoms in the unit cell below the plane of paper are shown.

1.94 ± 1 Å (mean value), very close to the corresponding distance (1.95 ± 1 Å, mean value) in $K_3[FeCN_6]$,[11] but longer than that (1.91 ± 1 Å, mean value) in $Na_4[Fe(CN)_6].10H_2O$.[12]

The sodium coordination is octahedral, each sodium ion being surrounded by four nitrogen atoms of cyanide groups and two oxygen atoms of water molecules. Although the octahedron is irregular, the Na – L distances are rather similar (2.5 Å). Bond distances and angles for the sodium ion coordination octahedra are listed in Table 6.

The sodium ion coordination octahedra are linked edgewise to form double chains parallel to the *a*-direction of the unit cell, the octahedral $[Fe(CN)_5NH_3]^{2-}$ ion linking these double chains together. Fig. 2 shows a projection of the structure along the *a*-axis. The $[Fe(CN)_5NH_3]^{2-}$-octahedra and two different sodium coordination octahedra are shown in perspective.

Fig. 3 is a perspective view along the *b*-axis, showing how the sodium ion coordination octa-

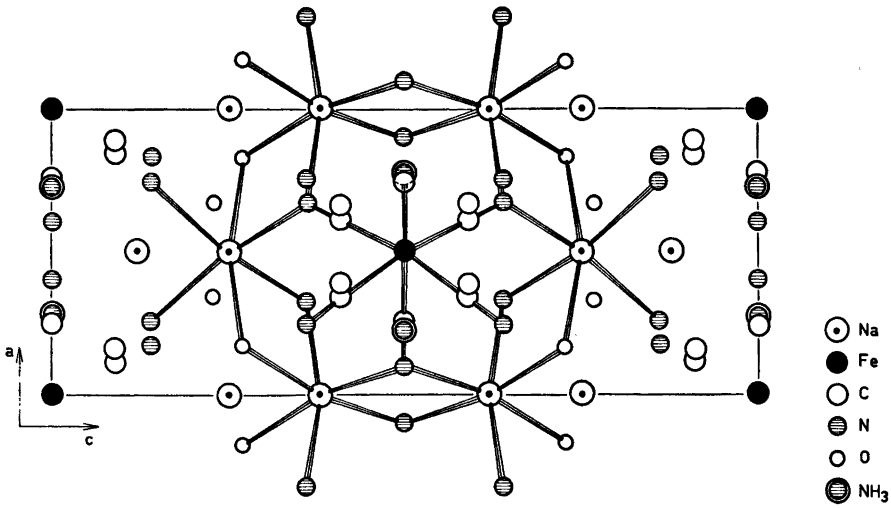

Fig. 3. Projection of the structure of $Na_3[Fe(CN)_5NH_3].2H_2O$ along the *b*-axis showing the arrangement of sodium ion coordination octahedra. Full lines indicate one unit cell. Some of the atoms belonging to the coordination octahedra lie in the unit cell below the plane of the paper.

hedra are linked to form double chains running along the *a*-direction of the unit cell.

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