The OD Structures of $K_3Fe(CN)_6$ and $K_3Co(CN)_6$

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The structures of potassium hexacyanoferrate(III) and hexa-cyanocobaltate(III) have been solved by three-dimensional X-ray methods. The crystals are built up of ordered layers whose stacking is disordered. The OD-groupoid can be formulated as

$$P\ (n);\ c;\ m$$
$$n_{1,}\ \bar{\tfrac{1}{4}};\ n\bar{\tfrac{1}{4}}_{,2};\ a_2$$

By comparison with other crystal structures and with IR data, and by ligand field calculations, it can be shown that the chemical bonds in these complex ions are mostly of σ-type with little or no π-contributions.

A review of earlier crystal structure work on hexacyanides, has been published previously,[1] together with a complete description of the OD-structure of $K_3Mn(CN)_6$. All the compounds studied so far, with the exception of $D_3Co(CN)_6$,[2] have disordered structures and are built up of ordered layers whose stacking is disordered. Despite this, it has been possible to determine the structure of the complex ions with an accuracy only slightly inferior to that usual in the determination of the structures of fully ordered compounds.[3]

In this paper, the OD-structures of two further compounds, *i.e.* $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, will be described. The investigation was undertaken in order to determine the influence of the number of d-electrons on the metal to ligand bond.

EXPERIMENTAL

Potassium hexacyanoferrate(III) and hexacyanocobaltate(III) were prepared according to methods given by Brauer.[4]

Accurate cell dimensions were determined from Guinier powder photographs, taken with potassium chloride as an internal standard (*cf.* Tables 1 — 3).

Several single crystals of both the iron and the cobalt compounds were rotated about all the crystallographic axes and the corresponding Weissenberg zones were registered. After several attempts, crystals which gave rise to rather welldeveloped spots on the diffuse streaks (see below) were found. These crystals were then used for the structure

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Table 1. Powder diffraction data for $K_3Fe(CN)_6$, orthorhombic indices.

$h\,k\,l$	$\sin^2\theta_{obs} \times 10^5$	$\sin^2\theta_{calc} \times 10^5$	Rel. intensity
3 1 0	3483	3488	100
1 0 2	3704	3704	80
1 1 2	4262	4255	30
2 1 2	5232	5235	50
2 3 0	6248	6231	60
3 0 2	6330	6319	50
3 1 2	6854	6870	90
3 2 2	8502	8515	60
1 3 2	8628	8640	60
0 4 0	8766	8754	30
3 2 3	11248	11255	30
1 4 2	12470	12474	60
0 0 4	13488	13510	80
5 2 2	13763	13745	60
4 4 0	13984	13984	60
3 1 4	16997	17006	60
4 0 4	18728	18740	50
3 5 2	19984	20017	30
4 2 4	20969	20943	30
4 4 4	27494	27525	60

determinations. The X-ray data were collected with a Philips Pailred Diffractometer, the iron hexacyanide being rotated about the crystallographic a axis and the cobalt compound about the c axis.

The diffractographs had the following feature in common: All reflections for which $l = 2L$, where L is an integer, were sharp and distinct and could be given the coordinates $H\,k\,L$ in reciprocal space. The indices $H\,k\,L$ correspond to axes of lengths 13.504 Å,

Table 2. Powder diffraction data for $K_3Co(CN)_6$, orthorhombic indices.

$h\,k\,l$	$\sin^2\theta_{obs} \times 10^5$	$\sin^2\theta_{calc} \times 10^5$	Rel. intensity
3 1 0	3531	3549	100
1 0 2	3742	3722	80
1 1 2	4282	4275	30
4 0 0	5356	5327	50
2 3 0	6336	6303	60
3 0 2	6418	6386	50
3 1 2	6946	6939	90
3 2 2	8618	8596	60
1 3 2	8748	8694	60
3 3 2	11383	11358	30
5 1 2	12272	12266	60
0 0 4	13600	13559	80
3 1 4	17143	17108	60
4 0 4	18899	18887	50
0 4 4	22366	22397	20
4 4 4	27763	27725	60

Table 3. The elementary cell dimensions for the MDO_1 and MDO_2 structures of $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, all distances in Å.

	$K_3Fe(CN)_6$	$K_3Co(CN)_6$
	MDO_1	MDO_1
a	13.504 ± 0.003	13.342 ± 0.019
b	10.401 ± 0.004	10.363 ± 0.008
c	8.360 ± 0.003	8.367 ± 0.006
	MDO_2	MDO_2
a	7.070 ± 0.002	6.994 ± 0.010
b	10.402 ± 0.004	10.363 ± 0.008
c	8.360 ± 0.003	8.367 ± 0.006
β	$107.20° \pm 0.02$	$107.40° \pm 0.04$

10.401 Å, and 4.180 Å (iron compound) and 13.342 Å, 10.363 Å, and 4.183 Å (cobalt compound). For both compounds the relative intensities of this type of reflection were the same for all crystals. The reflections for which $l = 2L + 1$ were situated on diffuse streaks whose reciprocal coordinates could be expressed as ξ, k, l where ξ may take any real number. One unit in the ξ-direction is defined so as to correspond to a distance a_0 in direct space. This distance corresponds to the separation between two of the layers from which the structures are built up.[3] In the iron compound a_0 is 4.180 Å while in the cobalt compound it is 4.183 Å.

The crystals used also showed distinct intensity maxima on the diffuse streaks. These intensity maxima constituted a reciprocal lattice with unit cell dimensions corresponding to a monoclinic cell with the dimensions $a = 7.070$ Å, $b = 10.402$ Å, $c = 8.360$ Å and $\beta = 107.20°$ (iron compound) and $a = 6.994$ Å, $b = 10.364$ Å, $c = 8.367$ Å and $\beta = 107.40°$ (cobalt compound).

The extinction rules for the two structures are the same as those found and discussed previously for $K_3Mn(CN)_6$ (see Table 4).

Table 4. Conditions limiting possible reflections.

i	$\xi \, k \, l$	only for	$\xi = H$	if	$l = 2L$
ii	$H \, k \, L$	»	»		$H + L = 2n$
iii	$\xi \, 0 \, l$	»	»		$l = 2n$
iv	$0 \, k \, l$	»	»		$k + l = 2n$

The so-called superposition structures were first solved from the family reflections, using Patterson and least squares methods.[1] (Tables 5 – 6). The structure factors of the so-called MDO_2 (monoclinic) structure [1,3] space group $P2_1/c$ could be estimated from the

Table 5. The atomic coordinates in the superposition structure of $K_3Fe(CN)_6$.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Mv	0.0	0.0	0.0	0.0	0.0	0.0	1.37	0.05
K1	0.2506	0.0003	0.2268	0.0004	0.0	0.0	1.80	0.07
C1	0.9422	0.0014	0.1648	0.0020	0.0	0.0	1.35	0.21
C2	0.0918	0.0009	0.0536	0.0013	0.3207	0.0031	1.56	0.16
N1	0.9027	0.0014	0.2634	0.0033	0.0	0.0	2.53	0.34
N2	0.1479	0.0010	0.0827	0.0015	0.4855	0.0173	3.22	0.31

Table 6. The atomic coordinates in the superposition structure of $K_3Co(CN)_6$.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Mv	0.0	0.0	0.0	0.0	0.0	0.0	1.36	0.06
K1	0.2507	0.0004	0.2269	0.0004	0.0	0.0	1.79	0.08
C1	0.9421	0.0016	0.1645	0.0022	0.0	0.0	1.42	0.24
C2	0.0918	0.0010	0.0539	0.0015	0.3205	0.0034	1.57	0.18
N1	0.9027	0.0015	0.2651	0.0032	0.0	0.0	2.45	0.37
N2	0.1478	0.0011	0.0823	0.0016	0.5131	0.0207	3.11	0.34

family reflections and the intensity maxima of the spots in reciprocal space with the coordinates $\xi = n + (l/4)$ ($n =$ integer), k and $l = 2L + 1$. The MDO_2 structure, like the superposition structure, is fully ordered and can be solved by ordinary methods (Tables 7 − 8). The R-factors could be refined to 0.069 for the cobalt compound and to 0.087 for the iron compound. The best fit between observed and calculated structure factors were in both cases obtained with the scattering factors for the 1 + charged central ions (Tables 9 − 10). Distances between atoms and bond angles can be found in Tables 11 and 12.

Table 7. Positional and thermal parameters of the atoms including their standard deviations for $K_3Fe(CN)_6$ MDO_2.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.0	0.0	0.0	0.0061	0.0036	0.0015	− 0.0015	0.0037	0.0
K1	0.0	0.0	0.5	0.0143	0.0071	0.0074	0.0046	0.0009	0.0
K2	0.5023	0.2278	0.6247	0.0121	0.0075	0.0054	− 0.0034	0.0038	0.0017
C1	0.8854	0.1689	0.9680	0.0033	0.0047	0.0022	− 0.0031	0.0206	0.0021
C2	0.1869	0.0500	0.2135	0.0088	0.0085	0.0039	0.0030	− 0.0022	− 0.0106
C3	0.1896	0.0576	0.8835	0.0097	0.0066	0.0006	− 0.0050	0.0180	− 0.0018
N1	0.7998	0.2614	0.9525	0.0183	0.0073	0.0099	− 0.0066	0.0016	0.0085
N2	0.2930	0.0837	0.3363	0.0217	0.0136	0.0067	0.0020	− 0.0117	0.0007
N3	0.3028	0.0894	0.8131	0.0119	0.0082	0.0093	0.0004	0.0270	− 0.0105

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{32})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Fe	0.0	0.0	0.0	0.0008	0.0003	0.0004	0.0008	0.0011	0.0
K1	0.0	0.0	0.0	0.0019	0.0006	0.0008	0.0016	0.0024	0.0
K2	0.0007	0.0004	0.0005	0.0009	0.0006	0.0004	0.0010	0.0016	0.0007
C1	0.0025	0.0014	0.0017	0.0038	0.0011	0.0015	0.0031	0.0057	0.0024
C2	0.0027	0.0019	0.0019	0.0045	0.0014	0.0019	0.0040	0.0068	0.0030
C3	0.0034	0.0016	0.0017	0.0051	0.0016	0.0014	0.0044	0.0076	0.0028
N1	0.0028	0.0016	0.0020	0.0049	0.0015	0.0024	0.0047	0.0081	0.0033
N2	0.0032	0.0018	0.0020	0.0068	0.0021	0.0021	0.0058	0.0083	0.0038
N3	0.0032	0.0017	0.0022	0.0057	0.0016	0.0023	0.0049	0.0100	0.0033

Table 8. Positional and thermal parameters of the atoms including their standard deviations for $K_3Co(CN)_6 \cdot MDO_2$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.0	0.0	0.0	0.0054	0.0043	0.0032	0.0	0.0021	0.0
K1	0.0	0.0	0.5	0.0182	0.0062	0.0071	0.0015	0.0095	0.0
K2	0.5018	0.2279	0.6251	0.0130	0.0097	0.0061	-0.0025	0.0051	0.0011
C1	0.8820	0.1642	0.9755	0.0085	0.0048	0.0057	-0.0024	0.0056	-0.0003
C2	0.1834	0.0520	0.2063	0.0077	0.0066	0.0060	0.0011	0.0072	-0.0082
C3	0.1852	0.0545	0.8849	0.0091	0.0049	0.0064	-0.0021	0.0064	-0.0021
N1	0.8029	0.2638	0.9537	0.0142	0.0063	0.0118	-0.0015	0.0043	0.0010
N2	0.2939	0.0795	0.3379	0.0133	0.0075	0.0087	0.0002	0.0013	-0.0063
N3	0.2928	0.0868	0.8159	0.0152	0.0121	0.0086	0.0	0.0117	0.0024
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Co	0.0	0.0	0.0	0.0003	0.0002	0.0005	0.0005	0.0005	0.0
K1	0.0	0.0	0.0	0.0011	0.0004	0.0009	0.0012	0.0015	0.0
K2	0.0005	0.0004	0.0003	0.0006	0.0004	0.0002	0.0007	0.0008	0.0005
C1	0.0015	0.0011	0.0013	0.0017	0.0009	0.0010	0.0023	0.0027	0.0016
C2	0.0016	0.0013	0.0013	0.0019	0.0010	0.0011	0.0025	0.0030	0.0019
C3	0.0016	0.0011	0.0013	0.0019	0.0010	0.0011	0.0025	0.0052	0.0019
N1	0.0018	0.0011	0.0015	0.0027	0.0011	0.0014	0.0024	0.0045	0.0025
N2	0.0016	0.0011	0.0017	0.0023	0.0011	0.0015	0.0027	0.0036	0.0022
N3	0.0018	0.0013	0.0017	0.0025	0.0016	0.0016	0.0035	0.0043	0.0027

DESCRIPTION OF THE STRUCTURES

As is obvious from the appearance of the diffraction intensities, the crystals are built up of planes stacked parallel to the a_0-axes. In the orthorhombic packing (see Fig. 1), every second layer is stacked directly over each other, while, in the monoclinic packing, each fourth plane coincides with the first.

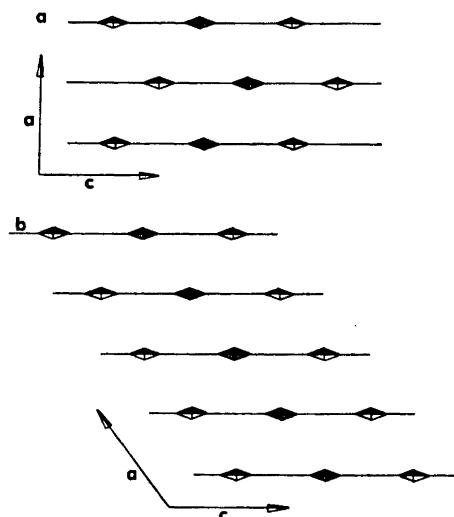*Fig. 1.* The sequence of layers in the structures of maximum degree of order MDO_1 and MDO_2 in the OD-groupoid family $P(n)cm/n_{1,\frac{1}{3}}n^-_{\frac{1}{2},2}a_2$. An open triangle corresponds to a structural element at y, a filled triangle to one at $\bar{y}$, a horizontally shaded triangle to one at $\frac{1}{2}+y$ and a vertically shaded triangle to one at $\frac{1}{2}-y$.

Table 9. Observed and calculated structure factors for the MDO$_2$ structure of K$_3$Fe(CN)$_6$. The columns are: Index, F_{obs} and F_{calc}.

Column group 1

index	Fobs	Fcalc
-2 K 9		
7	23	26
5	15	10
2	14	11
7	24	26
3	13	7
2	12	11
-2	12	-11
-7	23	26
-1 K 5		
9	11	-12
7	32	27
4	13	-14
3	23	24
2	10	11
1	18	16
-1	19	16
-2	12	-11
-3	25	24
-4	15	14
-6	11	-8
-7	34	27
-8	15	14
-9	13	-12
-11	15	16
0 K 1		
11	17	19
9	13	-14
8	15	-16
7	34	30
6	10	12
4	23	-22
3	31	27
2	15	15
-2	16	-15
-5	9	-4
-6	12	-12
-7	40	30
-8	17	16
-9	16	-14
-11	24	19
-1 K 7		
-6	11	-9
-5	21	18
-4	23	21
-1	26	23
1	24	23
4	20	-21
5	21	18
0 K 3		
-9	18	18
-6	27	-26
-5	37	32
-3	18	-11
-2	24	-21
-1	9	9
1	9	9
2	23	21
3	15	-11
5	31	32
6	22	26
7	13	8
9	11	18
-1 K 9		
4	14	12
1	17	17
-1	13	17
-4	13	-12
0 K 5		
-10	15	12
-9	12	16
-8	16	-12
-6	19	19
-5	20	22
-1	17	23
1	22	23
5	17	22
6	11	-19
8	11	12
1 K 1		
8	12	20
6	16	-26
2	8	-12
-2	11	12
-5	30	30
-6	31	26
0 K 7		
-7	16	19

Column group 2

index	Fobs	Fcalc
1 K 3		
-8	18	-21
-10	11	15
0 K 9		
3	18	20
1	20	18
-1	19	18
-3	19	20
1 K 5		
-11	12	13
-7	22	20
-6	10	-10
-4	20	17
-3	21	17
3	21	17
4	23	-17
7	16	20
11	13	13
1 K 7		
6	14	9
5	20	18
2	12	12
-2	18	-12
-4	13	7
-5	22	16
-6	12	-9
-9	25	21
2 K 3		
4	19	-16
3	15	11
2	21	17
1	47	33
-1	49	33
-2	23	-17
1 K 9		
5	14	15
2 K 5		
-5	13	15
2 K 5		
-9	23	20
-8	14	-12
-5	25	22
5	23	22
8	11	12
9	20	20
3 K 1		
9	23	23
8	13	16
5	23	23
4	10	13
-3	9	7
-4	13	-13
-5	30	23
-8	18	-16
-9	31	23
2 K 7		
3	11	17
-1	10	9
-3	12	17
3 K 3		
-3	12	26
-1	7	11
1	7	11
2	8	-10
3	20	26
8	10	8
3 K 5		
-7	15	15
-6	17	-14
-3	18	20
2	12	12
3	21	20
6	17	14
11	17	10
4 K 1		
10	12	11
7	15	18
6	16	19
3	23	29
2	11	13
-2	14	-13
-3	29	29
-6	20	-19
-7	22	18
-10	13	-11
-11	15	10

Column group 3

index	Fobs	Fcalc
5 K -1		
5	9	14
-5	12	14
-6	12	-10
-9	15	16
4 K 5		
-5	11	9
-4	13	-13
-3	13	8
-1	17	15
1	16	15
3	11	8
4	14	13
5	11	9
5 K 1		
6	13	-9
5	11	14
4	16	16
3	15	13
2	10	-8
-2	11	8
-3	19	13
-4	19	-16
-5	14	14
-6	10	9
-8	11	-10
4 K 7		
-3	16	14
5 K 3		
-7	23	19
-4	12	-15
-3	13	14
3	13	14
4	16	15
7	20	19
4 K 9		
3	14	9
5 K 5		
3	12	13
-3	14	13
-7	16	10
6 K 1		
-8	11	10
-7	11	10
-3	12	14
6 K 3		
5	12	15
1	11	11
-1	11	11
-5	17	15
-2 K 8		
-8	23	22
-6	10	11
-4	41	39
0	67	68
4	40	37
6	11	11
8	24	22
-1 K 6		
-8	7	15
-1 K 4		
-12	25	22
-10	24	21
-8	41	38
-6	14	13
-4	71	71
0	135	146
4	70	71
6	12	13
8	38	38
10	20	21
12	21	22
0 K 0		
-12	23	21
-10	14	16
-8	33	34
-4	95	104
-2	39	36
0 K 2		
-12	19	20
-11	7	4
-10	18	21

Column group 4

index	Fobs	Fcalc
-9	10	9
-8	33	36
-1 K 8		
8	15	13
6	38	37
4	12	9
2	46	45
0	14	13
-2	46	45
-4	12	9
-6	38	37
-8	17	13
-9	11	-8
0 K 4		
10	22	23
8	23	23
7	11	7
6	62	64
4	21	21
3	22	-22
2	81	79
1	11	9
0	16	13
-1 K 10		
4	19	20
5	14	14
0 K 5		
-10	24	20
-8	23	19
-7	16	17
-6	26	23
-5	8	-7
-4	27	27
-3	39	38
-2	45	42
-1	40	-40
0	55	52
1	42	40
2	45	42
3	38	-38
4	23	27
5	25	23
6	25	23
7	16	-17
8	21	19
10	16	20
1 K 2		
-12	23	20
-10	27	26
-8	26	25
-7	14	13
-6	34	33
-5	41	-36
-4	39	38
-3	41	39
-2	87	84
-1	99	-96
0	113	112
1	98	96
2	86	84
3	39	-39
4	37	38
5	37	38
6	30	33
7	13	-13
8	24	25
10	22	26
12	17	20
0 K 8		
8	19	21
6	16	17
4	42	44
1	11	10
0	44	47
-2	12	11
-4	42	44
-6	15	17
-8	23	21
1 K 4		
12	10	10
10	14	15
8	29	30
6	30	31
5	9	6
4	71	74
3	11	10
2	19	20
1	24	24
0	77	75
-1	25	-24
-2	20	20

Column group 5

index	Fobs	Fcalc
-3	13	-10
-4	73	74
-5	10	-6
-6	35	31
-8	32	30
-10	15	15
-12	14	10
2 K 0		
12	16	15
10	20	23
8	40	45
7	7	-7
6	41	45
5	8	-9
4	77	88
3	6	-6
-3	6	6
-4	87	88
-5	10	9
-6	49	45
-8	49	45
-10	27	23
-12	15	15
0 K 10		
2	25	27
1	13	-12
0	22	23
-1	13	12
-2	25	27
-3	12	-11
1 K 6		
-4	19	18
-10	26	25
-8	29	26
-7	14	-16
-6	34	33
-5	26	25
-4	29	24
-3	12	-9
-2	35	33
-1	31	29
0	17	16
1	31	-29
2	36	33
3	12	9
4	27	24
5	26	-25
6	33	33
7	13	16
8	27	26
10	21	25
2 K 2		
12	13	13
10	20	22
8	23	24
7	22	24
6	37	41
5	34	-35
4	39	40
3	14	14
2	84	81
1	55	-51
0	56	54
-1	55	51
-2	86	81
-3	14	-14
-4	41	40
-5	38	35
-6	42	41
-7	24	-24
-8	28	24
-10	23	22
-12	15	13
1 K 8		
2	53	56
0	10	11
-2	52	56
-6	26	25
-8	15	8
2 K 4		
-12	13	13
-10	23	22
-6	37	37
-5	9	8
-4	9	7
-3	12	-9
-2	101	97
0	23	21
2	100	97
3	12	9
6	36	37

Table 9. Continued.

```
 10   20   22            4 K 0              4 K 6            0   16   14
 12   11   13      12    9   10       -8   12   13           1   19  -18
                   10   18   18       -6   10   10           2   23   23
       3 K 0        8   30   34       -5   13  -10           3   12   12
 12   16   17       7   13   14       -4   26   25           4   22   24
                    6    7    7       -3   23   23           6   23   24
 10   30   32       4   57   67       -2   29   29
  8   23   23       3    6    5       -1   13  -14                 5 K 8
  6   45   51       2   16   18        0   39   39           2   24   27
  3   23   26      -2   18   18        1   12   14           6   19   16
  2   94  106      -4   66   67        2   26   29
 -2  107  106      -6    8    7        3   24  -23                 6 K 4
 -3   27  -26      -7   13  -14        4   24   25          10   13   12
 -6   53   51      -8   39   34        5   10   10           6   22   23
 -8   26   23     -10   20   18        6   11   10           2   40   41
-10   37   32     -12   11   10                             0   13   13
-12   21   17                               5 K 2          -2   41   41
                        2 K 10       12   12   11
       1 K 10       2   16   17      10   17   18                 7 K 0
  2   17   21       1   13  -15       8   20   23          -3   13   11
  1   12   13      -1   13   15       7    9  -10          -2   39   36
  0   13   15      -2   15   17       6   16   16           2   34   33
 -1   16  -13      -3   10  -11       5   15   16           3   10  -11
 -2   19   21                         4   28   29           6   24   25
 -3   12   12            3 K 6        3   28  -29          10   12   16
 -4   21   19     -10   12   12        2   27   27
                   -8   17   17        1   20   19                7 K 2
       2 K 6       -6   13   14        0   42   37          -4   15   16
-10   20   16      -4   29   30       -1   20  -19          -2   20   21
 -8   26   27      -3   33  -32                             -1   12  -15
 -6   32   30      -2   36   30       -2   28   27           0   23   23
 -5   18  -19      -1   19   18       -3   31   29           1   13   15
 -4   35   34       0   38   39       -4   31   29           2   17   21
 -2   28   28       1   20  -18       -5   18  -16
 -1   29  -26       2   36   36       -6   18   16                6 K 8
  0   12   12       3   31   32       -7    9   10           4   14   16
  1   27   26       4   29   30       -8   25   23           0   20   21
  2   28   28       6   11   14      -10   21   18          -4   17   18
  4   34   34       7   11    8      -12   12   11
  5   18   19       8   17   17                                   7 K 4
  6   30   30                               4 K 8          -8   13   11
  8   25   27            4 K 2        0   32   31          -6   14   12
 10   17   16      12   12   13        4   23   26          -4   24   23
                   10   14   18                             0   30   29
       3 K 2        9   10   -9            5 K 4            4   23   23
 12    9    8       8   24   27       10   15   12           6   13   12
 10   14   18       6   17   17        8   21   22           8   13   11
  8   25   27       5   20  -20        6    9   10
  7    9   -8       4   36   38        4   36   36                8 K 0
  6   37   39       3   36   39        3    9    7           8   17   16
  5    9    9       2   40   39        2    8    7           6   13   17
  4   50   52       1   33  -30        0   46   47           4   19   23
  3   22  -23                         -2    8    7          -4   24   23
  2   48   49       0   45   44       -3    9   -7          -6   19   17
  1   33   32      -1   33   30       -4   39   38          -8   22   16
  0   26   25      -2   42   39       -6    9   10         -10   12   10
 -1   34  -32      -3   38  -35       -8   24   22
 -2   50   49      -4   40   38      -10   12   12                8 K 2
 -3   24   23      -5   20   20                             1   13  -14
 -4   55   52      -6   17   17            6 K 0
 -5   11   -9      -8   29   27       -8   20   21                7 K 6
 -6   42   39      -9   10    9       -7   14   13           0   13   13
 -7   10    8     -10   20   18       -6   44   42           3   11   10
 -8   29   27     -12   14   13       -2   14   15
-10   22   18                         2   12   15                8 K 2
                        3 K 8        4   36   42          10   11    8
       2 K 8        2   29   29        7   12  -13           5    9   -9
  8   20   22      -2   30   29        8   17   21           4   10   10
  4   33   36      -4   11   12       10   12   11           3    9    9
  2    9    9      -6   26   24       12   11    9           2   19   18
  1    9   -7      -8   16   15                             1   13  -14
  0   39   41                               5 K 6           0   23   23
 -4   34   36            4 K 4        8   10   13          -1   14   14
 -8   21   22     -10   19   17        6   15   19          -2   20   18
                   -8   24   22        5   10  -11          -3    9   -9
       3 K 4       -6   36   35        4   18   18          -4   10   10
 12   10   12      -4   21   19        2   21   19          -5   10    9
 10   14   18      -2   43   40        1   19  -17
  8   30   31       0    8   -7        0   14   14          -6   12   12
  5   16  -15       2   41   40       -1   19   17          -8   12    8
  4   53   53                         -2   19   19
  3   10  -10            5 K 0       -4   19   18
  2   14   12       2   53   61       -5   12   11
  1   17  -16      -4   29   29       -6   20   19
  0   71   66      -6   37   35       -8   13   13
 -1   18   16      -8   17   17
 -2   15   12     -10   13   12            6 K 2
 -3   10   10     -12   10    8      -10   12   11
 -4   54   53                         -8   22   18
 -5   17   15            3 K 10      -6   28   24
 -8   33   31       2   12   13       -4   24   24
-10   18   18       0   14   14       -3   14  -12
-12   12   12      -1   12   -9       -2   25   23
                                     -1   20   18
```

Table 10. Observed and calculated structure factors for the MDO$_2$ structure of K$_3$Co(CN)$_6$. The columns are: Index, F_{obs} and F_{calc}.

```
 H 14  0        H 10  2         4  41  44        H  0  4          H  1  6
 4   9  11      6  11  11       3  23  24       8  10   7       0  39   38
 3  11  11      5  17  18       2  54  54       7  31  29       1  29  -28
 2  12  12      4  15  19       1 115 113       6  13  12       2  25   26
 1  10   9      3  16  19                       5  44  42       3  16  -17
 0  13  13      2  19  21       H  2  2         3  72  68       4  12   13
                1  20  24       1  85  84       2  24  24       5  17  -17
 H 12  0        0  13  20       0  30  28       1  78  77       6   9   10
 6  10   8                                      0  14  13       7  10  -10
 5   8   7      H  9  2         H 14  4
 4  11  12      0   9  -8       2  10  10       H 12  6          H  0  5
 3  19  14                      1  10  11       4   8   7       8  14   13
 2  14  14      H  8  2                         2   9   8       7  15   13
 1  18  13      8  10   7       H 12  4         1  13  13       6  13   13
 0  22  21      7  10   9       5  10  10       0  15  16       5  15   16
                6  18  13       4   9   9      -1  11  12       4  38   37
 H 11  0        5  21  22       3  12  11      -1  14  12       3  35   35
 3   8  -4      4  25  26       2  12  12                       2  13   12
                3  26  28       0  16  17       H 11  6         1  20   20
 H 10  0        2  22  23      -1  19  23       3   7  -2       0  57   56
 7  17  15      1  22  24
 6  10   9      0  32  40       H 11  4         H 10  6          H 12  6
 5  11  12                      0   9  -4       4   8  10       1  11    9
 4  21  20      H  7  2         1   9  -7       3  12  12      -1  13   13
 3  25  34      1   9 -13                       2  20  18      -2  14   16
 2  26  25      2  21  21       H 10  4         1  25  24
 1  22  20                      6  13  12       0  21  15       H 11  6
 0  15  12      H  6  2         5  14  13      -1  10   9      -2   9    3
                7  20  20       4  17  17
 H  9  0        6  25  25       3  18  17       H  9  6         H 10  6
 1   8  10      5  15  15       2  22  20      -1   8  -6       3  10   11
                4  15  18       1  17  15                       2  14   13
 H  8  0        3  30  41       0  22  22       H  8  6         1  16   15
 8  19  17      2  40  42      -1  23  22       5  11  12       0  11   11
 7  11   9      1  32  34                       4  12  12      -1  16   15
 6  20  19      0  51  53       H  9  4         3  18  16      -2  14   14
 5  19  17                      6   9   1       2  26  26
 4  36  33      H  5  2                         1  27  26       H  8  8
 3  26  25      0   8 -10       H  8  4         0  21  20       4  16   14
 2  49  47      1  35  38       7  13  11      -1  21  18
 1  25  24      2  33 -35       5  21  23                       3   9   13
 0  34  31      3   8   7       4  22  23       H  7  6         2  20   20
                4  17 -10       3  30  28       0  16 -16       1   9   10
 H  7  0        5  13  15       2  10   9       1  12  14       0  24   21
 2  10  -9                      1  32  31       3   8   9      -1  14   16
 4  14  14      7  16  14       0  27  27       4  10  -3      -2  24   24
 6  13 -12                     -1  42  40
                H  4  2                         H  6  6         H  6  8
 H  6  0        9  10  12       H  6  4         7  12  12       6  12   10
 9  20  21      8  10  10       9  16  17       6  16  16       5  14   16
 8  15  18      7  15  16       6  23  22       5  19  17       3  23   22
 7  24  25      6  24  25       5  12  10       3  11  13       1  26   26
 6   7   8      5  29  31       4  35  35       2  32  31       0  18   20
 5  36  35      4  37  35       3   8   7       1  33  34      -1  38   38
 4   9   8      3  50  51       2  37  36       0  27  24      -2  11   10
 3  52  52      2  39  41       1  33  33      -1  37  33
 2  51  49      1  39  37       0  64  64                       H  4  8
 1  78  73      0  69  70      -1  15  15       H  5  6         6  17   16
                                              -1  19 -17       4  25   26
 H  5  0        H  3  2         H  5  4         0   8   7       3  15   13
 1  24 -26      0  68  70       2  10  -6       1  26 -25       2  35   34
 2  10 -10      1  37 -33       3  17 -17       2  16  16       1   7    7
 6   9   5      2  12  14       5  12  11       3   8  -6       0  41   42
                3  22 -21                       4  11  10      -1  12   12
 H  3  0        4  35  36       H  4  4         5  10  -9      -2  42   39
 1  63 -78      5  26 -29       7  22  22
 2   9  -8      6  11  10       5  36  38       H  4  6         H  3  8
 3  26  27                      4  20  22       7   8   8      -1   9   -8
                H  2  2         3  52  53       6  12  12
 4   7   7      9  11  10       2   8   9       5  19  19       H  2  8
 7  12 -12      8  19  20       1  73  72       4  24  25      -1  44   44
                7  20  22       0  22  22       3  29  29       0   9   10
 H  2  0        6  22  22      -1  75  71       2  34  34       1  51   52
 9  18  16      5  27  28                       1  26  25       2  10    9
 7  42  41      4  40  40       H  3  4         0  28  26       3  30   30
 6  16  16      3  47  49       0  22 -20      -1  47  44       5  27   26
 5  60  60      2  81  81       1  12  12                       7  13   15
 4  13  20      0  27  28       2  11  10       H  3  6
 0  47  39                      3   9 -10      -1  28  28       H  1  8
                H  1  2                         0  36 -36       1   6    4
 H  1  0        1  95  95       H  2  4         1   9   9       0   9    9
 2  29  27      2  49 -49       8  19  20       2   7  -7
 3  16  14      3  31  32       6  38  39       3  31  32       H  0  8
 4  15 -13      4  30 -30       4  40  40       4  18 -20      -1  10   11
                5  17  18       3  18  16       6   8  -9       0  45   46
 H  0  0        6  17 -18       2  98  98                       1  12   10
 8  23  22      7  13  16       1  20  20       H  2  6         2  41   40
 7  12  12      8  17 -13       0  81  78       7  11  12       4  31   31
 6  63  62                                      6  14  13       6  20   20
 5  10  11      H  0  2         H  1  4         5  19  20
 4  88  87      9  16  16       0   9   9       4  27  28       H 12 10
 3   9  -7      8  21  24                       3  34  34      -2  11   10
 2  60  57      7  23  22       1  24  24       2  27  27      -1   9   10
 1  45  40      6  16  16       2  10  -7       1  35  34
                5  40  40       3  16 -15       0  44  44
                                              -1  38  39
```

Table 10. Continued.

H 10 10
-2	10	12
-1	11	10
0	10	9
2	9	11
3	13	11

H 8 10
-2	18	17
-1	12	13
0	10	10
1	11	11
2	12	12
3	14	14

H 7 10
2	8	2
1	8	-4

H 6 10
-2	23	25
-1	17	17
0	15	17
1	15	14
2	9	9
3	10	10
4	12	13

H 5 10
2	10	-11
0	11	-11
-1	14	13
-2	7	-4

H 4 10
-2	21	22
-1	17	18
0	17	17
1	20	20
2	17	15
3	13	15
4	11	13
5	9	10

H 3 10
3	12	-12
2	12	10
1	9	-11
0	9	10
-1	9	-9
-2	19	19

H 2 10
-2	13	15
-1	24	24
0	26	25
1	21	21
2	16	17
3	10	12
4	13	12
5	15	13
6	11	11

H 1 10
4	12	-9
3	8	8
2	12	-13
1	12	14
0	13	-13
-1	22	22

H 0 10
-1	30	30
0	24	23

H 12 12
0	8	8

H 10 12
-1	10	8
0	10	12
1	9	8

H 9 12
0	8	2

H 8 12
-3	9	10
-2	9	6
-1	12	13
0	11	10
1	15	13

H 6 12
-2	19	19
-1	11	10
0	15	16
2	13	12
4	11	10

H 5 12
-1	7	-4

H 4 12
-3	22	22
-2	8	6
-1	22	21
1	20	20
2	7	9
3	16	16
5	10	10

H 3 12
-2	6	-6

H 2 12
-3	9	8
-2	26	25
0	24	23
1	8	5
2	21	21
4	14	14

H 10 14
-3	10	6

H 9 14
0	8	8
-3	7	7

H 6 14
0	10	9
-1	10	11
-2	9	9
-3	10	11

H 5 14
2	8	3

H 4 14
0	10	11
-1	9	10
-2	8	9
-3	10	13

H 3 14
-3	6	7
-2	8	-7
2	8	-5

H 2 14
4	9	7
2	9	8
0	9	11
-1	10	11
-2	12	11
-3	10	10

H 1 14
-2	9	9
-1	7	-6
0	7	8

H 0 14
1	8	9
0	7	8
-1	9	11
-2	13	14

H 12 1
-3	10	6

H 10 1
1	15	-14

H 9 1
7	11	11
3	26	25
1	18	15
0	13	-14
-1	11	9

H 8 1
-7	10	6
-2	16	-17
0	14	-11
1	16	17
3	11	14
4	9	-9

H 7 1
8	13	13
6	11	11
4	20	19
2	22	21
0	31	32
-2	26	26
-4	16	19
-6	13	15

H 6 1
-6	10	9
-5	13	-11
-3	13	-13
-2	28	26
0	8	11
1	22	-26
2	9	10
3	10	-8
4	20	19
8	10	7

H 5 1
7	17	16
6	8	4
5	14	14
3	24	26
1	28	30
-3	28	31
-5	15	17
-7	15	18
-9	12	13

H 4 1
-6	10	-9
-4	11	-13
-3	19	19
-1	27	26
0	21	-22
2	27	-27
3	9	9
5	15	14

H 3 1
8	9	6
6	13	18
5	15	17
4	31	30
2	19	20
1	7	-10
0	29	25
-2	21	21
-4	28	31
-5	15	16
-6	24	24
-10	10	9

H 2 1
-9	11	-3
-8	10	4
-6	9	10
-5	8	-6
-3	15	-17
-2	9	7
-1	8	-6
0	13	12
1	14	-13
2	15	14
4	13	14
7	9	-8

H 1 1
6	13	14
5	21	21
4	8	9
1	33	29
-5	19	19
-6	13	14
-7	16	15
-8	11	8

H 12 3
2	9	-6

H 11 3
5	11	12
2	10	-7
1	10	8
0	9	6
-1	22	21

H 10 3
-5	9	-10
-2	15	15
0	9	5
1	11	-12
4	10	10

H 9 3
4	18	19
2	12	14
0	14	16

H 8 3
-5	13	13
-4	9	-8

H 7 3
-2	24	-23

H 7 3
7	12	9
5	21	22
3	12	12
2	11	-11
1	22	23
0	9	8
-5	16	18
-7	14	14

H 6 3
-7	12	-12
-6	9	10
-4	16	17
-3	18	-19
-1	14	-13
0	20	20
2	13	13
3	12	-15
6	12	11

H 5 3
8	13	13
6	16	17
4	17	18
2	25	25
0	30	29
-2	29	28
-4	16	19
-6	16	15
-8	10	13

H 4 3
-8	9	-13
-7	9	-6
-6	12	-11
-5	25	24
-3	9	8
-2	28	-27
-1	13	13
1	22	24
2	14	-13
3	9	-6
5	15	14
6	11	8

H 3 3
7	16	13
5	15	16
3	30	32
2	12	13
0	12	-11
-1	6	7
-3	32	31
-4	20	19
-5	26	24
-7	12	12
-8	9	6

H 2 3
-7	9	-5
-6	13	10
-4	8	6
-3	29	-25
-2	9	-8
-1	15	-16
0	20	19
1	12	12
2	17	19
3	11	-10
6	10	4

H 1 3
8	15	14
7	14	16
6	14	15
2	38	37
-2	17	16
-3	30	26
-4	35	31
-8	16	17
-9	12	16
-10	11	10
1	19	17

H 3 3
1	26	25

H 3 7
-2	17	17
-4	12	13
-5	8	7
-6	19	17
-7	10	10
-8	11	11

H 2 7
-4	8	-9
-3	9	11
-2	6	-4
1	11	12

H 1 7
4	10	9
3	12	11
-3	11	14
-6	11	8
-7	9	11

Table 11. Bond distances and bond angles in $K_3Fe(CN)_6$.

Fe1 – C1	1.927 ± 0.014 Å	C1 – Fe1 – C1	180.00 ± 0.00°
C2	1.952 ± 0.016	C2	91.56 ± 0.69
C3	1.971 ± 0.019	C2	88.44 ± 0.69
N1	3.050 ± 0.017	C3	88.67 ± 0.70
N2	3.081 ± 0.017	C3	91.33 ± 0.70
N3	3.138 ± 0.018	C2 – Fe1 – C2	180.00 ± 0.00
K1 – N1	2.827 ± 0.017	C3	89.94 ± 0.67
N2	2.927 ± 0.018	C3	90.07 ± 0.67
N3	2.993 ± 0.017	N1 – K1 – N1	180.00 ± 0.00
C2	3.119 ± 0.016	N2	85.99 ± 0.51
C3	3.150 ± 0.013	N2	94.01 ± 0.51
C1	3.531 ± 0.014	N3	87.27 ± 0.49
K2 – N3	2.809 ± 0.018	N3	92.73 ± 0.49
N1	2.860 ± 0.018	N3	92.73 ± 0.49
N2	2.861 ± 0.017	N2 – K1 – N2	180.00 ± 0.00
N1	2.946 ± 0.017	N3	84.49 ± 0.48
N3	3.211 ± 0.017	N3	95.51 ± 0.48
N2	3.280 ± 0.018	N3 – K1 – N3	180.00 ± 0.00
C1	3.365 ± 0.015	N1 – K2 – N1	92.76 ± 0.53
C3	3.367 ± 0.019	N2	154.35 ± 0.52
C2	3.434 ± 0.019	N2	74.15 ± 0.47
C1	3.500 ± 0.016	N3	82.40 ± 0.50
N2	3.528 ± 0.019	N3	135.06 ± 0.48
C1 – N1	1.131 ± 0.022	N2	82.26 ± 0.52
C2	2.705 ± 0.022	N2	139.57 ± 0.50
C3	2.724 ± 0.025	N3	149.43 ± 0.53
C2	2.780 ± 0.022	N3	77.09 ± 0.49
C3	2.788 ± 0.022	N2 – K2 – N2	124.76 ± 0.70
K2	3.365 ± 0.015	N3	89.17 ± 0.51
K2	3.500 ± 0.016	N3	68.43 ± 0.48
K1	3.531 ± 0.014	N3	67.98 ± 0.49
C2 – N2	1.131 ± 0.023	N3	85.68 ± 0.44
C3	2.772 ± 0.020	N3 – K2 – N3	126.60 ± 0.71
C3	2.775 ± 0.028	Fe1 – C1 – N1	171.44 ± 1.50
C1	2.780 ± 0.022	C2 – C1 – C3	60.47 ± 0.54
N1	3.549 ± 0.025	C3	59.79 ± 0.62
C3 – N3	1.167 ± 0.026	Fe1 – C2 – N2	176.58 ± 1.76
N1	3.582 ± 0.024	C3 – N3	179.06 ± 1.59

Table 12. Bond distances and bond angles in $K_3Co(CN)_6$.

Co1 – C1	1.876 ± 0.011 Å	C1 – Co1 – C1	180.00 ± 0.00
C2	1.896 ± 0.011	C2	90.16 ± 0.49
C3	1.916 ± 0.011	C3	91.12 ± 0.47
N1	3.035 ± 0.011	C2	90.16 ± 0.49
N3	3.045 ± 0.013	C2 – Co1 – C2	180.00 ± 0.00
N2	3.069 ± 0.012	C3	90.09 ± 0.45
K1 – N1	2.779 ± 0.011	C3 – Co1 – C3	180.00 ± 0.00
N2	2.903 ± 0.011	N1 – K1 – N1	180.00 ± 0.00
N3	2.959 ± 0.013	N2	85.62 ± 0.34
C2	3.140 ± 0.010	N3	87.76 ± 0.37
C3	3.142 ± 0.010	N2 – K1 – N2	180.00 ± 0.00
K2 – N2	2.859 ± 0.013	N3	86.17 ± 0.35
N3	2.866 ± 0.014	N3 – K1 – N3	180.00 ± 0.00
N1	2.881 ± 0.013	N1 – K2 – N1	92.08 ± 0.36
N1	2.944 ± 0.013	N2	153.55 ± 0.34

Table 12. Continued.

K2 −N3	3.202 ± 0.014	N1 −K2 −K3	83.43 ± 0.36
N2	3.286 ± 0.012	N2	81.95 ± 0.34
C3	3.372 ± 0.012	N3	149.55 ± 0.38
C1	3.382 ± 0.010	N2 −K2 −N3	88.77 ± 0.37
C2	3.394 ± 0.012	Co1 −C1 −N1	176.95 ± 1.01
C1	3.447 ± 0.010	Co1 −C2 −N2	176.83 ± 1.10
N2	3.467 ± 0.012	Co1 −C3 −N3	179.41 ± 1.12
C1 −N1	1.160 ± 0.016		
C3	2.655 ± 0.016		
C2	2.663 ± 0.015		
C2	2.671 ± 0.016		
C3	2.707 ± 0.015		
C2 −N2	1.174 ± 0.016		
C3	2.694 ± 0.015		
C3	2.698 ± 0.016		
C3 −N3	1.128 ± 0.017		

The planes are composed of nearly octahedral metal cyanido complex and potassium ions. The former are surrounded by 12 potassium ions while the latter are surrounded by 4 complex groups in such a way that each potassium ion has six nitrogen atoms as nearest neighbours.

In both the iron and the cobalt compounds, the symmetry of the complex groups is very nearly octahedral, so that the angles between the metal-carbon bonds are not significantly different from 90 or 180°. The metal-carbon bond lengths within each complex ion differ, however, significantly from one another.

DISCUSSION

As was pointed out in the case of the manganese compound it is possible to attribute the deviation in bond lengths to a Jahn-Teller splitting.[1] However, the same difference between the bond lengths is found in the cobalt compound which has a d^6-configuration. This ought to mean that the splitting is due to low site symmetry at the position of the complex ion or more probably to overestimated accuracy.

There are few systematic investigations on transition metal-ligand bond lengths to be found in the literature. For the most carefully studied ligand, the carbonyl group, the coordination number and the formal oxidation number varies in such a way that a comparison is very difficult. In Table 13 the mean values of the metal-cyanide bond length in the hexacyanides are compared with Me − F bond lengths and with the metal-cyanide bond lengths in the pentacyanonitrosyl ions. The infrared frequencies for the C≡N M − C stretching vibration and M − C≡N bending vibration and stretching vibrations for some hexacyanide and pentacyanide compounds are also listed. It should be noted that it is at the moment not clear which of the two bands observed between 300 and 600 cm^{-1} that can be attributed to the stretching vibration.[11,14] As both bands are displaced in the same way for different central ions this does, however, not effect the discussion below.

Accompanied by the increasing nuclear charge of the central atom in the series Mn − Fe − Co there is a decrease in the ligand-metal bond length. This

Table 13. Some interatomic distances in different compounds, distances in Å.

Metal	Me(II) – F MeF$_2$	Me(III) – F MnF$_3$ or (MnF$_b$)$_n^{2n-}$	Me(II) – C Me(CN)$_6^{4-}$	Me(III) – C Me(CN)$_6^{3-}$	Me – C Me(CN)/NO^{n-}
Mn	2.12^5 (mean)	1.96^6 (mean)	1.94^8 (mean)	2.00^1 (mean)	1.98^9 (mean)
Fe	2.07^5 (mean)	1.92^7	1.92^8 (mean)	1.95 [a] (mean)	1.90 (mean)[10]
Co	2.04^5 (mean)	1.89^7	–	1.89 [a] (mean) 1.88^2	–

[a] This paper.

can be described as a decrease in the radii of the atoms or, equivalently, as an increase in bond strength. The decrease is of the same order in the fluorides as in the cyanides. The Me – C infrared frequencies for the hexacyanides increase on going from Mn(III) to Co(III), which shows that there is an in-

Table 14. Infrared data for some hexacyano complexes and pentacyanonitrosyl complexes (frequencies in cm^{-1}).

Complex	v_6 (C≡N stretch)	v_7 (M – C≡N bend)	v_6 (M – C stretch)	Ref.
Cr(CN)$_6^{5-}$	2121, 2119	456	339	14
Mn(CN)$_6^{3-}$	2120, 2116, 2108	484	361	11
Fe(CN)$_6^{3-}$	2118	506	389	11
Co(CN)$_6^{3-}$	2143, 2129, 2126	564	416	11
Mn(CN)$_6^{4-}$	2030	535	< 500	12
Fe(CN)$_6^{4-}$	2094 – 2006	583	416	11
Mn(CN)$_6^{5-}$	1960	609	< 500	12
Mn(CN)$_5$NO^{3-}	2135, 2100, 2080	(500)	< 500	13
Fe(CN)$_5$NO^{2-}	2140 – 2182	470 – 515	420 – 450	13

crease in bond strength (Table 14). Some chemical evidence, *e.g.* the free energies for the formation of the hexacyanides, also support the fact that Co – C forms the strongest bond (Table 15).

Table 15. Thermodynamic data for the formation of cyanide complexes of transition metals in kcal/mol or cal/mol and degree.

Metal	Ionic medium	Temp.°C	$\Delta H°$	$\Delta G°$	$\Delta S°$	Ref.
Mn^{2+}	–	25.4	– 36.8	–	–	15
Fe^{2+}	a	25	– 85.77	– 48.22	– 125.9	16
Fe^{3+}	a	25	– 70.14	– 59.59	– 35.7	17
Co^{3+}	b	2	–	– 80.6	–	18

[a] Corrected to 0 ionic strength.
[b] Ionic medium varied.

COMPARISON WITH OTHER CYANIDES CONTAINING COMPLEX IONS OF THE SAME ELEMENTS

There are a few crystal structure determinations of hexacyanide complex ions containing Mn(II) and Fe(II) central atoms. As is evident from Tables 13 and 14 the bonding between the central atom and the ligand is in these cases stronger (the bond lengths are shorter and the stretching vibrations higher) than in the trivalent complex ions. The simple electrostatic rule that the bonding strength ought to increase as the charge increases is thus not obeyed. The structures of the complex ions $Mn(CN)_5NO^{3-}$ and $Fe(CN)_5NO^{2-}$ have been determined (Table 13). As is evident the central atom-ligand bond lengths in the manganese compound are about the same as in the $Mn(CN)_6^{3-}$ ion, $1.98-2.00$ Å, while for the iron compound the bond lengths correspond to those of the $Fe(CN)_6^{4-}$ ion, $1.90-1.92$ Å. It is tempting to conclude that the nitrosyl group should be regarded as a NO^+ ion in the iron compound, but as being more like NO^- in the manganese compound. This qualitative picture is somewhat supported by the NO distances in the two compounds, i.e. 1.12 Å in the iron compound $(N\equiv O^+)$, but 1.21 Å in the manganese compound $(N=O^-)$. In any case, the physical meaning of the oxidation number is obscure in compounds where the extent of double bonding is as large as in the penta-cyanonitrosyl compounds.

THE CHEMICAL BONDING IN THE HEXACYANO COMPLEXES

The electron distribution in hexacyanocobaltate(III) and hexacyano-ferrate(II) has been discussed, on the basis of ligand field calculations, by Alexander and Gray.[19] They found that the degree of π-bonding between the metal and cyanide groups was slight. The net charge on the central atom is small due to the extensive carbon to metal σ-bonding. This is in accordance with the present investigation. The metal to ligand bond lengths vary in much the same way as in the fluoride compounds, where no double bonding can be expected to take place. The cyanide bond lengths are the same or even shorter than in the corresponding pentacyanonitrosyl complexes in which $Me-C$ π-bonding is effectively prevented due to the strong $Me-N$ π-bonding, which also shows that back donation is slight. The same result is obtained from the IR data.

When the charge on the central atom decreases, the σ-bond strength also decreases, but, obviously, at the same time the π-bonding increases to such extent as to decrease the metal to ligand bond length. The calculations of Alexander and Gray show a larger degree of π-bonding in $Fe(CN)_6^{2-}$ than in $Co(CN)_6^{3-}$, which supports the arguments given above.

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