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The Crystal Structure of Potassium Hexacyanochromate(III), $K_3[Cr(CN)_6]$

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The crystal structure of potassium hexacyanochromate(III), $K_3[Cr(CN)_6]$, has been determined by single crystal X-ray methods. $K_3[Cr(CN)_6]$ crystallizes with an OD structure characterized by the OD groupoid symbol.

Pma(n)
$\{c_2\ n_{2,\frac{1}{2}}\ (n_{\frac{1}{2},1})\}$

The ordered orthorhombic form (MDO_1) has a unit cell with the dimensions $a = 8.5256(9)$ Å, $b = 10.6000(12)$ Å, and $c = 13.6840(13)$ Å, belonging to space group *Pcan*, with $Z = 4$. Its crystal structure has been solved from diffractometer data and refined by the method of least squares to a final R value of 0.046 based on 694 independent reflections. The complex ion has octahedral symmetry with Cr – C bond lengths of 2.057(12) Å, 2.075(7) Å, and 2.100(10) Å.

Much attention has been given in recent years to σ and π contributions to metal-ligand bonds in transition metal cyanocomplexes. Correlation of the bond lengths and geometries of the complex ions and information concerning the charges on the central metal atoms and ligands, obtained from crystal structure studies and X-ray photoelectron spectra, with existing semi-empirical molecular orbital calculations [1–4] ought to permit a determination of the relative variations of these contributions. In connection with such an investigation, in progress at this department, the crystal structures of several hexacyanides [5–8] and monosubstituted hexacyanides, *e.g.* pentacyanonitrosyls [9–11], have been studied. In the transition metal pentacyanonitrosyls, metal-cyanide π bonding is effectively prevented by the strong Me $\rightarrow \pi^*$ (NO) transfer, the strength of which varies in a predictable way with Me.[2–4, 12] π Bonding contributions to Me – CN bonds would, however, appear to be slight even in some hexacyanides, and, in order to examine their variation more closely, hexacyanides of the same transition metal atom with different formal oxidation numbers [5–8] have been studied as well as hexacyanides of different transition metals.

Since the majority of transition metal hexacyanides appear to crystallize with disordered crystal structures, it has not until fairly recently [13] been possible to determine their structures by appropriate methods. Previous crystallographic work has consisted mainly of determinations of unit cell dimensions and space groups (*cf.* Ref. 7). The crystal structures of $K_3[Me(CN)_6]$, where Me = Mn, Fe, and Co, have recently been determined.[7,8] To complete this series for the first row of transition metals, the crystal structures of $K_3[Cr(CN)_6]$ and $K_3[V(CN)_6]$ were of interest. The crystal structure of the former is presented in this paper. Attempts by Bennett and Nicholls [14] to prepare the latter compound yielded, however, $K_4[V(CN)_7].2H_2O$ whose crystal structure has now been determined.[15,16]

Attempts are now being made by the authors to prepare suitable single crystals of $K_4[Cr(CN)_6]$, in order to be able to compare Cr(III) with Cr(II) and $[Cr(CN)_6]^{4-}$ with other first row $[Me(CN)_6]^{4-}$.

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PREPARATION AND ANALYSIS

Potassium hexacyanochromate(III) was prepared according to the method described by Brauer.[17] Crystals suitable for single crystal X-ray work were obtained by precipitating $K_3[Cr(CN)_6]$ from aqueous solution with ethanol, instead of evaporating the solution, and then recrystallizing the crude product twice from aqueous solution.

The *chromium* content was determined gravimetrically as $PbCrO_4$ by oxidation of the compound to chromate with boiling conc. perchloric acid and subsequent precipitation with an aqueous solution of lead nitrate. The *potassium* content was determined by means of atomic absorption spectroscopy using a Perkin Elmer 403 spectrometer (Found: Cr 15.97; K 35.8. Calc. for $K_3[Cr(CN)_6]$: Cr 15.98; K 36.0).

The infra-red spectrum, registered with a Beckman IR 9 spectrophotometer, showed complete agreement with that given by Jones.[18]

OD STRUCTURE

Crystals of $K_3[Cr(CN)_6]$ were mounted along the needle-axis which will, in the following, be defined as the crystallographic a axis. Rotation photographs taken about this axis showed layer lines composed of discrete reflections for $A \approx 4.25$ Å and weak streaks corresponding to $a = 2A \approx 8.5$ Å. It was thus apparent that $K_3[Cr(CN)_6]$ crystallized with an OD structure,[13] *i.e.* a structure which can be described in terms of ordered layers whose mode of stacking is disordered. Weissenberg photographs of the weak layer lines showed that there were intensity maxima on the streaks, the majority of which had orthorhombic symmetry while the remainder had monoclinic symmetry. The orthorhombic intensity maxima corresponded to a unit cell with the approximate dimensions $a = 8.5$ Å, $b = 10.6$ Å and $c = 13.6$ Å, the monoclinic maxima requiring an apparent doubling of the c-axis, *i.e.* $c \approx 27.2$ Å.

If, as is usual in OD structures,[13] the c direction is assumed to be that of non-periodicity, the conditions limiting reflection for $K_3[Cr(CN)_6]$ may be summarized:

(i) discrete reflections, hkl, for $h = 2H$
diffuse streaks, $hk\zeta$, for $h = 2H + 1$, where ζ can take any value

(ii) Hkl: $H + l = 2n$

(iii) $hk0$: $h + k = 2n$

(iv) $h0\zeta$: $h = 2n$

$K_3[Cr(CN)_6]$ thus crystallizes as a family of structures characterized by the same OD groupoid as that which characterizes the structures of $K_3[Mn(CN)_6]$,[7] $K_3[Fe(CN)_6]$, and $K_3[Co(CN)]_6$.[8]

As described in detail in Ref. 7, reflection conditions (i) and (ii) indicate that the superposition structure, corresponding to the family reflections, Hkl, has an a axis of one-half 8.5 Å and is B face-centred with $Bmmb$ and $B2_1mb$ as possible space groups [*cf.* also reflection condition (iii)]. According to reflection conditions (iii) and (iv), the minimum layer symmetry is $P2a(n)$, but for the same reasons as given in Ref. 7, *i.e.* the high symmetry of the building units, the layer symmetry has here been assumed to be $Pma(n)$.

The B face-centring of the superposition structure requires that one layer be related to the next by the translation $-\vec{a}/4 + \vec{c}_0$ or $+\vec{a}/4 + \vec{c}_0$, where $\vec{c}_0$ is the unit vector perpendicular to the layers in the direction of non-periodicity[13] and $c_0 \approx 6.8$ Å. This means that the symmetry elements converting one layer, L_0, into the next, L_1, can be expressed as ${}_{0,1}[c_2\, n_{2,\frac{1}{2}}\, (n_{\frac{1}{2},1})]$ or ${}_{0,1}[c_2\, n_{2,\bar{\frac{1}{2}}}\, (n_{\bar{\frac{1}{2}},1})]$, respectively. These symmetry elements are illustrated by means of asymmetric triangles in Fig. 1.

$K_3[Cr(CN)_6]$ may thus be said to crystallize as a family of structures characterized by the OD groupoid

$$\begin{matrix} Pma(n) \\ \{c_2\, n_{2,\frac{1}{2}}\, (n_{\frac{1}{2},1})\} \end{matrix}$$

the symbol giving the total symmetry of any pair of consecutive layers, L_p and L_{p+1}.

Successive layers may thus, alternatively, be regarded as being related to one another by the translation $\alpha\vec{a}/4$ where α can take the value $+1$ or -1. As described in Ref. 7, there are two ordered extreme structures, or "structures of maximum degree of order" (MDO),[13] one orthorhombic, MDO_1, obtained by a zig-zag stacking of layers, *i.e.* α = alternately -1 and, $+1$ (*cf.* Fig. 1), and the other monoclinic, MDO_2 obtained by an oblique stacking of layers ($\alpha = +1$ or -1, only). The unit cell of the MDO_1 structure has the approximate dimensions $a = 8.5$ Å, $b = 10.6$ Å, and $c = 2c_0 = 13.6$ Å, the space group being $Pcan$, while the unit cell of the MDO_2 structure[7,8] is defined by $\vec{a}_{mon} = \vec{a}$, $\vec{b}_{mon} = \vec{b}$, $\vec{c}_{mon} = \vec{a}/4 + \vec{c}_0$ with $\beta \approx 107°$, the

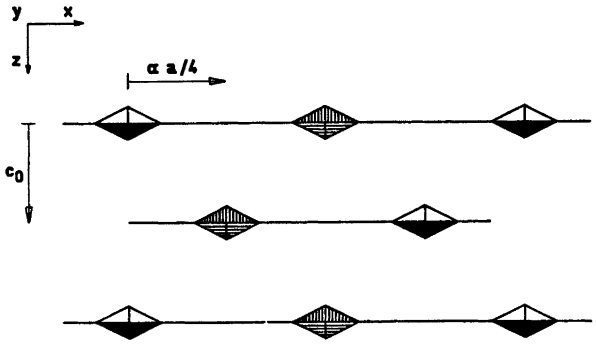

Fig. 1. Schematic representation of the ordered orthorhombic structure of $K_3[Cr(CN)_6]$, space group *Pcan*. $\vec{c}_0$ is the unit vector perpendicular to the layers in the non-periodic direction, while α is a factor which can take the value $+1$ or -1. *Notation:* empty triangles: y, filled triangles: $-y$, vertically shaded triangles: $\frac{1}{2}-y$, and horizontally shaded triangles: $\frac{1}{2}+y$.

space group being $P2_1/a$. In principle, each crystal of $K_3[Cr(CN)_6]$ can exhibit a different stacking sequence and thus be described in terms of larger or smaller contributions from the different MDO structures.

The fictitious superposition structure, $\hat{\varrho}(x,y,z)$, which is the same for all members of the OD groupoid family, is related to the real structure, $\varrho(x,y,z)$ by

$$\hat{\varrho}(x,y,z)=\tfrac{1}{2}[\varrho(x,y,z)+\varrho(x+\tfrac{1}{2},y,z)].$$

It has the approximate cell dimensions $a=4.25$ Å, $b=10.6$ Å, and $c=13.6$ Å and belongs to space group *Bmmb*.

Unlike the crystals of $K_3[Mn(CN)_6]$,[7] $K_3[Fe(CN)_6]$, and $K_3[Co(CN)_6]$,[8] the crystals of $K_3[Cr(CN)_6]$ studied showed a predominance of more or less discrete non-family reflections with orthorhombic symmetry, the streaks joining them being exceedingly weak. This indicates the presence of large regions of MDO_1 type structure.[13] The intensity maxima with mono-

Table 1. X-Ray powder diffraction data for $K_3[Cr(CN)_6]$. Guinier camera, Cu$K\alpha_1$ radiation ($\lambda=1.54050$ Å).

$h\ k\ l$	$10^5 \sin^2\theta_{obs}$	$10^5 \sin^2\theta_{calc}$	I_{calc} (relative scale)	I_{obs}
0 0 2	1261	1267	35	vvw
0 2 2	3380	3379	1450	vvs
0 0 4	5078	5069	68	w
2 2 1	5689	5694	100	w
0 3 2	6022	6020	435	s
2 2 3	8233	8228	445	s
2 3 1	8338	8334	75	w
0 4 0	8444	8448	27	vw
0 4 2	9715	9716	10	vvw
2 3 3	10870	10869	45	w
2 4 1	12033	12030	175	m
4 0 0	13059	13060	53	w
4 2 2	16443	16439	91	w
4 0 4	18125	18129	12	vvw
2 4 5	19629	19634	24	vw
0 0 8	20277	20278	50	w
2 2 7	20904	20902	30	vw
4 6 2	33338	33336	24	vw

clinic symmetry were so few in number that it was not considered profitable to attempt to determine the MDO_2 structure.

ACCURATE UNIT CELL DIMENSIONS

Powder photographs of $K_3[Cr(CN)_6]$ were taken in a Guinier focusing camera with $CuK\alpha_1$ radiation, using lead nitrate as an internal standard ($a = 7.8564$ Å).[19] $\sin^2\theta_{obs}$ values were obtained from the measured s values by means of the program PEPP [20] and eighteen family reflections were indexed and used to refine the cell dimensions of the MDO_1 structure with the program POWDER.[20] The following values were obtained (standard deviations, $\times 10^4$, in parentheses): $a = 8.5256(9)$ Å, $b = 10.6000(12)$ Å, and $c = 13.6840(13)$ Å. Observed and calculated $\sin^2\theta$ values are listed in Table 1. The calculated density corresponding to a cell content of four formula units is 1.75 g cm^{-3}. The experimental density, as determined by the method of flotation using bromoform and carbon tetrachloride is 1.74 g cm^{-3}.

DETERMINATION OF THE MDO_1 STRUCTURE

A crystal of $K_3[Cr(CN)_6]$ with the approximate dimensions $0.05 \times 0.02 \times 0.01$ cm was mounted along the a axis and the intensities of the family reflections (hkl, $h = 2H$) and the streaks, $hk\zeta$, at the reciprocal lattice points corresponding to the unit cell of the MDO_1 structure, were measured with an Arndt-Phillips linear diffractometer at the Department of Inorganic Chemistry, University of Aarhus. $MoK\alpha$ radiation selected by a graphite monochromator was employed, data being collected for the layers $0kl - 10kl$. Symmetry related reflections were averaged and correction was made for Lorentz and polarisation effects, assuming the graphite monochromator to behave as an ideal mosaic crystal, using the program G4.[21] A total of 694 independent reflections for which $F_o^2 > 2.5\ \sigma(F_o^2)$, according to counting statistics, were regarded as being observed and were used in the subsequent calculations. No correction was made for absorption (linear absorption coefficient for $K_3[Cr(CN)_6]$ in $MoK\alpha$ radiation = 19.3 cm^{-1}).

A Patterson function and subsequent electron density calculations based on the family reflections only, using the program FORDAP,[21] confirmed that the superposition structure of $K_3[Cr(CN)_6]$ was isomorphous with those of $K_3[Mn(CN)_6]$,[7] $K_3[Fe(CN)_6]$,[8] and $K_3[Co(CN)_6]$.[8] No attempt was made to refine the atomic and thermal parameters of this structure.

A Patterson function based on the non-family reflections (hkl, $h = 2H + 1$) only, was then calculated. Since such a calculation [13] yields vectors between atoms within a single layer, it was possible to obtain the positions of the potassium atoms relative to chromium and thus eliminate the other potential relative positions afforded by the superposition structure. The chromium atom, which is situated at the origin of the superposition structure, was assigned the position *Pcan*,* 4*c*, with $x = 1/8$, $y = 0$, and $z = 1/4$, and the two potassium atoms were assigned a fourfold and an eight-fold position in accordance with the vectors obtained from the Patterson synthesis. An electron density calculation using the signs obtained with the chromium and potassium atoms in these positions revealed the positions of all the ligand atoms.

Atomic and anisotropic thermal parameters were then refined using the full matrix least squares program LINUS [21] and assigning the reflections unit weights. The atomic scattering factors due to Cromer and Mann [22] were used for all atoms. As is necessary in OD structures, the family and non-family reflections were assigned separate scale factors. No layer scale factors were, however, refined. An isotropic extinction coefficient was refined assuming unit path length for all reflections, a final g value of $4.1(5) \times 10^{-7}$ being obtained. During the refinement, x_{Cr} was held fixed at 0.125 in order to obtain convergence. If this parameter was refined extremely large shifts were obtained for x_{Cr} and x_{K1} and the standard deviations for all parameters were considerably larger than when x_{Cr} was fixed. This is probably because the origin is not properly defined for the family reflections unless either x_{Cr} or x_{K1} is fixed. As expected, there were large correlations between many of the x parameters.

A final R value of 0.046 was obtained ($R = 0.037$ for the 372 family reflections and $R = 0.074$

* Equipoints of general position of *Pcan* (conventional setting,[19] No. 60, *Pbcn*): $\pm(x,y,z;\ \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}-x, \frac{1}{2}+y, \bar{z};\ x, \bar{y}, \frac{1}{2}-z)$.

Table 2. Atomic coordinates, expressed as fractions of the cell edges, and mean square vibration amplitudes, U_{ij}, (Å²) for $K_3[Cr(CN)_6]$. The estimated standard deviations of the parameters ($\times 10^4$) are given in parentheses.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	4*c*	0.1250	0.0000	0.2500	0.0168(7)	0.0256(8)	0.0235(8)	0.0000	0.0000	0.0012(7)
K(1)	4*c*	0.6297(4)	0.0000	0.2500	0.0232(12)	0.0372(13)	0.0408(15)	0.0000	0.0000	0.0070(12)
K(2)	8*d*	0.6263(30)	0.2329(3)	0.5021(1)	0.0249(7)	0.0722(16)	0.0358(8)	0.0074(55)	0.0008(32)	−0.0100(10)
N(1)	8*d*	0.1254(28)	0.2730(7)	0.1474(4)	0.0458(37)	0.0368(43)	0.0391(33)	0.0064(81)	−0.0056(89)	0.0057(30)
N(2)	8*d*	0.3991(18)	0.0857(9)	0.3980(7)	0.0227(95)	0.0629(52)	0.0469(46)	−0.0114(46)	−0.0110(53)	−0.0081(41)
N(3)	8*d*	0.3623(32)	0.4108(9)	0.4019(6)	0.0450(74)	0.0687(54)	0.0387(42)	0.0096(66)	0.0011(82)	0.0080(41)
C(1)	8*d*	0.1248(17)	0.1771(6)	0.1853(5)	0.0309(34)	0.0354(37)	0.0260(32)	0.0069(62)	−0.0037(56)	−0.0004(29)
C(2)	8*d*	0.2971(12)	0.0565(10)	0.3458(8)	0.0312(58)	0.0397(53)	0.0296(58)	0.0033(40)	0.0020(44)	0.0002(46)
C(3)	8*d*	0.4519(10)	0.4431(9)	0.3499(7)	0.0192(47)	0.0309(45)	0.0357(62)	0.0046(35)	0.0020(41)	0.0057(43)

Table 3. Observed and calculated structure factors ($\times 10$) for the MDO_1 structure of $K_3[Cr(CN)_6]$.

K	L	FOBS	FCALC
*	H=	0	*
0	4	940	969
0	6	176	156
0	8	1597	1657
0	10	195	-164
0	12	1018	1059
0	14	124	-100
0	16	346	366
1	4	551	530
1	6	270	-268
1	8	342	-351
2	2	2382	-2403
2	4	73	-53
2	6	2023	-2057
2	8	286	293
2	10	1047	-1082
2	12	197	193
2	14	585	-628
3	2	1680	1627
3	4	82	-105
3	6	493	-494
3	8	120	111
3	14	175	210
4	0	1932	1960
4	2	511	-504
4	4	1705	1732
4	8	1167	1200
4	10	434	-445
4	12	685	705
4	16	345	399
5	2	442	449
5	4	166	-174
5	14	134	76
5	16	291	-33
6	0	83	-94
6	2	1408	-1416
6	4	810	826
6	6	914	-924
6	8	106	74
6	10	617	-643
6	12	122	120
6	14	440	-482
6	16	173	250
7	4	90	-185
7	8	105	107
7	12	242	-245
8	0	529	536
8	2	315	-305
8	4	882	911
8	6	452	-463
8	8	628	648
8	10	198	-203
8	12	384	319
8	14	165	-145
9	2	111	-113
9	4	106	-103
9	6	124	143
10	0	275	280
10	2	456	-461
10	4	361	379
10	6	547	-575
10	8	234	237
10	10	188	-198
10	12	180	159
11	2	92	-81
12	0	336	366
12	2	264	-267
12	4	313	310
12	6	257	-286
12	8	161	224
13	2	96	-59
14	0	191	211
14	2	185	-196
*	H=	1	*
1	2	402	-405
1	3	103	107
1	7	96	-36
1	9	157	-154
1	10	203	-196
1	11	127	133
1	12	107	95
1	13	104	-102
1	17	114	-62
1	18	103	-93
2	1	179	-181
2	3	202	-192
2	4	64	73
2	5	289	-195
2	6	122	-101
2	7	105	66
2	8	139	126
2	9	131	-123
2	11	151	-162
2	12	92	-83
3	0	388	378
3	1	115	-108
3	2	180	165
3	4	201	222
3	6	67	35
3	7	210	229
3	8	378	389
3	9	212	-196
3	10	121	-130
3	11	161	194
3	12	171	160
4	1	310	313
4	2	101	93
4	4	202	-198
4	5	342	350
4	7	164	170
4	9	94	38
4	10	113	-118
4	11	165	161
5	0	164	-143
5	1	135	-128
5	2	408	-413
5	3	141	130
5	5	226	-230
5	6	333	-338
5	8	110	-108
5	10	137	-123
5	13	142	-157
5	14	194	-197
6	1	113	-124
6	2	172	162
6	3	353	-354
6	5	233	-237
6	6	89	-82
6	8	150	163
6	9	170	-188
6	11	140	-143
7	0	391	385
7	1	137	-127
7	2	101	91
7	3	122	94
7	4	251	255
7	6	85	69
7	7	128	120
7	8	236	240
7	12	140	149
8	1	134	129
8	2	89	-84
8	3	243	255
8	5	107	109
8	9	126	122
8	11	132	112
9	0	225	-242
9	2	137	-150
9	3	111	89
9	4	85	51
9	5	218	-216
9	6	270	-318
9	10	111	-87
10	2	98	87
10	3	177	-185
10	9	124	-114
11	0	215	199
11	1	105	-109
11	4	142	138
12	3	129	145
*	H=	2	*
0	3	2162	2137
0	5	897	-914
0	7	428	443
0	9	713	-728
0	11	676	674
0	13	257	-248
0	15	473	444
0	17	348	-327
1	3	1959	1916
1	5	1042	1029
1	7	573	553
1	9	597	598
1	11	351	334
1	13	334	314
1	15	291	264
1	17	223	210
2	1	444	-440
2	3	1616	1595
2	5	1601	-1583
2	7	828	827
2	9	685	-681
2	11	408	393
2	13	439	-418
2	15	344	327
2	17	324	-285
3	1	1443	-1388
3	3	779	-752
3	5	279	-260
3	7	468	-474
3	9	626	-617
3	11	510	-513
3	13	282	-258
3	15	146	-105
4	1	1418	-1373
4	3	674	684
4	5	719	-715
4	7	948	941
4	9	619	-603
4	11	496	481
4	13	383	-363
4	15	269	265
5	1	287	276
5	3	782	773
5	5	697	691
5	7	183	167
5	9	361	364
5	11	329	319
5	13	136	77
5	15	187	165
6	1	1110	-1107
6	3	587	578
6	5	676	-659
6	7	673	651
6	9	318	-318
6	11	335	326
6	13	437	-443
6	15	291	281
7	1	225	-228
7	3	245	-233
7	5	468	-462
7	7	227	-230
7	11	196	-206
7	15	164	-145
8	1	672	-673
8	3	441	431
8	5	455	-434
8	7	496	497
8	9	510	-498
8	11	377	374
8	13	266	-243
9	1	227	245
9	9	124	148
9	11	179	144
10	1	428	-437
10	3	464	468
10	5	297	-305
10	7	272	267
10	9	273	-309
10	11	318	321
11	3	126	-119
12	1	311	-311
12	3	318	324
12	5	228	-249
12	7	174	166
12	9	254	-232
14	1	153	-169
14	5	289	-185
*	H=	3	*
1	2	58	57
1	3	151	167
1	4	191	-192
1	5	381	-398
1	6	387	396
1	7	222	237
1	10	116	-93
*	H=	3	*
1	13	145	-139
1	14	170	179
1	15	170	168
1	17	113	-102
2	1	211	-218
2	2	117	118
2	3	98	83
2	4	303	-294
2	5	328	-322
2	7	149	-155
2	8	133	127
3	1	74	68
3	2	210	-197
3	3	128	139
3	4	306	-314
3	5	217	-228
3	6	74	84
3	7	269	273
3	8	261	-271
3	9	128	-118
3	11	134	120
3	12	113	-104
3	15	105	72
4	1	143	144
4	2	184	179
4	3	376	383
4	4	100	-95
4	5	196	188
4	6	149	-122
4	7	103	-73
4	8	250	256
4	9	237	238
4	10	99	92
4	11	248	235
4	12	168	-156
4	13	107	-94
4	14	101	112
5	0	163	168
5	1	142	-143
5	2	363	367
5	3	216	215
5	5	175	-173
5	6	166	165
5	8	132	135
5	9	91	-84
5	10	171	163
5	11	91	58
5	13	122	-125
5	14	130	140
6	1	271	-277
6	2	102	93
6	3	105	-96
6	4	92	-109
6	5	215	-220
6	7	204	-199
6	9	99	-98
6	10	105	-63
6	13	134	-108
7	0	411	-431
7	1	250	-255
7	3	121	114
7	4	108	-112
7	6	223	-221
7	8	210	-217
7	9	151	-143
7	11	204	206
7	12	166	-157
8	2	170	173
8	3	297	305
8	5	146	137
8	7	86	65
8	9	129	124
9	1	88	-93
9	2	175	175
9	4	95	90
9	6	129	153
9	9	140	-150
9	10	170	171
10	3	220	-217
10	8	115	-102
10	9	146	-147
11	0	274	-280
11	1	187	-188
11	6	105	-103
11	8	145	-100
*	H=	4	*
0	4	1279	-1323
0	6	261	264
0	8	1161	-1175
0	12	792	-787
0	14	169	179
0	16	437	-434
1	2	203	206
1	4	381	-375
1	6	100	95
1	8	317	328
2	2	1594	1532
2	4	305	-315
2	6	1698	1718
2	8	179	-178
2	10	713	722
2	14	689	604
3	2	477	-469
3	4	171	-154
3	6	143	138
3	8	136	137
3	12	132	-116
4	0	1296	-1349
4	2	344	341
4	4	1316	-1323
4	6	112	81
4	8	954	-953
4	10	316	308
4	12	608	-587
4	16	370	-361
5	4	102	-66
5	6	116	-124
5	8	219	208
5	12	145	-118
6	0	186	-185
6	2	1162	1132
6	4	482	-489
6	6	658	646
6	8	141	-99
6	10	638	621
6	12	148	-145
6	14	384	387
6	16	181	-169
7	2	172	160
7	12	152	126
8	0	673	-675
8	2	331	322
8	4	586	-582
8	6	230	234
8	8	598	-580
8	10	318	303
8	12	333	-333
9	2	95	70
9	4	107	85
10	0	370	-399
10	2	448	443
10	4	228	-218
10	6	389	374
10	8	247	-231
10	10	298	278
10	12	198	-177
12	0	361	-370
12	2	272	258
12	4	239	-229
12	6	197	207
12	8	230	-218
*	H=	5	*
1	2	349	323
1	3	173	-171
1	4	105	-102
1	7	84	80
1	9	143	149
1	10	233	224
1	11	127	-125
1	12	104	-102
2	1	163	153
2	3	96	91
2	7	78	-63
2	8	151	-153
2	9	123	120
2	11	161	151
2	12	93	97
3	0	314	-313
3	1	72	79
3	2	56	-43
3	4	182	-198
3	7	156	-152
3	8	284	-290
3	9	139	143
3	10	184	100
3	11	149	-128
3	12	149	-161
4	1	145	-130
4	4	172	178
4	5	260	-262
4	7	160	-157
4	8	80	-72
5	1	115	111
5	2	294	296
5	5	118	138
5	6	284	314
5	7	86	-60
5	11	93	58
5	13	126	135
5	14	190	185
6	2	95	-120
6	3	236	240
6	5	178	174
6	8	114	-117
6	9	121	128
6	11	117	136
7	0	321	-307
7	1	96	68
7	4	206	-218
7	5	81	47
7	7	86	-131
7	8	195	-204
7	12	121	-130
8	1	129	-125
8	3	153	-158
8	6	86	50
8	9	105	-116
9	0	181	186
9	1	95	-75
9	2	122	133
9	5	164	182
9	6	262	266
9	10	105	94
10	3	142	127
11	0	158	-151
11	4	132	-135
12	2	97	74
*	H=	6	*
0	3	859	-877
0	5	220	222
0	7	288	-278
0	9	640	610
0	11	602	-608
0	13	196	198
0	15	236	-221
1	3	731	-730
1	5	540	-534
1	7	471	-456
1	9	361	-349
1	11	212	-206
1	13	292	-282
1	15	206	-178
2	1	658	667
2	3	721	-721
2	5	613	610
2	7	468	-467
2	9	611	595
2	11	415	-405
2	13	305	291
2	15	158	-155
3	1	462	457
3	3	734	726
3	5	268	236
3	7	112	115
3	9	504	494
3	11	424	405
4	1	782	772
4	3	478	-471
4	5	458	443
4	7	568	-574
4	9	440	436
4	11	392	-373
4	13	274	258
4	15	180	-187
5	1	403	-393
*	H=	6	*
5	3	139	-156
5	5	416	-414
5	7	351	-337
5	9	167	-134
5	11	150	-155
5	13	192	-180
5	15	124	-97
6	1	547	544
6	3	469	-461
6	5	573	565
6	7	468	-460
6	9	167	176
6	11	196	-189
6	13	323	322
7	1	85	87
7	3	291	274
7	5	283	286
7	9	104	101
7	11	192	196
8	1	291	281
8	3	370	-374
8	5	506	498
8	7	408	-413
8	9	282	266
8	11	192	-179
9	1	136	-147
9	11	132	-97
10	1	212	207
10	3	380	-371
10	5	350	356
10	7	251	-253
10	9	160	157
11	7	109	99
12	1	196	284
12	3	253	-254
12	5	210	233
*	H=	7	*
1	4	55	-74
1	5	61	70
1	6	85	-105
1	7	127	-128
2	2	87	103
2	3	94	108
2	4	84	98
2	5	178	197
2	6	106	-87
3	0	124	119
3	1	88	85
3	2	62	61
3	3	91	-96
3	4	101	100
3	5	85	76
3	7	163	-146
3	8	161	153
3	9	135	135
3	11	140	-136
4	1	212	-217
4	2	112	99
4	3	67	-43
4	5	92	-102
4	7	85	-69
4	9	189	-94
4	10	102	-74
5	0	157	-131
5	1	72	73
5	2	199	-192
5	3	169	-173
5	5	148	132
5	6	88	-78
5	8	119	-106
5	9	106	83
5	10	116	-108
6	1	96	117
6	3	154	172
6	4	75	15
6	5	139	125
6	9	137	128
7	0	127	120
7	1	83	77
7	3	136	-128
7	4	159	147
7	8	188	116
8	2	82	-85
8	3	153	-163
8	5	116	-108
8	7	107	-99
9	0	117	-114
9	5	148	136
9	6	147	-147
9	7	116	-101
10	3	113	119
*	H=	8	*
0	4	765	846
0	6	169	-163
0	8	611	628
0	12	478	483
1	2	110	-124
1	4	133	142
1	8	129	-155
2	2	765	-786
2	4	198	215
2	6	894	-917
2	8	96	93
2	10	449	-451
3	2	82	54
3	4	68	84
3	8	106	-90
4	0	792	734
4	2	172	-174
4	4	711	711
4	6	108	-87
4	8	573	578
4	10	145	-167
4	12	367	379
5	2	97	-89
5	6	108	188
5	8	116	-132
6	0	229	219
6	2	670	-649
6	4	213	201
6	6	410	-391
6	10	412	-406
7	2	118	-94
8	0	516	472
8	2	207	-218
8	4	343	325
8	6	142	-134
8	8	391	385
10	0	299	276
10	2	311	-298
10	4	156	131
*	H=	9	*
1	2	105	-127
1	4	169	180
1	5	135	-120
1	6	151	-135
2	1	74	-140
2	2	130	-130
3	0	78	109
3	4	171	181
3	7	92	91
3	8	160	171
4	2	117	-118
4	3	152	150
4	5	159	151
4	6	89	72
4	8	96	-65
5	0	87	58
5	1	109	-92
5	2	193	-189
5	6	173	-181
6	1	113	-109
6	5	115	-98
6	7	113	-72
7	0	262	288
7	1	121	-107
7	4	95	98
8	3	183	182
9	2	124	-133
*	H=	10	*
0	3	336	410
0	5	257	-261
0	7	254	256
0	9	233	-245
1	3	332	357
1	5	223	236
1	7	216	215
1	9	215	222
2	3	336	354
2	5	373	-389
2	7	299	304
2	9	280	-276
3	1	224	-258
3	3	247	-264
3	5	179	-181
3	7	163	-163
3	9	172	-176
4	1	337	-343
4	3	269	288
4	5	260	-282
4	7	298	302
4	9	246	-229
5	1	152	163
5	3	172	171
5	5	191	190
5	7	108	182
6	1	313	-313
6	3	275	275
6	5	260	-269
6	7	234	216
7	1	134	-103
7	3	99	-75
7	5	157	-141
8	1	228	-219

for the 322 non-family reflections. The corresponding R_w values were 0.049, 0.044, and 0.093, respectively. The final ratio between the scale factors for the non-family and family reflections was 1.04, which is in accordance with the observation that the structure of the crystal studied closely approximated the MDO_1 structure. An $F_o - F_c$ Fourier synthesis, calculated with the program JIMDAP,[21] showed a maximum electron density of 0.5 e/Å^3.

Atomic and thermal parameters are listed in Table 2 and observed and calculated structure factors in Table 3. Distances and angles within the $[Cr(CN)_6]^{3-}$ complex ion, as calculated by the program ORRFE,[21] are given in Table 4.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A projection of a unit cell of $K_3[Cr(CN)_6]$ along [010], drawn by the program ORTEP,[21] is shown in Fig. 2. By comparing Fig. 2 with Fig. 1 it is seen that a layer of the OD structure is composed of the two $[Cr(CN)_6]^{3-}$ complex

Table 4. Bond distances (Å) and angles (°) within the $[Cr(CN)_6]^{3-}$ complex ion. Standard deviations of the distances ($\times 10^3$) and the angles are given in parentheses.

Distances			
Cr – C(1)	2.075(7)	C(1) – N(1)	1.141(9)
Cr – C(2)	2.057(12)	C(2) – N(2)	1.167(17)
Cr – C(3)	2.100(10)	C(3) – N(3)	1.099(22)
Angles			
Cr – C(1) – N(1)	178.2(0.6)	C(1) – Cr – C(3)	91.0(0.4)
Cr – C(2) – N(2)	177.3(1.0)	C(1) – Cr – C(3)	90.0(0.4)
Cr – C(3) – N(3)	178.5(1.0)	C(2) – Cr – C(2)	88.9(0.5)
C(1) – Cr – C(1)	179.9(0.8)	C(2) – Cr – C(3)	90.2(0.2)
C(1) – Cr – C(2)	90.5(0.4)	C(2) – Cr – C(3)	179.0(0.5)
C(1) – Cr – C(2)	89.5(0.4)	C(3) – Cr – C(3)	90.7(0.5)

ions in the upper half ($0 < z < 0.5$) of the unit cell, together with the four K(2) ions directly above and below the K(1) and Cr atoms in the c direction. The second layer, which is identical with the first, is obtained from the latter by a translation of $-\vec{a}/4+\vec{c}_0$, while the third layer is obtained from the second by the translation $\vec{a}/4+\vec{c}_0$.

As is apparent from Table 4, the $[Cr(CN)_6]^{3-}$ ions are not significantly distorted from octahedral symmetry. Although there is no significant difference between them, the three Cr – C bonds show a spread in length [2.057(12) Å, 2.075(7) Å, and 2.100(10) Å] similar to that found for $K_3[(Mn(CN)_6]$, $K_3[Fe(CN)_6]$, and $K_3[Co(CN)_6]$.[7,8] The mean Cr – C bond length, 2.077(5) Å, is in agreement with mean Cr – C bond lengths found in $Cd_3[Cr(CN)_6]_2.xH_2O$ [2.047(19) Å],[23] $Mn_3[Cr(CN)_6]_2.6H_2O$ [2.063(11) Å],[24] and $[Co(C_2H_8N_2)_3][Cr(CN)_5NO].2H_2O$ [Cr – C_{eq} 2.033(7) Å and Cr – C_{ax} 2.075(14) Å].[25] A mean Cr – C bond length of 1.99(3) Å was found in $[K_3Cr(CN)_5NO]$.[10] This value represents, however, the mean including Cr – N(O), since $K_3[Cr(CN)_5NO]$ crystallizes with an OD structure and it was possible, at that time, only to solve the superposition structure. The cyanide bond lengths, which range from 1.099 – 1.167 Å with a mean value of 1.136(7) Å, are also in agreement with C – N distances found in other transition metal cyanocomplexes.[5–11,16,23–25]

Accompanying the increase in effective nuclear charge on the central metal atom from chromium(III) to cobalt(III), there is a decrease in Me – C bond length and an increase in the Me – C≡N bending and Me – C stretching frequencies, whereas the C≡N stretching frequencies and bond lengths are fairly constant (*cf.* Table 5). This would appear to indicate

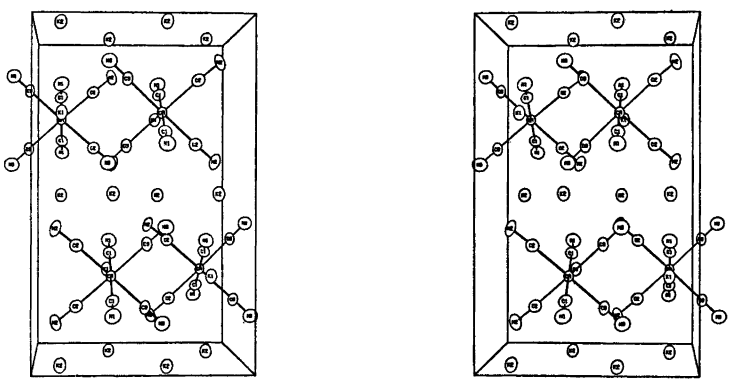

Fig. 2. Stereoscopic projection of the unit cell of $K_3[Cr(CN)_6]$ along [010]. The a axis is horizontal.

Table 5. Infra-red data [18] and bond distances (Å) for some Me(III) hexacyanides.

Compound	Mean Me – C (Å)	ν_7 cm^{-1} (Me – C≡N bend)	ν_8 cm^{-1} (Me – C stretch	Mean C≡N (Å)	ν_6 cm^{-1} (C≡N stretch
$K_3[Cr(CN)_6]$	2.08[a]	458	339	1.14[a]	2128
$K_3[Mn(CN)_6]$	2.00[7]	483	361	1.14[7]	2112
$K_3[Fe(CN)_6]$	1.95[8]	506	389	1.14[8]	2118
$K_3[Co(CN)_6]$	1.89[8]	564	416	1.15[8]	2129

[a] Present work.

that the π-bonding contribution to the Me – C bond is very slight, which is in accordance with molecular orbital calculations[1] on $[Co(CN)_6]^{3-}$. Moreover, there is no significant difference between the C≡N distances in the Me(III) hexaxyanides and those found in the corresponding pentacyanonitrosyls, in which Me – C π-bonding is regarded as being negligible.[2-4,12]

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