

The Crystal Structure of $K_3Cr(CN)_5NO$

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The crystal structure of $K_3Cr(CN)_5NO$ has been studied by three-dimensional X-ray methods. The space group is $Pcn2$ and the elementary cell dimensions $a = 13.38 \text{ \AA}$, $b = 10.37 \text{ \AA}$ and $c = 8.38 \text{ \AA}$. One of the three potassium ions in the formula unit and the complex ion form endless "chains" extending along the x -axis. The stacking of these chains is disordered. The remaining potassium ions connect the chains forming a three-dimensional structure.

Chromium, manganese, and cobalt all form pentacyanonitrosyl complexes with ionic charge -3 , *i.e.* $[Me(CN)_5NO]^{3-}$. There has been considerable controversy regarding the structures of these ions. Naiman¹ regards the complex ion $[Cr(CN)_5NO]^{3-}$ as being nearly octahedral while Ballhausen and Gray² postulate that the π -bonding in this complex should give a large tetragonal distortion. The visible absorption spectrum recorded both by the author and by Bernal and Harrison³ supports the latter theory. The spectrum is almost identical with the $[Cr(H_2O)_5NO]^{2+}$ spectrum but very different from that of $Cr(CN)_6^{3-}$. Moreover the pentacyanonitrosylferrate (II)-ion, the "nitroprusside" ion, has a large tetragonal distortion.⁴ It therefore seemed appropriate to determine the crystal structures of some salts containing the different complex ions in order to try to solve the problem.

$K_3Cr(CN)_5NO \cdot H_2O$ and $K_3Cr(CN)_5NO$ have been prepared by Griffith, Lewis and Wilkinson,⁵ who have also studied the infrared spectra and measured the magnetic susceptibilities of the compounds, and found them to be paramagnetic with susceptibilities indicating the presence of one unpaired electron.

EXPERIMENTAL

Potassium pentacyanonitrosylchromate was prepared according to a modified method of that due to Griffith *et al.*⁵ Potassium hexacyanidochromate reacts with hydroxylamine according to the equation:

$$Cr(CN)_6^{3-} + 2NH_2OH = Cr(CN)_5NO^{3-} + NH_3 + HCN + H_2O.$$

The potassium hexacyanidochromate was prepared from chromium trioxide, potassium hydroxide, and potassium cyanide. The product was purified by repeated recrystalliza-

tion and suitable crystals were picked out from the mother liquor as soon as they had reached an appropriate size.

Analysis. Chromium was determined gravimetrically as barium chromate. Cyanide was determined as silver cyanide. A small sample of the substance was dissolved in water and dilute sulfuric acid was added. The hydrogen cyanide gas evolved was driven over in a stream of nitrogen to an absorption column, where it was absorbed in slightly acid silver nitrate solution. The total nitrogen in the complex was determined by a micro-Kjeldahl method, the nitrogen being reduced by Devarda's alloy in alkaline solution to form ammonia, which was then driven off and estimated by titration with acid. (Found: Cr 15.8; CN⁻ 38.9; N 26.0. Calc for K₃Cr(CN)₅NO: Cr 15.9; CN⁻ 39.5; N 25.5).

STRUCTURE DETERMINATION

Single crystals of K₃Cr(CN)₅NO were rotated about the [001] and [302] directions. In the rotation photographs taken when the crystal was rotated about the [001] direction it was observed that each second layer line consisted of very weak continuous streaks, thus indicating the presence of disorder in the structure. CuK α radiation was used. No allowances were made for anomalous dispersion. The elementary cell dimensions were found to be

$$a = 13.38 \pm 0.02 \text{ \AA}, b = 10.37 \pm 0.01 \text{ \AA}, \text{ and } c = 8.38 \pm 0.01 \text{ \AA}.$$

Consideration of the systematic absences led to a choice of *Pnc2*, No. 30, or *Pncm*, No. 53, as space groups, but if the continuous layer lines were disregarded, spacegroup No. 65, *Cmcm*, was found to be applicable. The density was determined to be 1.92 g.cm⁻³, which corresponded to four formula units in the larger unit cells and two in the smaller unit cell.

As a first approximation the space group was assumed to have the symmetry *Cmcm*. From a three-dimensional Patterson synthesis it was then possible to locate four of the six potassium atoms. It was, however, evident, that two chromium atoms and two potassium atoms must be placed in the same crystallographic positions. With the aid of the heavy atom positions the signs of the structure factors could be determined, and the positions of the light atoms were then obtained from a three-dimensional Fourier synthesis performed with these signs. The positions of the light atoms were refined several times by difference synthesis, and an *R*-value of 0.24 was finally obtained.

A least squares refinement was then performed. Owing to the high degree of disorder in the structure, and since the space group *Cmcm* was employed, there is considerable overlap between certain atoms, and the refinement had, consequently, to be carried out in very small steps. Although it was evident that most of the atoms could be refined when placed in positions belonging to the subcell *Cmcm*, four of the six potassium ions could not and had thus to be placed statistically in an eightfold position. After about eight cycles of refinement, the *R*-factor dropped to 0.158 (Table 1). The standard deviations of the parameters of those atoms overlapping one another are large in the direction of overlap.

Table 1. Observed and calculated structure factors for $K_3Cr(CN)_6NO$.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	4483	5919	5	2	2	11716	13400
4	0	0	8395	9176	7	2	2	6679	6758
6	0	0	2232	— 2111	9	2	2	4852	4227
8	0	0	13856	13718	11	2	2	2454	2258
4	1	0	4834	5754	1	3	2	14705	13039
6	1	0	2539	2080	3	3	2	7823	— 7534
8	1	0	2620	— 2818	5	3	2	2306	2542
0	2	0	7897	5421	7	3	2	3708	— 3640
2	2	0	22029	23409	9	3	2	4926	5286
4	2	0	1863	— 868	11	3	2	3413	— 3525
6	2	0	16402	18213	1	4	2	12343	12292
8	2	0	1863	1883	3	4	2	6310	5167
10	2	0	6125	7704	5	4	2	5203	5518
2	3	0	16716	— 15262	7	4	2	7196	6824
4	3	0	1052	— 879	9	4	2	3948	3983
6	3	0	3708	4787	11	4	2	2638	2812
8	3	0	1402	1103	1	5	2	2454	— 2982
0	4	0	20443	18181	3	5	2	7543	7014
2	4	0	3653	4202	5	5	2	5793	— 5619
4	4	0	12767	15410	9	5	2	2675	— 2689
6	4	0	1199	— 1404	11	5	2	2435	2502
8	4	0	7583	9332	1	6	2	9077	8190
12	4	0	3616	4319	3	6	2	4594	4001
2	5	0	3875	— 3358	5	6	2	4373	5091
4	5	0	1993	— 1285	7	6	2	4188	4425
0	6	0	1624	— 2124	9	6	2	1790	1539
2	6	0	11568	11806	11	6	2	1956	1203
4	6	0	5959	6139	1	7	2	1771	1466
6	6	0	5424	7129	3	7	2	1900	— 2535
4	7	0	1144	— 1219	5	7	2	3070	3800
8	7	0	1144	1982	7	7	2	1587	— 1547
0	8	0	3450	4638	11	7	2	1162	— 1125
2	8	0	1273	1842	1	8	2	4336	4644
4	8	0	5461	5580	3	8	2	2657	2788
6	8	0	2528	2168	5	8	2	2417	2038
8	8	0	2657	3547	7	8	2	2694	2598
0	10	0	775	1105	9	8	2	2362	2493
2	10	0	1605	2113	11	8	2	2103	1745
4	10	0	1661	2123	1	9	2	1384	— 1450
6	10	0	2325	3415	9	9	2	1402	— 1016
0	12	0	1236	1733	1	10	2	1863	1689
4	12	0	1089	819	3	10	2	2159	2527
1	0	2	8838	12820	5	10	2	1513	1865
3	0	2	13782	19692	7	10	2	1162	1163
5	0	2	5609	7608	11	10	2	812	900
7	0	2	3229	2601	1	12	2	978	1468
9	0	2	4834	5492	3	12	2	1089	1341
11	0	2	4889	4328	0	0	4	17122	24224
1	1	2	3948	— 3752	2	0	4	1882	979
3	1	2	13229	18140	4	0	4	12657	10839
5	1	2	8247	— 9373	6	0	4	2583	1497
7	1	2	5221	4801	8	0	4	8561	8205
9	1	2	4760	— 4996	10	0	4	2011	— 1272
11	1	2	2970	2651	12	0	4	4262	4490
1	2	2	3893	4355	2	1	4	1845	1962
3	2	2	14391	14501	4	1	4	3487	3746

<i>h</i>	<i>k</i>	<i>f</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>f</i>	<i>F</i> _o	<i>F</i> _c
8	1	4	2306	— 2509	7	1	6	4354	2907
0	2	4	2214	— 1814	9	1	6	3745	— 2374
2	2	4	12620	12572	11	1	6	1974	1348
4	2	4	2085	2378	1	2	6	5092	3930
6	2	4	13653	13447	3	2	6	5387	4751
10	2	4	6089	4098	5	2	6	3247	3805
14	2	4	3764	3030	7	2	6	3007	2644
2	3	4	4483	— 3762	9	2	6	5111	2704
4	3	4	1697	1381	11	2	6	3044	1653
6	3	4	1513	1227	13	2	6	1919	901
8	3	4	1107	— 989	1	3	6	4520	3591
0	4	4	12620	10614	3	3	6	5756	— 5205
2	4	4	2399	2069	5	3	6	1679	1706
4	4	4	9686	10113	11	3	6	3745	— 2291
8	4	4	6125	6303	1	4	6	6771	5061
10	4	4	1919	1409	3	4	6	3284	2348
2	5	4	904	1124	5	4	6	2362	2126
6	5	4	1089	— 1000	7	4	6	3819	2947
8	5	4	1753	— 1561	9	4	6	3395	2132
2	6	4	8118	8083	11	4	6	2657	1590
4	6	4	2491	2823	13	4	6	1162	845
6	6	4	4520	4210	1	5	6	3653	— 2687
10	6	4	3137	3247	5	5	6	2565	— 2703
14	6	4	1827	1563	7	5	6	2214	1983
2	7	4	1144	1142	9	5	6	867	— 936
0	8	4	4059	4861	11	5	6	1365	1042
2	8	4	1827	1665	1	6	6	4446	2896
4	8	4	2638	2952	3	6	6	2768	2217
6	8	4	941	484	5	6	6	2768	2991
8	8	4	2288	2866	7	6	6	2509	2206
10	8	4	1624	1270	3	7	6	1734	— 2026
2	9	4	904	984	5	7	6	1624	1889
2	10	4	1568	1842	1	8	6	1218	1434
2	11	4	683	— 515	3	8	6	1494	1652
2	12	4	572	1129	5	8	6	2048	1825
3	0	6	6310	5848	7	8	6	1605	1546
5	0	6	1125	988	9	8	6	1015	902
7	0	6	1919	889	1	9	6	1089	— 734
9	0	6	5351	3448	5	10	6	978	1525
11	0	6	4520	2905	8	0	8	3044	3015
1	1	6	3893	— 2934	6	2	8	5277	4480
3	1	6	5830	5788	8	4	8	2731	2439
5	1	6	3635	— 3860	6	6	8	2113	1733

DESCRIPTION OF THE STRUCTURE

The chromium atoms seem to be surrounded by six ligands which, within the limits of error, constitute a regular octahedron (Tables 3, 4). Due to the high degree of disorder, it was not possible to distinguish between the nitrosyl and the cyanide groups, although it is most likely that the atoms of the nitrosyl group replace the carbon and nitrogen atoms completely at random. The potassium ions are surrounded either by six nitrogen atoms which constitute an almost regular octahedron, or by six nitrogen atoms which constitute an almost regular trigonal prism.

Table 2. Fractional atomic parameters for $K_3Cr(CN)_5NO$.

Atom	Position	<i>y</i>	<i>z</i>	<i>x</i>
Cr(1)	<i>a</i>	0.0000	0.0000	0.0000
Cr(2)	<i>b</i>	0.5000	0.0000	0.2500
K(1)	<i>a</i>	0.0000	0.0000	0.5000
K(2)	<i>b</i>	0.5000	0.0000	0.7500
K(3)	<i>c</i>	0.2508	0.2297	0.5000
K(4)	<i>c</i>	0.7508	0.2269	0.7500
C(1)	<i>c</i>	0.0995	0.0553	0.1628
C(2)	<i>c</i>	0.5995	0.0553	0.4128
C(3)	<i>c</i>	0.0995	0.0553	0.8372
C(4)	<i>c</i>	0.5995	0.0553	0.0872
C(5)	<i>c</i>	0.4334	0.1709	0.2500
C(6)	<i>c</i>	0.9334	0.1709	0.0000
N(1)	<i>c</i>	0.1497	0.0904	0.2493
N(2)	<i>c</i>	0.6497	0.0904	0.4993
N(3)	<i>c</i>	0.1497	0.0904	0.7507
N(4)	<i>c</i>	0.6497	0.0904	0.0007
N(5)	<i>c</i>	0.4003	0.2621	0.2500
N(6)	<i>c</i>	0.9003	0.2621	0.0000

The disorder revealed in the rotation photographs apparently arises in the following way. In the structure there are long rows consisting of a complex group, a potassium ion, a complex group and so on, extending along the *c*-axis. Without loss of much energy these rows can be displaced by *c*/2. If we arbitrarily chose an origin in a row in a certain elementary cell there is about

Table 3. Bond distances in $K_3Cr(CN)_5NO$.

Cr(1)–C ₁ (1)	1.99 ± 0.03 Å	K ₁ (3)–N ₁ (1)	2.89 ± 0.10
Cr(1)–C ₁ (3)	1.99 ± 0.03	K ₁ (3)–N ₄ (1)	3.11 ± 0.10
Cr(1)–C ₁ (6)	1.98 ± 0.05	K ₁ (3)–N ₁ (3)	2.89 ± 0.10
		K ₁ (3)–N ₄ (3)	3.11 ± 0.10
K ₁ (1)–N ₁ (1)	3.05 ± 0.10	K ₁ (3)–N ₁ (5)	2.92 ± 0.03
K ₁ (1)–N ₂ (1)	3.05 ± 0.10	K ₁ (3)–N ₄ (5)	2.90 ± 0.03
K ₁ (1)–N ₁ (3)	3.05 ± 0.10		
K ₁ (1)–N ₂ (3)	3.05 ± 0.10	C ₁ (1)–N ₁ (1)	1.05 ± 0.12
K ₁ (1)–N ₃ (6)	2.80 ± 0.03	C ₁ (5)–N ₁ (5)	1.04 ± 0.06
K ₁ (1)–N ₄ (6)	2.80 ± 0.03		

Table 4. Bond angles in $K_3Cr(CN)_5NO$.

C ₂ (1)–Cr ₁ (1)–C ₁ (1)	93 ± 1°	N ₁ (1)–K ₁ (1)–N ₂ (1)	93 ± 3
C ₁ (3)–Cr ₁ (1)–C ₁ (1)	87 ± 1	N ₁ (1)–K ₁ (1)–N ₁ (3)	87 ± 3
C ₁ (6)–Cr ₁ (1)–C ₁ (1)	92 ± 1	N ₁ (1)–K ₁ (1)–N ₃ (6)	88 ± 3
C ₂ (6)–Cr ₁ (1)–C ₁ (1)	88 ± 1	N ₁ (1)–K ₁ (1)–N ₄ (6)	92 ± 3
C ₄ (1)–Cr ₁ (1)–C ₁ (1)	180 ± 0	N ₁ (1)–K ₁ (3)–N ₁ (3)	93 ± 3
		N ₁ (1)–K ₁ (3)–N ₁ (5)	82 ± 3
Cr(1)–C ₁ (1)–N ₁ (1)	176 ± 4	N ₁ (1)–K ₁ (3)–N ₁ (5)	150 ± 3
Cr(2)–C ₁ (5)–N ₁ (5)	178 ± 4	N ₁ (3)–K ₁ (3)–N ₁ (5)	154 ± 3
		N ₁ (3)–K ₁ (3)–N ₄ (5)	79 ± 3
		N ₁ (5)–K ₁ (3)–N ₄ (5)	92 ± 3

equal probability that the corresponding origin in the next elementary cell should be placed in the positions 000 or $00\ c/2$. The same type of disorder which characterizes this structure has previously been found in certain platinum and palladium complexes.⁶ The fractional atomic parameters in Table 2 refer to an ordered structure, belonging to space group $Pnc2$.

DISCUSSION

As mentioned above, the ligand positions in the complex groups constitute within the limits of error a regular octahedron. These results can, however, be interpreted in two ways. Either the complex ions have true octahedral symmetry, or they are tetragonally distorted with one short chromium-nitrogen (Cr—NO) bond and five longer chromium-carbon bonds (Cr—CN), the orientation of the ions being six-fold degenerate. The latter implies that in the structure determined the nitrosyl group can occupy any of the six positions reserved for the ligand groups. In the nitroprusside ion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ the iron-nitrogen bond distance is about 0.30 Å shorter than the iron-carbon distance.⁴ Thus if the chromium-carbon bonds are 2.09 Å⁷ the chromium-nitrogen bond can be expected to be about 1.79 Å which yields a mean value of 2.04 Å as compared with the distance 1.99 ± 0.03 Å found in this structure. Although it is not possible to distinguish between the cyanide and nitrosyl group positions it is evident from the structure investigated that both the Cr—N—O and Cr—C—N linkages are linear.

Further refinement of this structure was not considered to be worthwhile owing to the disorder. Work on the ordered structures of $\text{K}_3\text{Cr}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ and $\text{K}_3\text{Mn}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ is in progress and will be published shortly.

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