

The Crystal Structure of Sodium Hexacyanochromate(II) Decahydrate, $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$

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The crystal structure of sodium hexacyanochromate(II) decahydrate has been determined by single crystal X-ray methods using diffractometer data collected at -100°C . The crystals are monoclinic with $a = 9.866(4) \text{ \AA}$, $b = 11.502(4) \text{ \AA}$, $c = 9.152(4) \text{ \AA}$, $\beta = 98.30(3)^\circ$, and belong to space group $P2_1/n$. A final R value of 0.052 was obtained for 1210 independent reflections. The complex ion has nearly octahedral symmetry with mean Cr—C and C—N distances of 2.053(4) and 1.156(5) \AA , respectively.

As part of a systematic investigation of transition metal hexacyanides, the crystal structure of $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ has been determined. By correlating the M—C and C—N bond lengths and the geometries of the complex ions for various metals and oxidation states with other experimental data, such as IR and X-ray photoelectron spectra, and with molecular orbital calculations it should be possible to estimate the relative magnitudes of the σ and π contributions to the M—C(N) bonds. Structural data are now available for $\text{K}_4[\text{V}(\text{CN})_6]$,¹ $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$, $\text{Na}_4[\text{Mn}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$,² $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$,² $\text{K}_3[\text{Cr}(\text{CN})_6]$,³ $\text{K}_3[\text{Mn}(\text{CN})_6]$,⁴ $\text{K}_3[\text{Fe}(\text{CN})_6]$,⁵ and $\text{K}_3[\text{Co}(\text{CN})_6]$.⁵

EXPERIMENTAL

The compound was prepared by a modification of the method due to Ludi.⁶ 2.5 g $\text{Na}_2[\text{Cr}(\text{CN})_6]$ and 1.7 g NaCN were dissolved in 10 ml 0.2 M NaOH and an amalgamated aluminum sheet was added. After a few minutes the solution turned red and hydrogen gas was evolved. Within 10 h dark green crystals of $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ suitable for single crystal X-ray work

developed on the aluminum sheet and on the walls of the vessel. The amalgamation of the aluminum sheet, which seems to be the critical step in this synthesis, was accomplished by first washing the aluminum sheet (*ca.* $7 \times 15 \times 0.1 \text{ mm}$) in CCl_4 , dipping it into a 0.1 M solution of $\text{Hg}(\text{NO}_3)_2$ for 30 s, and finally rinsing it in water. The above method is to the author's knowledge the only way by which large single crystals of this compound can be prepared.

$\text{Na}_2[\text{Cr}(\text{CN})_6]$ was prepared by passing a solution of $\text{K}_3[\text{Cr}(\text{CN})_6]$ through a Merck No. 1 ion exchange column saturated with sodium ions. The resulting solution was filtered and evaporated *in vacuo* at 50°C . $\text{K}_3[\text{Cr}(\text{CN})_6]$ was prepared according to Brauer.⁷

The chromium content was determined gravimetrically as PbCrO_4 by oxidation with boiling perchloric acid and subsequent precipitation with an aqueous solution of lead nitrate. The water content was determined by drying the compound over P_2O_5 with gentle heating using argon as protective atmosphere and measuring the loss in weight. The sodium content was determined gravimetrically as sodium uranyl zinc acetate by precipitation with uranyl zinc acetate saturated with the sodium salt. [Found: Cr 10.98; Na 20.0; H_2O 36.5. Calc. for $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$: Cr 10.82; Na 19.15; H_2O 37.5].

The compound is very unstable in air due to loss of water of crystallization and oxidation of chromium to the trivalent state. Upon dissolution in water the compound is immediately oxidized and gives a yellow solution from which $\text{Na}_2[\text{Cr}(\text{CN})_6]$ can be crystallized. The compound is also sensitive to X-rays at room temperature.

Unit cell parameters were determined from Guinier powder photographs using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and SiO_2 as an internal standard. The powder samples were prepared in a glove-box filled with humid argon to prevent oxidation and loss of crystal water, and were covered with mylar film during exposure in the Guinier camera. 23 lines were

indexed and the cell parameters were refined using the program POWDER.⁸ A number of lines could not be indexed owing to too large deviations from possible $\sin^2\theta$ values or to calculated and observed intensities not matching each other. These lines probably originated from decomposition products.

An attempt was made to record the IR spectrum of $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ with the KBr disc technique. However, only the spectrum of the chromium(III) compound could be recorded and it is obvious that milling and exposure to infrared radiation caused rapid oxidation of the substance.

The crystal used in the investigation (approximate size $0.17 \times 0.18 \times 0.23$ mm) was picked out from the vessel where it was grown, dried with a filter paper, covered with epoxy resin and mounted on a glass fibre. The intensities were collected with a SYNTEX P2₁ automatic four circle diffractometer using monochromatized $\text{CuK}\alpha$ radiation. The $\omega-2\theta$ scan method was used and the 2θ scan speed was allowed to vary between 2 and $15^\circ/\text{min}$ depending on the intensity of the measured reflexion. Data were collected for $2\theta \leq 115^\circ$. During the data collection the crystal was cooled to -100°C using the SYNTEX LT1 low temperature device. Without cooling and an epoxy cover, the crystals lose their diffracting power in less than 30 min.

In order to minimize the expected radiation damage to the crystal no separate background counts were made. The scan range was instead increased slightly in order to obtain a representative background on each side of a reflexion. A profile analysis based on the Larsen-Lehmann method⁹ was then applied to the 96 step profile collected for each reflexion. It was thus possible to reduce the time required to collect the data by one third. The deterioration of the crystal appeared, however, to be slight since the periodically measured test reflexion did not show any significant decrease in intensity.

STRUCTURE DETERMINATION

1210 independent reflexions with $F_o^2 > 2.5 \sigma(F_o^2)$ were considered as being observed and were corrected for Lorentz, polarization and absorption effects. $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ was found to be isomorphous with $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ and $\text{Na}_4[\text{Mn}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$.² The positional parameters of the manganese compound were used to start a series of least squares refinements. The refinement of an over-all scale factor, atomic coordinates and isotropic thermal parameters using the block diagonal approximation yielded an R -value of 0.065. On introduction of anisotropic thermal parameters and using full matrix least squares refinement an R value of 0.052 was obtained for 124 parameters ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). Throughout the refinement Cruickshank's weighting scheme¹⁰ [$w = (a + F_o + cF_o + dF_o^2)^{-1}$] was used with $a = 15.0$, $c = 0.015$ and $d = 0.0$. The scattering factors for Cr^0 , O, N, C, and Na^+ were those of Doyle and Turner.¹¹ A difference synthesis calculated after the final cycle of refinement showed no peak higher than about $1.5 \text{ e}/\text{\AA}^3$. Such peaks were close to the oxygen atoms where the water hydrogen atoms would be expected to lie. No attempt was, however, made to locate the hydrogen atoms. Some crystallographic data are given in Table 1.

A list of observed and calculated structure factors is available from the author on request.

Table 1. Crystallographic data for $\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$.

Unit cell	monoclinic with $a = 9.866(4) \text{ \AA}$ $b = 11.502(4) \text{ \AA}$ $c = 9.152(4) \text{ \AA}$ $\beta = 98.30(3)^\circ$ $V = 1027.7(7) \text{ \AA}^3$
Formula weight	480.0
Density	$D_m = 1.54 \text{ g/cm}^3$ $D_x = 1.551 \text{ g/cm}^3$
Systematic absences	$h+l = 2n+1$ for $h0l$ $k = 2n+1$ for $0k0$
Space group	$P2_1/n$ (non-standard setting)
General positions	$\pm(x, y, z) \pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$
Crystal habit	dark green prismatic crystals
$\mu(\text{Cu})$	61.7 cm^{-1}

RESULTS AND DISCUSSION

The final atomic coordinates and thermal parameters are given in Tables 2 and 3, respectively. Some distances and angles are given in Table 4. The basic building unit in the structure is the almost octahedral $\text{Cr}(\text{CN})_6^{4-}$ ion. Due to the center of symmetry there are three crystallographically different cyanide groups. The mean Cr—C and C—N distances are 2.053(4) and 1.156(5) Å, respectively. The deviations from linearity of the cyanide groups are significant and are probably due to packing effects.

The N(3) atoms are in contact with three sodium ions while the N(2) atoms are in contact

with one sodium ion. The N(1) atoms have relatively short distances to some water oxygen atoms and appear to be involved in weak hydrogen bonding. Each sodium ion is surrounded by two nitrogen atoms from cyanide groups and four water oxygen atoms forming a distorted octahedron. The sodium ions thus link the complex ions together, forming a three-dimensional network. A stereoscopic projection of the unit cell along [010] is shown in Fig. 1.

The strength of the metal-carbon σ -bond is expected to be dependent on the effective nuclear charge of the metal atom and thus to increase from V to Co. For the same reason the σ -contributions are expected to be stronger for the M(III) complexes than for the M(II) complexes. One effect of the σ -bond is to reduce the positive charge on the metal atom.

d - π^* donation should be favoured by a low positive charge on the metal atom and a large number of metal d -electrons. Back-donation leads to increased strength of the metal-carbon bond, decreased strength of the carbon-nitrogen bond, and an increased positive charge on the metal atom.

In all cases where bond lengths are known for both the formally di- and trivalent states of a given metal atom, the M(III)—C bond is longer than the M(II)—C bond. From a simple electrostatic approach considering σ -bonding only one would expect the reverse situation. The short M(II)—C bonds must therefore be due to a strong π -contribution.

Table 2. Atomic coordinates with estimated standard deviations.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cr	0	0	0
Na1	0.5959(2)	0.3569(2)	0.0123(2)
Na2	0.7184(2)	0.1280(2)	0.4025(2)
C1	0.2043(6)	0.0122(4)	0.0743(6)
C2	0.4982(5)	0.3214(5)	0.4758(6)
C3	0.0435(5)	0.0189(4)	0.2118(7)
N1	0.3204(5)	0.0215(4)	0.1137(5)
N2	0.5040(5)	0.2207(4)	0.4672(6)
N3	0.9278(5)	0.0312(4)	0.3283(5)
O1	0.2967(4)	0.0376(3)	0.4439(4)
O2	0.6117(4)	0.0068(4)	0.2025(5)
O3	0.7663(4)	0.2782(4)	0.2142(5)
O4	0.1148(6)	0.2710(4)	0.3184(5)
O5	0.3866(4)	0.2793(3)	0.1004(5)

Table 3. Anisotropic thermal parameters ($\times 10^3$) with their standard deviations. The temperature factor is expressed as $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cr	5.5(7)	6.6(7)	9.4(8)	-0.5(9)	6.6(11)	0(9)
Na(1)	15(1)	19(1)	24(1)	2(2)	4(2)	6(2)
Na(2)	14(1)	16(1)	20(2)	3(2)	7(2)	3(2)
C(1)	21(4)	10(3)	13(3)	0(4)	23(5)	-2(4)
C(2)	8(3)	22(4)	17(3)	5(4)	20(5)	6(5)
C(3)	6(3)	7(3)	21(3)	1(4)	3(5)	1(4)
N(1)	13(3)	29(3)	32(3)	2(4)	17(5)	-1(4)
N(2)	19(3)	15(3)	47(4)	-1(4)	20(5)	-4(5)
N(3)	17(3)	21(3)	14(3)	4(4)	13(5)	2(4)
O(1)	21(2)	18(2)	22(2)	-5(3)	15(4)	0(3)
O(2)	17(2)	47(3)	29(3)	5(4)	3(9)	19(4)
O(3)	24(2)	27(2)	47(3)	-6(4)	19(4)	-30(4)
O(4)	72(4)	24(3)	42(3)	-14(5)	6(5)	9(4)
O(5)	28(2)	21(2)	37(3)	-9(4)	14(4)	12(4)

Table 4. Some distances (Å) and angles (°) in Na₄[Cr(CN)₆].10H₂O. Standard deviations are given within parentheses. No superscript, atom in x, y, z ; ', atom in $\bar{x}, \bar{y}, \bar{z}$; '', atom in $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; ''', atom in $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Cr—C(1)	2.037(6)	C(1)—N(1)	1.155(8)
Cr—C(2)	2.065(6)	C(2)—N(2)	1.163(8)
Cr—C(3)	2.057(6)	C(3)—N(3)	1.150(8)
C(1)—Cr—C(2)	92.3(2)	C(1)—Cr—C(3)	90.5(2)
C(2)—Cr—C(3)	90.2(2)	Cr—C(1)—N(1)	178.1(5)
Cr—C(2)—N(2)	176.3(5)	Cr—C(3)—N(3)	177.6(5)
Na(1)—N(3)'''	2.509(5)	Na(1)—N(3)''	2.537(5)
Na(1)—O(1)	2.479(4)	Na(1)—O(3)	2.483(5)
Na(1)—O(4)	2.334(5)	Na(1)—O(5)''	2.489(5)
Na(2)—N(2)	2.515(5)	Na(2)—N(3)''	2.525(5)
Na(2)—O(1)'	2.385(4)	Na(2)—O(2)''	2.417(5)
Na(2)—O(3)''	2.532(5)	Na(2)—O(5)''	2.511(5)
Some short oxygen-nitrogen distances			
N(1)—O(2)'''	3.081(7)	N(1)—O(2)''	2.877(7)
N(1)—O(4)	2.997(7)	N(1)—O(5)''	3.042(7)

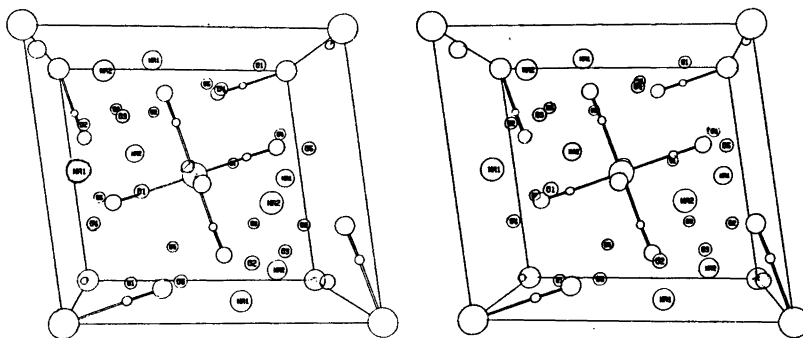


Fig. 1. Stereoscopic projection of the unit cell of Na₄[Cr(CN)₆].10H₂O along [010]. The a axis is horizontal. The labels of the chromium, carbon and nitrogen atoms have been omitted for clarity.

Graphical representations of the metal-carbon and carbon-nitrogen bond lengths for the hexacyano compounds mentioned in the introduction of this paper are shown in Figs. 2–3. The differences in carbon-nitrogen bond lengths are not significant but there is a tendency for the C–N bonds to weaken when going from V(II) to Fe(II). This is also supported by a decrease in the ν (C–N) IR stretch frequency.¹ No such trend is observed for the M(III) complexes.

The observed bond lengths indicate that π -bonding is strongest in the Mn(II) and Fe(II) complexes. Here the π -contribution almost

compensates for the decreased effective nuclear charge when going from Co(III) to Fe(II) (both d^5 ground state configuration) or from Fe(III) to Mn(II) (both d^5). This is in good agreement with the results of semi-empirical molecular orbital calculations made by Alexander and Gray.^{12,13} When comparing Mn(III) and Cr(II) (both d^4) it is seen that the decreased nuclear charge is not fully compensated for by π -bonding and the π -bonding seems to be weaker than in the Fe(II) and Mn(II) complexes. The largest difference in M–C bond lengths for metals with the same electronic ground state configuration is observed between V(II) and

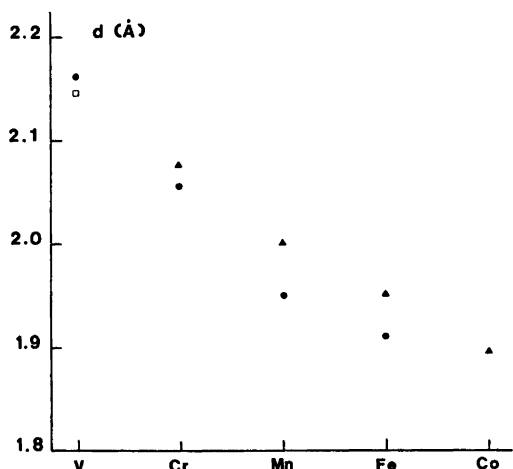


Fig. 2. Mean M-C bond lengths for some transition metal hexacyano complexes. ●, M(II)-C; ▲, M(III)-C. The seven-coordinated V(III) complex $K_4[V(CN)_7] \cdot 2H_2O$ is denoted by □.

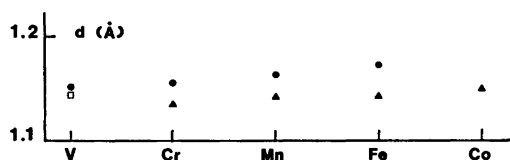


Fig. 3. Mean C-N bond lengths for some transition metal hexacyano complexes. ●, distance in M(II) complexes; ▲, distance in M(III) complexes. The seven-coordinated V(III) complex is denoted by □.

Cr(III) (both d^3). This means that the weakest π -contribution in the M(II) series is found in the V(II) complex. These observations are also supported by the tendency for the C-N bond length to increase when going from V(II) to Fe(II).

No structure of a hexacyano complex with V(III) is known but the structure of $K_4[V(CN)_7] \cdot 2H_2O$ has been solved,¹⁴ the complex ion having a pentagonal bipyramidal conformation. Although a comparison of bond lengths is not strictly relevant it is interesting to note that the V(III)-C bond is shorter than the V(II)-C bond. This also appears to indicate that the π -contribution in the V(II) complex is weaker than in the other M(II) complexes. The weak

bonding in the V(II) complex has been noted earlier.¹

An X-ray photoelectron investigation of transition metal hexacyanides confirms these conclusions.¹⁵

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