# The Crystal Structures of Hexacyanomanganate Decahydrate, $Na_4[Mn(CN)_6].10H_2O$ and Tetrasodium Hexacyanoferrate Decahydrate, $Na_4[Fe(CN)_6].10H_2O$

AINA TULLBERG and NILS-GÖSTA VANNERBERG

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structures of the isomorphous compounds $Na_4[Mn(CN)_6].10H_2O$ and $Na_4[Fe(CN)_6].10H_2O$ have been refined by single crystal X-ray diffraction methods. The crystals are monoclinic and belong to space group $P2_1/n$. $R$-values of 0.09 and 0.08 have been obtained for the manganese and iron compounds, respectively.

The structures are built up of almost regular octahedral $[Me(CN)_6]^{4-}$ ions, linked together in three dimensions by distorted sodium ion coordination octahedra. There are three crystallographically different cyanide groups. In each $[Me(CN)_6]^{4-}$ octahedron the nitrogen atoms of two cyanide groups are thus each linked to three sodium ions, the nitrogen atoms of two other cyanide groups are each linked to one sodium ion, while the nitrogen atoms of the remaining two cyanide groups would appear to participate in hydrogen bonding to water molecules.

The mean $Me-C$ distances are 1.95(3) Å and 1.91(1) Å and the mean $C-N$ bond distances are 1.16(3) Å and 1.17(1) Å for $Na_4[Mn(CN)_6].$- $10H_2O$ and $Na_4[Fe(CN)_6].10H_2O$, respectively.

The chemical bonding in hexacyanido complexes has been subject to much discussion. Many authors believe that the extreme stability and inertness of the complexes are due to appreciable $\pi$-bonding between the central ion and the cyanide ligand.[1,2] However, some theoretical calculations show little $\pi$-bonding in these complexes.[3] Qualitatively, it should be possible to determine the relative contributions of $\pi$- and $\sigma$-bonding if the variation in bond lengths of complex ions of the type $Me(CN)_6{}^{n-}$ can be expressed as a function of the

central ion and its oxidation state. This calculation has been performed in order to determine the bond distance in $Me(II)-CN$, where Me is Mn and Fe. The $Me(III)-CN$ distances have been previously determined by one of the authors.[4,5] A short communication regarding the work has been given previously.[6]

## EXPERIMENTAL

Crystals of $Na_4[Mn(CN)_6].10H_2O$ were prepared from $MnCO_3$ and $NaCN$, according to the method described by Brauer;[7] those of $Na_4[Fe(CN)_6].10H_2O$ were obtained by recrystallizing a commercial sample from water. Both compounds, and particularly $Na_4[Mn(CN)_6].10H_2O$, are unstable in air, due to high water vapor pressure.

*Crystal data.* The unit cell dimensions for the compounds were determined from Guinier powder photographs taken with $CuK\alpha_1$ radiation, using potassium chloride (Mn) and lead nitrate (Fe) as an internal standard.[8] The manganese compound reacted quantitatively with lead nitrate even in solid phase why potassium chloride has to be used in this case. About 20 lines were indexed and the cell parameters were refined with the program POWDER.[9] The following results were obtained: Mn: $a = 9.818(7)$ Å, $b = 11.460(8)$ Å, $c = 9.093(8)$ Å, $\beta = 97.95(6)°$ and $V = 1013.2$ Å$^3$, Fe: $a = 9.787(5)$ Å, $b = 11.448(6)$ Å, $c = 9.037(5)$ Å, $\beta = 97.49(4)°$ and $V = 1003.8$ Å$^3$. Observed and calculated $\sin^2\theta$ values, $d$-values and the corresponding intensities are listed in Tables 1a and 1b.

The measured density for $Na_4[Fe(CN)_6].$- $10H_2O$, 1.60 g cm$^{-3}$ was determined by the flotation method using carbon tetrachloride (density 1.60 g cm$^{-3}$). The calculated density,

*Table 1a.* X-Ray powder diffraction data for $Na_4Mn(CN)_6 \cdot 10H_2O$. Guinier camera; $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

| h k l | $10^5 \sin^2 \theta$ obs | $10^5 \sin^2 \theta$ calc | d (calc) Å | $I_{calc}$ | $I_{obs}$ |
|---|---|---|---|---|---|
| 1 1 0 | 1071 | 1079 | 7.443 | 43 | vs |
| 0 1 1 | 1179 | 1183 | 7.094 | 3 | vw |
| 1 0 1 | 1536 | 1547 | 6.215 | 9 | m |
| 0 2 0 | 1809 | 1807 | 5.727 | 8 | m |
| 0 0 $\bar{2}$ | 2906 | 2926 | 4.518 | 9 | m |
| 1 2 $\bar{1}$ | 2959 | 2979 | 4.478 | 3 | w |
| 2 1 $\bar{1}$ | 3301 | 3318 | 4.239 | 5 | m |
| 1 1 $\bar{2}$ | 3619 | 3631 | 4.049 | 15 | s |
| 2 1 1 | 4054 | 4069 | 3.826 | 6 | m |
| 0 3 1 | 4785 | 4797 | 3.521 | 17 | s |
| 3 1 0 | 6088 | 6099 | 3.122 | 10 | s |
| 1 0 $\bar{3}$ | 6647 | 6649 | 2.988 | 7 | m |
| 0 4 0 | 7213 | 7228 | 2.868 | 6 | m |
| 3 2 $\bar{1}$ | 7610 | 7624 | 2.792 | 8 | s |
| 2 2 $\bar{2}$ | 7975 | 7994 | 2.728 | 7 | s |
| 1 4 $\bar{1}$ | 8399 | 8398 | 2.658 | 4 | m |
| 3 2 1 | 8745 | 8749 | 2.605 | 5 | m |
| 3 2 $\bar{2}$ | 9242 | 9256 | 2.534 | 4 | m |
| 3 3 0 | 9708 | 9713 | 2.472 | 2 | w |
| 3 3 $\bar{1}$ | 9872 | 9882 | 2.451 | 2 | w |
| 1 4 $\bar{3}$ | 13867 | 13877 | 2.068 | 10 | s |

*Table 1b.* X-Ray powder diffraction data for $Na_4Fe(CN)_6 \cdot 10H_2O$. Guinier camera; $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

| h k l | $10^5 \sin^2 \theta$ obs | $10^5 \sin^2 \theta$ calc | d (calc) Å | $I_{calc}$ | $I_{obs}$ |
|---|---|---|---|---|---|
| 1 1 0 | 1093 | 1083 | 7.402 | 45 | vs |
| {1 0 $\bar{1}$ / 0 1 1} | 1205 | {1191 / 1192} | {7.057 / 7.056} | {1 / 3} | vw |
| 1 0 1 | 1554 | 1547 | 6.193 | 12 | m |
| 0 2 0 | 1819 | 1811 | 5.724 | 8 | m |
| 0 0 $\bar{2}$ | 2964 | 2954 | 4.480 | 9 | m |
| 1 2 $\bar{1}$ | 3013 | 3002 | 4.446 | 3 | vw |
| {2 1 $\bar{1}$ / 1 2 1} | 3360 | {3357 / 3358} | {4.204 / 4.204} | {5 / 4} | m |
| 1 1 $\bar{2}$ | 3673 | 3683 | 4.013 | 17 | m |
| 2 1 1 | 4077 | 4068 | 3.819 | 6 | w |
| 0 3 1 | 4814 | 4813 | 3.511 | 10 | s |
| 2 2 1 | 5434 | 5426 | 3.307 | 2 | diff. |
| 3 1 0 | 6128 | 6124 | 3.113 | 11 | m |
| 1 0 $\bar{3}$ | 6758 | 6748 | 2.965 | 10 | m |
| 0 4 0 | 7250 | 7243 | 2.862 | 10 | m |
| 3 2 $\bar{1}$ | 7695 | 7687 | 2.778 | 10 | m |
| 2 2 $\bar{2}$ | 8006 | 7999 | 2.723 | 9 | m |
| 1 4 $\bar{1}$ | 8444 | 8434 | 2.652 | 4 | vw |
| 1 2 $\bar{3}$ | 8569 | 8559 | 2.633 | 4 | w |
| 3 2 1 | 8763 | 8755 | 2.603 | 6 | w |
| 3 2 $\bar{2}$ | 9380 | 9371 | 2.516 | 4 | w |

based on two formula units in the unit cell, is 1.60 g cm$^{-3}$.

Conditions limiting possible reflections for crystals of both compounds are

$h0l : h+l = 2n$
$0k0 : k = 2n$

This is in accordance with space group $P2_1/n$.

## DETERMINATION OF THE STRUCTURE OF $Na_4[Mn(CN_6].10H_2O$

The structure of $Na_4[Mn(CN)_6].10H_2O$ was determined first. A crystal was mounted in a sealed glass capillary with rotation axis parallel to the c-axis and rotation and Weissenberg equi-inclination photographs were registered using multiple film techniques and $CuK\alpha$ radiation. Only the layers $hk0-hk4$, giving a total of 561 independent reflections, were recorded before the crystal decomposed. Attempts were made to mount other crystals but, before a satisfactory specimen was found, interest was focused on the isomorphous iron compound, which seemed to be more stable to X-ray exposure. Since the linear absorption coefficient for $Na_4[Mn(CN)_6].10H_2O$ in $CuK\alpha$ radiation is 69.3 cm$^{-1}$, the data are seriously effected by absorption. However, no corrections were made for this.

The relative intensities of the reflections $hk0-hk4$ were estimated visually by comparison with a logarithmic scale. After correction for Lorentz and polarisation effects, using the program DATA P2,[*] a three dimensional Patterson synthesis was computed with the program DRF.[*] Since the unit cell contains two manganese atoms and the general equivalent positions in space group $P2_1/n$ are fourfold, the manganese atoms must occupy one of the special twofold positions with site symmetry 1. The general positions of the sodium atoms and the orientation of the octahedral $[Mn(CN)_6]^{4-}$ ions were determined from the Patterson synthesis. Some C and N peaks were lower than expected and there was overlapping, probably due to the approximate scaling of the data, which had been carried out assuming that there were no fluctuations in the intensity from the X-ray tube.

Subsequent electron density calculations based on the contributions of the postulated atoms to the structure factor phases revealed the positions of the remaining non-hydrogen atoms. After a few cycles of isotropic block diagonal least squares refinement, using the program BLOCK,[*] the $R$-value converged to 0.089. A difference electron density calculation showed no spurious peaks, the highest being 1 e/Å$^3$. $F_c$ values were calculated for the unobserved reflections in the five layers registered. All were small.

Bond distances and angles were calculated with the program DISTAN.[*] The Mn$-$C bond distances vary between 1.91 and 1.98 Å (mean 1.95 Å) and the C$-$N distances between 1.14

*Table 2.* Final atomic fractional coordinates and isotropic thermal parameters for $Na_4Mn(CN)_6.10H_2O$. Standard deviations are given in parentheses. The temperature factor is exp $(-B \sin^2 \theta/\lambda^2)$.

| Atom | $x$ | $y$ | $z$ | $B$ Å$^2$ |
|---|---|---|---|---|
| Mn | 0 | 0 | 0 | 2.6(1) |
| Na(1) | 0.0948(6) | 0.1419(4) | 0.5122(8) | 3.9(1) |
| Na(2) | 0.7154(5) | 0.1285(4) | 0.3992(8) | 3.5(1) |
| C(1) | 0.303(1) | 0.510(1) | 0.431(2) | 2.8(2) |
| C(2) | 0.498(1) | 0.328(1) | 0.476(2) | 2.8(2) |
| C(3) | 0.542(1) | 0.517(1) | 0.300(2) | 2.5(2) |
| N(1) | 0.187(1) | 0.519(8) | 0.391(2) | 3.3(2) |
| N(2) | 0.502(1) | 0.228(1) | 0.472(2) | 3.6(2) |
| N(3) | 0.431(1) | 0.471(1) | 0.823(2) | 2.9(2) |
| O(1) | 0.302(1) | 0.038(1) | 0.444(1) | 3.5(2) |
| O(2) | 0.106(1) | 0.487(1) | 0.700(1) | 4.7(2) |
| O(3) | 0.267(1) | 0.219(1) | 0.715(2) | 4.8(2) |
| O(4) | 0.113(1) | 0.274(1) | 0.317(2) | 6.4(3) |
| O(5) | 0.383(1) | 0.278(1) | 0.099(1) | 4.3(2) |

and 1.19 Å (mean 1.16 Å). The Mn−C−N angles are 178.2°, 175.5°, and 178.5°. As there is no chemical reason why the $[Mn(CN)_6]^{4-}$ ions should not be close to regular, the observed distortion is probably due to absorption and termination errors in the data. Atomic parameters are listed in Table 2 and bond distances and angles within the complex $Mn(CN)_6^{4-}$ ion are listed in Table 5.

## DETERMINATION OF THE STRUCTURE OF $Na_4[Fe(CN)_6].10H_2O$

A crystal of $Na_4[Fe(CN)_6].10H_2O$ was first mounted to rotate about the c-axis on an

automatic single crystal diffractometer (Philips PAILRED) and the intensities of reflections in layers $hk0-hk9$ were measured with $MoK\alpha$ radiation. They were reduced to structure amplitudes using the program DATA P1.[3] It was then discovered that due to an instrumental error, several reflections had been wrongly indexed. A preliminary structure report based on selected data from the PAILRED data was published.[6] Refinement of the data gave an R-value of 0.13 and a distorted $[Fe(CN)_6]^{4-}$ octahedron with Fe−C bond distances varying between 1.90 and 2.04 Å and Fe−C bond distances between 1.12 and 1.21 Å.

Another crystal was mounted on an in-

*Table 3.* Atomic coordinates for $Na_4Fe(CN)_6.10H_2O$, expressed as fractions of the cell edges, and their standard deviations.

| Atom | $x$ | $y$ | $z$ |
|------|-----|-----|-----|
| Fe | 0 | 0 | 0 |
| Na(1) | 0.0935(4) | 0.1396(3) | 0.5098(4) |
| Na(2) | 0.7138(4) | 0.1285(3) | 0.3989(4) |
| C(1) | 0.3086(7) | 0.5088(8) | 0.4290(8) |
| C(2) | 0.5004(8) | 0.3333(6) | 0.4776(8) |
| C(3) | 0.5434(7) | 0.5174(5) | 0.3016(8) |
| N(1) | 0.1896(8) | 0.5175(7) | 0.3882(9) |
| N(2) | 0.5033(8) | 0.2318(6) | 0.4680(8) |
| N(3) | 0.4296(8) | 0.4705(6) | 0.8202(8) |
| O(1) | 0.3023(7) | 0.0388(6) | 0.4439(7) |
| O(2) | 0.1050(7) | 0.4902(7) | 0.7013(8) |
| O(3) | 0.2666(7) | 0.2201(6) | 0.7149(8) |
| O(4) | 0.1138(11) | 0.2724(7) | 0.3162(9) |
| O(5) | 0.3817(8) | 0.2785(6) | 0.0979(8) |

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

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| Fe | 0.0045(1) | 0.0031(1) | 0.0052(2) | −0.0005(3) | 0.0017(2) | −0.0006(3) |
| Na(1) | 0.0085(4) | 0.0061(3) | 0.0101(5) | −0.0001(5) | 0.0008(7) | 0.0002(6) |
| Na(2) | 0.0084(4) | 0.0050(3) | 0.0100(5) | 0.0009(5) | 0.0017(6) | 0.0007(5) |
| C(1) | 0.0049(6) | 0.0050(6) | 0.0055(7) | −0.0006(12) | 0.0001(10) | −0.0014(12) |
| C(2) | 0.0045(6) | 0.0045(6) | 0.0065(10) | −0.0009(11) | 0.0017(14) | −0.0002(10) |
| C(3) | 0.0034(6) | 0.0023(5) | 0.0078(9) | −0.0002(8) | 0.0014(10) | 0.0011(9) |
| N(1) | 0.0068(7) | 0.0067(7) | 0.0109(10) | 0.0010(12) | 0.0039(13) | 0.0007(13) |
| N(2) | 0.0072(8) | 0.0046(5) | 0.0114(2) | −0.0007(11) | 0.0045(16) | −0.0029(10) |
| N(3) | 0.0072(8) | 0.0055(6) | 0.0065(8) | 0.0012(9) | 0.0039(12) | 0.0015(9) |
| O(1) | 0.0104(9) | 0.0069(6) | 0.0081(8) | −0.0024(10) | 0.0037(13) | 0.0009(9) |
| O(2) | 0.0069(6) | 0.0115(7) | 0.0104(8) | 0.0037(14) | 0.0017(11) | 0.0063(14) |
| O(3) | 0.0093(8) | 0.0073(6) | 0.0132(11) | 0.0002(11) | 0.0010(14) | −0.0067(12) |
| O(4) | 0.0229(16) | 0.0070(6) | 0.0137(13) | −0.0067(17) | −0.0050(22) | 0.0014(14) |
| O(5) | 0.0117(9) | 0.0067(6) | 0.0112(10) | −0.0023(12) | 0.0029(14) | 0.0021(12) |

*Table 5.* Geometry of the $Fe(CN)_6^{4-}$ and $Mn(CN)_6^{4-}$ octahedra. Interatomic distances (in Å) and angles with their standard deviations in parentheses.

| Distance | | | Angle | |
|---|---|---|---|---|
| Fe − C(1) | 1.902(7) | | Fe − C(1) − N(1) | 177.7(8) |
| Fe − C(2) | 1.920(8) | | Fe − C(2) − N(2) | 178.0(7) |
| Fe − C(3) | 1.906(7) | | Fe − C(3) − N(3) | 179.2(6) |
| C(1) − N(1) | 1.180(10) | | C(1) − Fe − C(2) | 88.1(4) |
| C(2) − N(2) | 1.165(10) | | C(1) − Fe − C(3) | 89.6(3) |
| C(3) − N(3) | 1.174(10) | | C(2) − Fe − C(3) | 90.0(3) |
| Mn − C(1) | 1.95(1) | | Mn − C(1) − N(1) | 178(4) |
| Mn − C(2) | 1.98(1) | | Mn − C(2) − N(2) | 175(2) |
| Mn − C(3) | 1.93(2) | | Mn − C(3) − N(3) | 179(1) |
| C(1) − N(1) | 1.15(2) | | C(1) − Mn − C(2) | 88.4(5) |
| C(2) − N(2) | 1.15(2) | | C(1) − Mn − C(3) | 88.7(6) |
| C(3) − N(3) | 1.19(2) | | C(2) − Mn − C(3) | 89.8(6) |

*Table 6.* Geometry of the sodium ion coordination octahedra in $Na_4[Fe(CN)_6].10H_2O$. Interatomic distances (in Å) and angles with their standard deviations in parentheses.

| Coordination of Na(1) | | | | Coordination of Na(2) | | | |
|---|---|---|---|---|---|---|---|
| Atom | x | y | z | Atom | x | y | z |
| Na(1) | 0.0935 | 0.1396 | 0.5098 | Na(2) | 0.7138 | 0.1285 | 0.3989 |
| N(3) | 0.0704 | − 0.0295 | 0.6798 | N(2) | 0.5033 | 0.2318 | 0.4680 |
| N(3)′ | − 0.0704 | 0.0295 | 0.3202 | N(3)″ | 0.9296 | 0.0295 | 0.3202 |
| O(1) | 0.3023 | 0.0388 | 0.4439 | O(1)′ | 0.6977 | − 0.0388 | 0.5561 |
| O(3) | 0.2666 | 0.2201 | 0.7149 | O(2) | 0.6050 | 0.0098 | 0.2013 |
| O(4) | 0.1138 | 0.2724 | 0.3162 | O(3)′ | 0.7666 | 0.2799 | 0.2149 |
| O(5) | − 0.1183 | 0.2215 | 0.5979 | O(5)′ | 0.8817 | 0.2215 | 0.5979 |

| Distance | | | Distance | | |
|---|---|---|---|---|---|
| Na(1) − N(3) | | 2.500(8) | Na(2) − N(2) | | 2.524(8) |
| Na(1) − N(3) | | 2.526(8) | Na(2) − N(3)″ | | 2.576(8) |
| Na(1) − O(1) | | 2.486(8) | Na(2) − O(1)′ | | 2.402(8) |
| Na(1) − O(3) | | 2.517(8) | Na(2) − O(2) | | 2.382(8) |
| Na(1) − O(4) | | 2.346(9) | Na(2) − O(3)′ | | 2.503(8) |
| Na(1) − O(5) | | 2.498(8) | Na(2) − O(5)′ | | 2.510(8) |
| | Mean | 2.479 | | Mean | 2.483 |

| Angle | | Angle | |
|---|---|---|---|
| N(3) − Na(1) − N(3)″ | 86.0(3) | N(2) − Na(2) − N(3)″ | 177.6(3) |
| N(3) − Na(1) − O(1) | 86.0(3) | N(2) − Na(2) − O(1)′ | 96.2(3) |
| N(3) − Na(1) − O(3) | 86.4(3) | N(2) − Na(2) − O(2) | 98.8(3) |
| N(3) − Na(1) − O(4) | 169.6(3) | N(2) − Na(2) − O(3)′ | 94.9(3) |
| N(3) − Na(1) − O(5) | 87.1(3) | N(2) − Na(2) − O(5)′ | 95.9(3) |
| N(3)′ − Na(1) − O(1) | 94.3(3) | N(3)″ − Na(2) − O(1)′ | 86.1(3) |
| N(3)′ − Na(1) − O(3) | 171.5(3) | N(3)″ − Na(2) − O(2) | 81.1(3) |
| N(3)′ − Na(1) − O(4) | 85.7(3) | N(3)″ − Na(2) − O(3)′ | 82.7(3) |
| N(3)′ − Na(1) − O(5) | 85.6(3) | N(3)″ − Na(2) − O(5)′ | 84.3(3) |
| O(1) − Na(1) − O(3) | 81.4(3) | O(1)′ − Na(2) − O(2) | 86.1(3) |
| O(1) − Na(1) − O(4) | 88.3(3) | O(1)′ − Na(2) − O(3)′ | 168.7(3) |
| O(1) − Na(1) − O(5) | 173.1(3) | O(1)′ − Na(2) − O(5)′ | 90.1(3) |
| O(3) − Na(1) − O(4) | 101.4(3) | O(2) − Na(2) − O(3)′ | 90.5(3) |
| O(3) − Na(1) − O(5) | 97.8(3) | O(2) − Na(2) − O(5)′ | 165.1(4) |
| O(4) − Na(1) − O(5) | 98.6(3) | O(3)′ − Na(2) − O(5)′ | 90.6(3) |

tegrating Weissenberg equiinclination camera. The layers $hk0 - hk10$ were recorded using $MoK\alpha$ radiation. There were 1283 independent reflections. Multiple film techniques were used and the intensities of the reflections were estimated visually by comparison with a logarithmic scale. The data were corrected for Lorentz and polarisation effects with the program DATA P2.[9] No absorption corrections were made. The linear absorption coefficient for $Na_4[Fe(CN)_6].10H_2O$ in $MoK\alpha$ radiation is 9.2 cm⁻¹. The structure refined to $R = 0.109$ with block diagonal least squares refinement using the program BLOCK[9] and isotropic temperature coefficients. 162 reflections were omitted in this stage of the refinement because their intensities had been estimated with less precision than the others.

The parameters were then further refined with the full matrix least squares program LALS,[9] an $R$-value of 0.089 being obtained. When anisotropic thermal parameters were assigned to all atoms the $R$-value dropped to 0.077. After refinement with the 162 reflections mentioned earlier included the $R$-value was 0.084.

The atomic scattering factors used for $Fe^+$, $Na^+$, C, N, and O were those given in the International Tables.[8] The $Fe^+$ values were corrected for anomalous dispersion according to Cromer and Waber.[10] A weighting scheme of the form proposed by Cruickshank[11] ($s = [10.0 + |F_o| + 0.05|F_o|^2]^{-1}$) was employed.

The 830 unobserved reflections were then assigned values by taking $I = 0.5I_{min}$ for each reciprocal lattice layer. A difference synthesis was calculated with the program DRF with these reflections included. This showed a

*Table 7.* Water contact distances (in Å) shorter than 3.10 Å in $[Na_4Fe(CN)_6].10H_2O$ with their standard deviations given in parentheses.

| Distances | |
| --- | --- |
| $O(1) - N(1)$ | 3.02(1) |
| $O(1) - N(2)$ | 2.95(1) |
| $O(2) - N(1)$ | 3.07(1) |
| $O(2) - N(1)$ | 2.89(1) |
| $O(2) - O(3)$ | 2.97(1) |
| $O(4) - N(1)$ | 2.95(1) |
| $O(5) - N(1)$ | 3.08(1) |

maximum peak height of 1.4 e/Å³. No attempts were made to locate the hydrogen atoms.

Atomic parameters for the structure are given in Tables 3 and 4. Bond distances and angles are listed in Tables 5, 6, and 7, and observed and calculated structure factors are listed in Table 8.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The unit cell is body-centered with respect to the nearly octahedral $[Me(CN)_6]^{4-}$ ions. These are linked together in three dimensions by sodium ions in distorted coordination octahedra, each involving two nitrogen atoms of cyanide groups and four oxygen water atoms at a mean distance of 2.5 Å.

Due to the centre of symmetry there are three crystallographically different cyanide groups in the unit cell, so that two opposite cyanide groups in each $[Me(CN)_6]^{4-}$ octahedron are each linked through nitrogen atoms N(3) to three different sodium ions while two other cyanide groups are each linked through nitrogen atoms N(2) to one sodium ion. The remaining two nitrogen atoms N(1) are not coordinated to sodium ions but would appear to participate in hydrogen bonding to water molecules which are corners of sodium ion octahedra (Fig. 1).

The distances and angles within the $[Fe(CN)_6]^{4-}$ octahedron are illustrated in Fig. 2.

There are five water contact distances to nitrogen or oxygen atoms shorter than 3.1 Å, indicating the possibility of hydrogen bonding, as mentioned above. These distances are listed in Table 10.

Few structure investigations of hexacoordinated transition metal cyanide compounds have been described, probably because many of these compounds are unstable and tend to crystallize with disordered structures. However, a neutron diffraction study of $K_4[Fe(CN)_6].3D_2O$ by Taylor, Mueller and Hitterman[12] was published in 1970. The results presented here are in good agreement with those found in that investigation. Fe−C bond distances varying between 1.908(4) and 1.956(4) Å [mean 1.927(3) Å] are reported for $K_4[Fe(CN)_6].3D_2O$. The corresponding distances in $Na_4[Fe(CN)_6].10H_2O$ are 1.907(7), 1.906(7), and 1.920(8) Å. In $K_4[Fe(CN)_6].3D_2O$ the C−N

*Table* 8. Observed and calculated structure factors for the structure Na$_4$[Fe(CN)$_6$].10H$_2$O.

```
 H  0  0       H  8  0        6  70  65      -1  20  22       5   -   5*        H  4  2
 4  41  41    0  84  82      7   -  -6*      0   -  11*       6   -   3*     -10  15  13
 6   -   7*    1  13 -15      8  35  33       1  28  34       7  16  15      -9   -   1*
 8  20  20     2  16  17                      2  76 -74                      -8   -   2*
10  48  43     3   9 -11       H  2  1        3  58  57       H 13  1        -7   -   5*
12   -   9*    4  19  18     -8  29  27       4   -   9*     -1   -  -4*      -6   -  79*
               5  18  20    -7  26  26       5  34  36      0  15  16       -5   8  -9
 H  1  0       6  11  10    -6   -  -8*       6  11 -10      1   -  -5*      -4  31  33
 2  20 -24     7   -   2*    -5  15  18       7  15  16                      -3  23 -23
 3 118 105     8  11   9    -4  16 -16       8  32  30       H 14  1        -2  19  22
 4   9 -11     9   9   8    -3 149 -103       9  15  16     -4   -  -3*      -1  53  46
 5   -  -1*   10  18  17     1  45  40      10   -  -1*     -3  15  14       0  26 -21
 6   -  -1*                   2  35  36                      -2   -  -2*      1   3  -5
 7  30  31     H  9  0        3 101  86       H  7  1       -1   -   5*       2  23  25
 8  12  12     1  10  10      4   -  -5*    -10  15  12                       3   9  10
 9   -   3*    2  10  -9      5  14  16      -9   -   3*      H  0  2         4  66  63
10   -   2*    3  15  16      6   -   7*     -8  13  12     -12  18  20       5  24 -26
11  13  13     4   -   3*     7   -   2*     -7   -   4*    -10  22  25       6  40  37
12   -  -3*    5   7   9      8   -  -7*     -6  38  35     -8  27  25        7   -  -4*
               6   8   8      9  15  15     -5   -  -3*     -6  39  45        8  24  24
 H  2  0       7  11  11                    -4  27  29     -4  87  76        9   -   1*
 2  23  20     8  11  12      H  3  1       -3   -   0*      4  22  25       10  11  12
 3  14 -16                  -10  21  20     -2  35  37      6  58  58       11   -   1*
 4  26  26     H 10  0       -9   -   8*    -1  14 -17      8  15  16       12   -   9*
 5   -   4*    0   -  11*    -8  14  12      0  27  30     10  52  45
 6  31  30     1   -   6*    -7   -  -5*      1   -   3*    12  13  13        H  5  2
 7   6   8     2  12  13     -6  25 -22       2  24  27                    -13   9  10
 8  16 -19     3   9  12     -5  21  20       3  20 -19      H  1  2       -12   -   0*
 9   -   6*    4  15  15     -4  28  27       4  36  38    -11  22  22     -11   8   8
10  16  16     5   -   7*    -3  68 -59       5   -   2*   -10   -   6*    -10   -  -1*
11   -   2*    6  16  16      0 136 111       6  42  44     -9  18  18      -9  21  20
               7   -   0*     1   -   1*      7   -   7*    -8  15 -16      -8  11  12
 H  3  0       8   9   7      2  30  28       8  22  24     -7  39  41      -7  28  28
 1  21  21                   3   -   2*                     -6  19  20      -6   7   9
 2   8  -9     H 11  0        4   -   6*      H  8  1       -5   3   8      -5  25  25
 3  58  56     1  17  19      5   -   6*     -7  13  14     -4  26  29      -4   8  -9
 4   -   7*    2   -   8*     6  37  40      -6  16  18     -3   -   9*     -3   5   5
 5  66  62     3  14  15      7  15 -15      -5  32  30      3  67  55      -2  10 -10
 6   -   3*    4   -   7*     8  15  14      -4   -  -6*     4  16  13      -1  28  30
 7   -   7*    5  44  38      9   -   8*     -3  20  22      5   -  -4*      0  18 -17
 8  17  18     6   -   3*    10  22  23      -2   -  -8*     6   -  -5*      1  42  38
 9   -   5*    7  10  10                    -1  12   8      7  22  21       2  67  55
10   -  -6*    8   -   4*     H  4  1        0  38 -43      8   8   8       3  17  17
11   -  -4*    9  12  12    -11  23  23       1  25  26      9  43  39       4  11 -11
12   -   1*                 -10   -  -4*      2  18  20     10   -   4*      5  27  26
               H 12  0      -9   -   5*       3  19  21     11  21  20       6   5  -7
 H  4  0       0   -   4*    -8   -  -5*      4   -  11*    12   -   0*      7  12  12
 0 146 130     1   -  -2*    -7  31  30       5  46  47     13  11  10       8  15 -13
 1  18 -16     2  26  25     -6  16  20                                     9  27  27
 2  52  47     3   8   9     -5   -   1*      H  9  1        H  2  2        10   -  -3*
 3  13  13     4  13  14     -4   -   1*    -6  13  13     -12   8   9      11  15  15
 4  22  22     5  12  10     -3  31  33     -5   -   9*    -11   -   4*
 5  23  23     6  19  20     -2  15  12     -4   -   1*    -10  16  14       H  6  2
 6  38  37     7   -  -1*    -1  76  70     -3  28 -28     -9  20 -19     -12  13  14
 7   7  -8     8  12  11      0  78 -65     -2  16  17     -8   -  -3*    -11   -   1*
 8  16  16                   1  24  30     -1   -  -3*     -7   -   6*    -10  17  18
 9   -   2*    H 13  0        2   -  -3*      0  11  13     -6  16  18      -9   -   0*
10   8  11     1  12  12      3  82  74      1   -  -6*     -5  15 -14      -8  10  11
               2   -   8*     4   -   5*      2   -   6*    -4  44  49      -7   -  -2*
 H  5  0       3   -   6*     5  39  41      3   -   9*     -3  77  72      -6  12  13
 1  35  35     4   -   5*     6   -   2*      4  15  17     -2  17  13      -5  10  11
 2  57  51     5  13  14      7  15  17                     1  31 -29      -4  31  32
 3  42  41     6   -   7*     8   -   8*      H 10  1        2   -  -96*    -3  10 -12
 4   -  -6*                   9  19  19     -3  13  14      3  17 -16      -2  36  33
 5  39  40     H 14  0       10   -   3*    -2   -  -3*     4  36  36      -1   -   0*
 6  22  23     0  17  18     11  15  12     -1  21  20      5  14 -15       0  45  42
 7  15  16     1   -  -3*                    0  12 -11      6  44  37       1   7  -8
 8  18 -19     2   -   8*     H  5  1        1  19  21      7  19  20       2   -  -1*
 9   8   8     3  13  13    -10  22  22      2   -  -2*     8  22  19       3   -   0*
                           -9   -  -4*      3  16  17      9   -   2*       4  19  21
 H  6  0       H  0  1      -8   -   3*                    10   8   9       5  10  12
 0  75  71   -13  16  13    -7   -   0*      H 11  1       11   -   3*       6  30  29
 1  24 -24   -11  16  13    -6   -   5*     -4  22  22     12   -   6*       7  29 -28
 2  37  37    -9  20  22    -5   -  -6*     -3   -  -11*                     8  18  20
 3  94  86    -7  36  37    -4  30  30     -2  16  16       H  3  2         9   -   6*
 4  24  24    -5  94  87    -3  47  45     -1   -   3*     -9  12  12       10  17  17
 5   -  -3*   -3  83  67    -2  14  16      0   -  50*     -8  10  -5      11   -  -1*
 6  21  20     3  75  66    -1  24 -26      1  15 -13      -7  41  39      12   8  10
 7  13 -15     5   - 175*    0  75  65      2  13  12      -6  21 -22
 8   -   4*    7   -  15*    1   -  -7*      3   -  -7*     -5  22  21       H  7  2
 9   -   3*    9  26  27      2  21  23      4  16   4      -4  34  30     -11  26  25
10  20  19                   3  46 -41      5   -   2*     -3  40  36     -10   -  -3*
               H  1  1       4  32  34      6  18  17      -2   6  -5      -9  11  12
 H  7  0     -12  13  14      5   -   1*      7   -   2*    -1   -  -18*    -8   -   7*
 1  55  55   -11   -   6*     6  38  38      8   -  10*     0  28  27      -7  26  25
 2  27  25   -10  19  19      7  18  20      9   -   7*     1   -  10*     -6   7  -7
 3  50  47    -9   -   9*     8  13  14     10  21  18      2  67 -57      -5   7  10
 4   -  -7*   -8  12   9      9   -   4*                    3  18  18      -4   7   8
 5  14  18    -7   -  10*    10  17  16      H 12  1        4  14 -12      -3  17  19
 6  18  19    -6  33  35                   -3  14  15      5  49  47      -2   9   8
 7  17  16    -5   -   5*     H  6  1       -2   -   1*     6   -   2*     -1  73  67
 8   -  -2*   -4  26  25    -7  29  29     -1  25  27      7  19  19       0  10 -11
 9   -  11*   -3  22 -22    -6   -   0*      0  16 -16      8   -   2*      1  22  21
10   -   0*    2  72  61    -5  34  31      1  14  15      9  19  19       2   6   8
11  14  13     3  25  24    -4   -   0*      2   -  -5*    10   -   3*      3  44  41
               4  57  57    -3   -  -5*      3  24  26     11  13  13       4  13 -15
               5   -  12*   -2  25  21      4   -   0*                     5  14  15
```

*Table 8. Continued.*

```
 6   -   -1*      7   -   -5*      1  26  28       4  47  47      -3  12  11           H  5  4
 7  16  16       8  12  13       2  76  76       5   -   1*     -2  11   9       -11  15  16
 8   -   -3*                      4  14 -13       6  10  10      -1   -   4*     -10   -   3*
 9  25  25           H 13  2      5  21  23       7   -   1*      0   -   6*      -9   -   5*
10   -  -1*      -1  17  17       6   -   7*      8  15  17       1   -  -2*      -8   -   2*
11  15  16       0   -  -7*      7  19 -19                       2   -   4*      -7  33  33
                  1  15  16       8   -   3*          H  8  3     3   -   3*      -6  10  11
     H  8  2      2   -   7       9   -  -7*     -11  12  10       4  13  14      -5  24  25
-10  11  11       3   -   7*     10  15  15      -10   -   2*      5   -  -2*      -4   -  -7*
 -9   -  -2*      4   -  -5*     11   -   0*      -9  11  10       6  15  10      -3  45  42
 -8  15  16       5  10  10      12  15  14       -8  13  11                      -2   -  -5*
 -7   -   4*                                      -7  28  26          H 14  3     -1   -   4*
 -6   -   2*          H 14  2          H  4  3    -6   -   2*      3  16  10       0   -  -2*
 -5   -  -1*     -2   9   9      -11  31  30      -5  15  14                       1  26  26
 -4  28  31      -1   -   1*     -10   -  -3*     -4   -  -4*          H 15  3     2   -   5*
 -3   6   7       3  10  12       -9  13  14      -3  30  31       3   -   2*      3  28  29
 -2  13  12       1   -  -4*      -8   -   1*     -2  13  15       4  16  13       4  24  25
 -1  41  38       2  14  15       -7  10  12      -1   9   9                       5  29  27
  0  33  33                       -6   8  -8       0   -  -2*          H  0  4     6   -  -6*
  1   7  -8           H 15  2      -5  16  15       1  22  23     -12  21  21       7  14  13
  2  27  27      -1  15  15       -4   -   4*      2  14  15     -10  14  17
  3   -  -7*      0   6  -8       -3   8  -7       3   9   8      -8  45  42           H  6  4
  4   7   9       1   -   8*      -2  27  23       4  18  20      -6  23  32      -8  25  27
  5  19 -21       2   -   0*      -1 169 161       5  21  22      -4  15  18      -7   -  -1*
  6  24  24       3  11  11       0   9 -12       6  10 -10      -2  91  83      -6  22  20
  7   -   6*                      1  11  12       7  15  15      -2  98  76      -5   -  -7*
  8   -   7*          H 16  2      2  10 -11                      4  45  43      -4   -  11*
  9   -   6*      0   9  10       3  17  18           H  9  3     6   -   2*      -3   -   2*
 10  19  18                       4  12  14     -10  12  10       8  17  21      -2  38  36
                      H  0  3      5   -  -3*      -9  12  10                      -1  21 -20
     H  9  2     -13  14  14       6   9 -10       -8   -   6*         H  1  4     0  35  34
 -7  11  11     -11  28  27       7   -   7*      -7   -  -5*    -11  21  22       1  11   9
 -6   -   1*      -9  15  18       8   -   5*      -6  15  14     -10   -  -1*     2   -  42*
 -5  10  10      -7  51  46       9  31  31       -5   -   7*     -9  18  21       3   -   3*
 -4  17  18      -5  37  36      10   -  -8*      -4  11  12      -8   -   4*      4  14  14
 -3  13 -15      -3  55  49      11  12  11       -3  11 -11      -7   -  12*      5   -   3*
 -2   -   5*      3  22  25                       -2  11  12      -6  11 -12      6   -   4*
 -1  33  33       5  43  42           H  5  3     -1   -   0*     -5  43  39       7   -   2*
  0  10  10       7  30  32     -12  16  15       0   9  10      -4  76  73       8  12  12
  1   -   3*      9  23  22     -11   -   3*      1  22  22      -3   -  30*
  2  18 -18      11  15  17     -10  12  10       2   -  -9*      1  47  40           H  7  4
  3  17  15                      -9   -  -3*      3   -   0*      2  33 -33     -11  16  17
  4   8  -7           H  1  3     -8  30  28       4  19  21      3  17  17      -10   -   0*
  5   -   5*     -14  14  13      -7   -  -8*      5  12  12      4  15  17       -9  19  19
  6   -  -4*     -13   -   2*     -6   -   5*      6   -   4*      5  35  33       -8   -  -1*
  7   -   1*     -12  12  10      -5   -   4*      7  11  -9       6  24  25       -7   -   6*
  8   -   5*     -11   -  -2*     -4  50  48                       7   -   9*      -6   -  10*
  9  15  15     -10  14  13      -3  13  14          H 10  3      8   -   2*      -5  28  28
                 -9  29  27      -2  32  29      -9  12  10       9  18  17       -4  15 -15
     H 10  2     -8  22  23      -1  35  32      -8   -   7*                      -3  15  17
 -9   9 -10      -7   -  -3*      0  21  20      -7   -   9*          H  2  4     -2   -   5*
 -8   7   7      -6  46  45      1   6  -7       -6   -   3*     -9  12 -13       -1  97  81
 -7   -   3*     -5  12  16      2  25  24       -5   -   6*     -8  29  32        0   -   4*
 -6  16  17      -4  72  61      3  17 -18       -4  25 -24      -7   -   2*       1  15  15
 -5   7  -6      -3  45 -36      4   8  11       -3  11  11      -6  23  32        2   -   2*
 -4  10  12      -2  24  30      5   -  -7*      -2   9   7      -5   -   5*       3  11  10
 -3  21  22       1  56  49      6  23  23       -1  26  27      -4  18 -18        4   -   2*
 -2  10  10       2  35  41      7  15  16       0  14 -16      -3  23  28        5  16  16
 -1   -  -6*      3   -  -5*     8   -   7*      1  10  10      -2  29  27        6   -  -3*
  0   -   1*      4  49  49      9   -  -3*      2  12  13      -1  58  30        7   -  11*
  1  15 -14       5  12  13     10  13  13      3  10   9       0  17  16        8   -   5*
  2   9  13       6  18  19     11   -  -3*     4   -   5*      1  60 -51        9  19  20
  3   9 -10       7   -  -9*    12  13  11      5   -   5*      2  55  49
  4  16  17       8  15  16                     6  12 -12       3   9  11           H  8  4
  5   6  -7       9   -   5*         H  6  3     7   -   7*      4  22  24      -8  25  22
  6  18  18      10   -   6*    -11  16  17      8   -  -3*      5  13 -14       -7   -   8*
                 11   -   0*    -10   -  -5*     9  12  10       6   -  -1*       -6   -  10*
     H 11  2      12  14  14     -9  11  11                      7  24  24       -5   -  10*
 -9   9  10                      -8   -   4*         H 11  3                      -4   -  11*
 -8   -   1*         H  2  3     -7  30  28      -8  14  15          H  3  4      -3  18  19
 -7  18  17     -11  22  21      -6   -  -6*     -7   -  -6*     -7  29  28       -2  44  37
 -6   -   1*     -10   -   1*    -5  30  29      -6  17  18      -6   -  -4*      -1   -  -7*
 -5  20  20      -9   -   2*     -4   -  -5*     -5   -   6*     -5  28  28        0  16  16
 -4   -   2*     -8  15  16      -3  24  26      -4  11  10      -4   -  -7*       1   -   2*
 -3  19  19      -7  20  19      -2   -   3*     -3   -  -2*     -3  43  44        2  38  36
 -2   -  -2*     -6  15  16      -1  30  32      -2  18  19      -2  14 -13
 -1   9  10      -5  21  20      0   -   1*     -1   -   1*      -1  17  18           H  9  4
  0   -  -3*     -4  62 -57      1  29  12      0  24  23       0  15  17       -7  15  13
  1  20  20      -3   -   5*     2   9   5      1   -   5*       1   -   4*      -6   -  -2*
  2   -  -4*     -2  19  18      3  18  19      2  25  26       2   7  -9       -5  18  19
  3  18  16      -1  74  64      4   -  -5*     3   -  -8*       3  15  17       -4  21  18
  4   -  -1*      0  36 -30      5  29  32      4   -  11*       4  22 -25       -3   -   7*
  5  33  32       3   -   0*     6   -  -5*     5   -   1*       5  35  34       -2   -   4*
  6   9 -10       4   -   6*     7   -   7*     6   -  10*       6   -   4*      -1  15  14
  7   9  10       5  20  23      8   -   0*                      7  24  25        0   -   7*
  8   -  -2*      6  12 -13      9  18  18         H 12  3                       1   -   0*
  9  11  11       7  13 -17     10   -   0*     -7  14  14          H  4  4       2   -  -9*
                  8   -  -3*    11  12   9      -6   -   0*     -10  14  13       3  14  13
     H 12  2      9  27  25                     -5  16  16       -9   -   1*      4   -   1*
 -8   9   8                         H  7  3     -4   -   8*      -8  26  22       5  15  14
 -7   -   5*         H  3  3    -10  15  15      -3  11  11      -7   -  11*
 -6   -  16*     -12  14  13     -9   -  -3*     -2  13  12      -6  51  51           H 10  4
 -5   -   2*     -11   -  -1*    -8  13  13      -1  20  20      -7   -  11*      -6  15  16
 -4  12  13     -10  10   9      -7   -  -1*      0   -   1*     -5   -  -3*      -5   -  -4*
 -3   6  -7      -9   -   2*     -6  56  56      1  14  12      -4  27  28       -4  20  19
 -2  22  20      -8  25  25      -5   -   4*     2   -  -4*      -3   -   2*      -3   -   6*
 -1   9   9      -7   9 -10      -4  21  22      3  14  15      -2  14  13       -2   -   9*
  0  10  13      -6   -   5*     -3   -   3*     4   -   4*      -1  36 -29       -1   -   4*
  1   -   3*     -5  10   9      -2  18  18      5  11  13       0  23  25        0   -   9*
  2  13  13      -4  31  31      -1   -  -8*                     1   7  10        1  18 -18
  3   -   0*     -3  16 -17      0  12  14         H 13  3       2  13  10        2  13  12
  4  23  22      -2  32  30      1   -   7*     -6  13  11       3   8   9        3   -   4*
  5   -  -7*     -1  54 -51      2  26  31      -5   -   2*      4  83  74        4  17  16
  6  12  12       0  26  25      3   -   2*     -4  12  12
```

*Table 8. Continued.*

```
    H 11   4       0   24   22      10    7    7       7    8    7       0   19   20        H 13   6
 -7  18   18       1    -   -5*                        H 14   5        1   13    9       -1   12   11
 -6   -   -5*      2   45   40        H  8   5       1    -   10*       2    -   -5*       0    -   3*
 -5  16   17       3   13  -13     -7   22   21       2    -   2*       3   42   39       1    -   2*
 -4   -    0*      4    -    4*     -6    -   -3*      3    9   10       4    9   11       2    -   1*
 -3  24   23       5    -    5*     -5   17   17                        5   16   16       3   15   14
 -2   -   -3*      6    -    2*     -4    -   -4*      H 15   5        6    -   -2*
 -1  23   23       7    -   -1*     -3   26   26      0    9    8       7   17   17        H  0   7
  0   -    1*      8   21   19      -2   14   16                                         -11   12   13
  1   -    5*      9    -   -6*     -1    6    9       H  0   6        H  6   6          -9   14   16
  2   -   -1*     10   10    9       0    -    6*    -12   25   24     -5   23  -30       -7   40   36
  3  17   15                        1    8    9*    -10    -    6*     -4    9    9       -5    -   6*
  4    -    0*      H  4   5         2   14   17     -8    -    6*     -3    -   2*       -3    -   6*
  5  17   16      -9   13   13       3   31   30     -6    -   10*     -2   45   46       1    9   11
  6    -    1*     -8    -   -4*     4    -   2*     -4    -   -4*     -1   25  -27       3   65   55
  7  16   15      -7    6    8       5   15   14     -2    -  107*      0   24   24       5    8    8
                  -6   10  -11       6    -    3*     2   45   41      1   13   22       7   24   25
    H 12   4      -5   39   36       7   13   14      4   21   20      2   21   21
 -6  15   15      -4    -    1*                       6    -   4*      3    -   7*        H  1   7
 -5   -    3*     -3   20   20       H  9   5        8   30   30      4   23   18      -13   12    3
 -4  17   15      -2   25   24     -6    -    9*                       5    -   -6*      -12   14   14
 -3   -    2*     -1   60   50     -5    -   -4*      H  1   6        6    -   9*       -11    -   6*
 -2  16   15      0    9   -8     -4    -   -2*     -8    -   -1*     7    -   1*       -10    -   9*
 -1   -   -5*      1   42   43     -3    -   -1*     -8   15   18      8   19   19       -9   19    6
  0  17   18      2    -    1*     -2   22   24     -7    -   -2*                        -8   20   20
  1   -   11*      3   11   12     -1    9   -9     -6    -   1*       H  7   5         -7   11   13
  2   -   10*      4   12  -13      0   21   23     -5   21   24     -9   15   13       -6   13   14
  3   -    8*      5   27   29      1   23   24     -4   15   10     -8    -   -6*       -5    -   9*
  4  17   15       6    -    4*     2    9   10     -3    -   29*      -7   10   12      -4   26   28
                   7    -    0*     3    -    3*     -1   69    9     -6    -   4*        -3    -   5*
    H 15   4       8    -    3*     4    -    6*      1    -    1*     -5    -   6*        2   23   21
 -1  18   17       9   21   20      5    -    4*      2    -    1*     -4    -   -7*       3   30   28
                                   6    -   -1*      3   15   16     -3   19   17        4   33   30
    H  0   5       H  5   5        7    -   -1*      4   15  -16     -2   13  -15        5    -   2*
-11   9    9     -12    8    8      8   11   10      5   22   21     -1   24   23        6   27   27
 -9   -    2*     -11    -   -2*                      6   23   24      0    -   9*        7    -   4*
 -7  61   58      -10   10    8       H 10   5       7    9    9      1   43   49        8   10   10
 -5  51   50      -9    6   -9     -9    8    7       8    -   7*       2    -   -7*
 -3  50   51      -8   20   21     -8    -   -9*      9   13   12      3   11   13        H  2   7
  3  70   61      -7    -   -6*     -7    8    7     10    -   4*       4   13   14      -7   12   12
  5  46   44      -6   18   17     -6    -   -2*     11   13   11      5   11   11       -6    -   3*
  7  29   27      -5   12   14     -5    7    4                                         -5    -   -2*
  9   9   12      -4    -   -2*     -4   12  -14      H  2   6        H  8   6          -4    -   2*
                  -3    -    0*     -3   14   14     -7   10   -9     -3    9   10        -3   14   15
    H  1   5      -2   74   64     -2    -    0*     -6   11   12     -2   35   32       -2   20  -20
-16   8    8      -1   10   11     -1   20   18     -5   12   11     -1    -   -2*       -1   11   10
 -9   6    9       0   26   27      0    -   -5*     -3    -   4*       0   14   14        0   15   14
 -8  31   30       1    -    0*     1   19   21     -2    -   1*       1    -   5*        1   22   21
 -7  21   23       2   44   39      2    -   -2*     -1   13   16      2   21   19        2    -   6*
 -6  24   25       3    -   -3*     3    8    9      0   22   19      3   10   10        3   33   30
 -5   -   -3*      4    -    0*     4    -    5*      1   14  -14      4   13   12        4   10   10
 -4  43   42       5    -   -2*     5   10    9      2   16   13      5    -   -2*       5    7    8
  1  80   73       6    8    7      6   10   -9      3    -   -3*      6    -   5*        6    -   -2*
  2  32   26       7    -    2*     7    -    5*      4   31   28      7    -  11*       7   15   13
  3  13   16       8   23   22      8    -    4*     5    -   5*       8   17   16        8    -   -3*
  4  34   28       9    -    5*     9    7    7      6    -    2*                        9   10   11
  5   4    6      10    8    9                       7    -    5*      H  9   6
  6  16   18                        H 11   5        8   24   22     -5   13   12        H  3   7
  7   5   -8       H  6   5       -8    9   10                      -4    -   4*      -12   14   14
  8  20   20     -11    7    7     -7    8   -6       H  3   6       -3   10   11      -11    -   1*
  9   -    1*     -10   13  -13    -6   10   10     -7   22   23     -2    -   2*      -10    -  14*
 10  10   10      -9    -    5*     -5    -   -6*    -6    -   -5*      3   16   17       -9    -   0*
 11   7    7      -8    6   -4     -4    9    9     -5   15   17      4    -   -2*       -8    -   3*
                  -7   28   26     -3    -    3*    -4    -   7*       5   12   13       -7    8    8
    H  2   5      -6   14  -15     -2   25   27     -3   15   15      6    -  12*       -6    9   10
-11   9    7      -5   33   32     -1   15   -9     -2   24  -24      7    -   7*       -5   19  -19
                  -4   18   17      0   15   14     -1    -   3*      8    -   2*       -4    -   1*
    H  1   5      -3   29   30      1    -    0*     0   10  -10      9    -   5*       -3    6   -7
-10   -    8*     -2    8    9      2   20   20      1   33   34                        -2   40   35
                  -1   22   20      3    -   -2*     2    -   -6*      H 10   6         -1    -   5*
    H  2   5       0   11   -9      4   15   16     3    -   -4*     -7   11  -10        0   13   13
 -9   -   -3*      1   13   13      5    -   -1*     3   41   38     -6    -   8*        1    5    7
 -8   -    0*      2    6   -6     6    -    4*     4    -   -7*     -5    -   -7*       2    8   10
 -7  22   22       3   31   29      7    -    2*     5   14   14     -4   13   12        3    7   -8
 -6  13   14       4   13  -14     8   11   11      6    -   1*      -3    -   -8*       4   19   17
 -5  33   36       5   29   26                      7   15   14     -2   11   12        5    8   -9
 -4  26  -24       6    6    5       H 12   5                       -1    -   -6*       6   10   12
 -3  27   30       7   15   16    -9   11    5       H  4   6        0    -   6*        7    -   -1*
 -2   -    2*      8    -    5*    -5   14   14     -8   14   14      1    -   -7*       8   16   16
 -1   -   39*      9    7    6     -4    -   5*     -7    -    1*      2   12   11
  0   7    8                       -3   10   12     -6    9    8      3    -   -2*       H  4   7
  1  12  -10       H  7   5        -2    7    8     -5   13  -15      4   15   16       -9   21   20
  2  13   14     -12    8    7     -1   14   17     -4   31   29      5    -   -2*       -8    -   3*
  3  28   29     -11    -   -1*     0   16    3     -3    -   -2*      6   12   13       -7   10   12
  4  24   21     -10    -    5*     1   17   16     -2   27   26                        -6    -   0*
  5   4   19      -9    -   -4*     2    -    1*    -1   14  -14       H 11   6         -5    9  -11
  6  17  -18      -8   19   19     3   12   19     0   21   19     -7   21   20        -4    -   6*
  7  11   12      -7    7  -11     4    -    0*      1    -    9*     -6    -   -5*       -3   24   22
  8   5    5      -6   22   23     5   12   12      2   16   17     -5    -   7*        -2    -   -3*
  9   6    7      -5    5    6                       3   12   13     -4    -   -8*       -1   12   12
                  -4   39   38      H 13   5        4   36   31     -3    -   9*        0   13  -11
    H  3   5      -3    -   -2*    -8    9    8      5    9  -10     -2    -   -6*       1   47   40
-12  10   10      -2   12   13    -7    -   -5*     6   18   19     -1    -  10*        2    -   -7*
-11   -   -6*      -1   11   12    -6    -   9*      7    -   1*      0    -   -5*       3   10   12
-10   -    3*      0   21   20    -5    -   2*      8   12   12      1   12   11        4    -   -6*
 -9   -    3*      1    7   -8     -4    -   1*                       2    -   -1*       5    -   3*
 -8  20   21       2   13   14    -3    -   3*       H  5   6        3   23   23        6    -   5*
 -7  14  -17       3    -    1*    -2   17   17     -7   11    9                        7   13   15
 -6   -    4*      4   49   44    -1    -   6*     -6    -   4*       H 12   6         8    -   2*
 -5   -   -5*      5    -    2*     0    9    9     -5   21   23     -4   16   15        9   12   12
 -4  16   18       6   12   12     1    -   -3*    -4   20  -22     -3    -   -1*
 -3   -    2*      7    -    3*     2   11   12     -3   22   22     -2    -   4*        H  5   7
 -2  73   58       8   13   13     3    -   4*     -2    -   -6*     -1    -   -6*      -10   10   10
 -1   6   -4       9    -    1*     4    9    8     -1   21   21      0   13   13       -9    -   1*
```

*Table 8. Continued.*

```
-8  11  12      0   -   6*      -4   -   0*      -2   8   -9      -9   7   7       6    8    9
-7   -  -4*      1   -  -8*      -3  21  22      -1  19  19      -8   -   0*
-6  17  17      2   -   8*      -2  10 -12       0  10  12      -7   8   9        H  7 10
-5  19  20      3   -  -4*      -1  15  16       1  11  11      -6   9  11      -7   7   7
-4   -   8*      4   -   8*       0  19  20       2  11  11      -5   8   8      -6   -   0*
-3   -  -1*      5   -  -5*       1   -  10*      3  10   8      -4   4   4      -5   5   5
-2  16  13      6   -   7*       2   -   0*       4   -   2*      -3  13  15      -4   -  -1*
-1   -   4*      7   -   1*       3   -   6*       5   -   0*      -2   -   8*      -3  20  18
 0  16  16      8  12  12        4   -   2*       6   -   3*      -1   -  16*      -2   -   0*
 1  21 -22                       5   -   7*       7  13  13       0   -  -1*      -1  10   9
 2  18  17      H 12  7          6   -  -9*                       1  16  16       0   -   0*
 3   -  -6*      -3  13  14      7  16  14       H  3  9          2   -   2*       1  12  12
 4  25  26      -2   -   2*                      -4  15  17       3  13  17       2   -   2*
 5   -   6*      -1   -   7*      H  6  8        -3  12 -14       4   6   6       3  12  10
 6   -   7*       0   -  -3*     -8  18  17      -2  12  13       5   8   8       4   -   2*
 7   -   1*       1  14  14      -7   -   5*     -1   -   6*       6   -   4*       5   -   5*
 8  15  16                      -6  16  17       0  45  35       7  10   9        6   -   4*
                 H 13  7        -5   -  -9*       1   -  -4*                       7   8   8
 H  6  7        -6  11  11      -4  16  17       2   -   7*       H  2 10
-13  13  10                     -3   -  -6*       3  11  12      -10  13  11       H  8 10
-12   -   1*     H  0  8        -2  15  14                       -9   -   2*      -10   -   8
-11   -   8*     -6  24  26      -1   -   2*      H  4  9        -8   9  10       -9   -   2*
-10   -  -5*     -4   9  13       0  16  15      -3  40  33       -7   -   1*      -8   6   5
-9  16  17       2   -   5*      1   -   2*      -2   -  -4*      -6   7   7       -7   -   2*
-8   -   4*      4  19  19      2  12  14       -1  12  13      -5   -   5*       -6   -   2*
-7  17  16       6   -   4*      3   -   1*       0   -   5*      -4  15  15      -5   -   5*
-6   -   0*      8  19  19      4   -  10*        1  15  16      -3   5   8       -4  12  12
-5  12  13                      5  14 -13        2   -   4*      -2   9  12       -3   -   4*
-4   8  10      H  1  8                          3  12  12       -1   -  -6*      -2   7   7
-3  14  15      -9  21  23      H  7  8                          0  11  12       -1   -  -1*
-2   -   0*      -8   -   5*     -9  16  14       H  5  9         1   -   5*       0  18  18
-1   8   8      -7  13  14      -8   -  -2*      -6  14  16       2  29  26        1   -   2*
 0  23 -25      -6   -  11*     -7   -  11*     -5   -   1*       3   -  -4*       2   6   6
 1  17  16      -5   -   9*     -6   -   4*      -4  18  18       4  10   9        3   -   0*
 2   -   3*      -4   -   6*     -5   -   8*     -3   -   5*       5   6   6        4   -   4*
 3  29  27      -3  33  35      -4   -   8*     -2  13  14        6  12  10        5   -  10
 4  12 -14      -2   -  13*     -3  26  23      -1   -   4*                        6   8   6
 5  11  12      -1   -  11*     -2   -   0*      0  21  19       H  3 10
 6   -   9*       0   -   9*     -1   -  10*      1   -  -2*      -9   9   8        H  9 10
 7  14  15       1  26  25       0   -   9*      2  14  14       -8   -  -4*      -7   9   9
                 2   -   5*      1  17  15                        -7   7   7       -6   -   1*
 H  7  7         3   -  -2*      2   -  -4*      H  6  9         -6   -   1*       -5   -   6*
-8  15  14       4   -   3*      3  11  11      -7  16  12       -5  18  16       -4   -   0*
-7   -   2*      5   -   3*                     -6   -   -3*     -4   -  -6*       -3  11  11
-6  12  13       6   -   1*      H  8  8        -5   -  13*      -3  10  10       -2   -   2*
-5   -   6*      7  19  18      -6  15  13      -4   -   1*      -2   -   2*       -1   6   7
-4  20  19                     -5  14  13      -3  29  26       -1   5   5        0   -  -1*
-3   -  -6*      H  2  8        -4   -  10*     -2   -   4*       0   -  -2*       1  10   9
-2  18  19      -8  27  24      -3  16  17      -1  12  12       1  15  14        2   -  -3*
-1   -   4*      -7   -  -5*     -2  14  13       0   -  -3*      2   7  -8        3  13  12
 0   -  -1*      -6  27  26      -1   -   6*      1  11  11       3  16  14        4   -   4*
 1   -  -4*      -5  11  12      0  12  11       2   -   2*       4   -   3*       5   -   3*
 2  12  14      -4  19  19                       3  11  11       5  19  17        6   -   3*
 3   -  -8*      -3  14  14      H  9  8                                          7   9   8
 4  19  19      -2   9   9     -3  19  20       H  7  9         H  4 10
 5   -   2*      -1   -   3*    -2   -  11*     -8  15  15      -10   7   6        H 13 10
 6  23  23       0   -   1*    -1   -   7*     -7   -   0*      -9   -   0*       -6   9   9
                 1   -   2*     0   -   0*     -6  12  11       -8  13  12       -5   -   0*
 H  8  7         2  15  18      1  14  11      -5   -   0*      -7   -  -2*       -4  15  10
-9  11  10       3   -  -14*                   -4  13  13       -6   -   4*       -3   -  -0*
-8  11  11       4  16  12      H 10  8        -3   -   0*      -5   -  -2*       -2   7   7
-7  13  14                     -4  13  12      -2  11  10       -4   9   9        -1   -  -0*
-6   -   8*      H  3  8        -3   -   5*     -1   -   5*      -3   4  -4        0   8   8
-5   -   8*     -9  18  16      -2   -   5*      0  11  11       -2  14  11       1   -   0*
-4   -   6*     -8   -  -10*    -1   -   0*      1   -   4*      -1   6  -5        2   9  10
-3   8   8      -7  16  15      0   -   8*      2  16  17                         3   -  -3*
-2   -  -4*      -6   -   5*     1   -  -1*                     H  5 13          4   -   4*
-1  10  10      -5  25  27      2  13  10      H  8  9          -9   8  10        5   -   2*
 0   -   2*     -4   -  -1*                    -5  17  16       -8   -   4*       6   8   8
 1   -   7*     -3   9  10      H 11  8        -4   -   4*      -7   9   8
 2   -   4*     -2  13  14      2   -  -1*     -3   -   9*      -6   -  -3*       H 11 10
 3  20  19      -1   -   6*     3  17  16      -2   -  -2*      -5  15  14       -5   8   9
 4   -   3*      0  13 -15      4   -  -5*     -1   -   9*      -4   5  -5        -4   -  -4*
 5   -   8*      1   -   0*                     0  14  16       -3   9   9        -3  10   9
 6   -   5*      2   -  -8*     H 12  8         1   -   7*      -2   6  -5        -2   -  -3*
 7  11  12      3  15  17      1   -   4*      2  13  13       -1  11  11        -1   -   3*
                4   -  -5*     2  14  12                        0   -  -2*       0   -  -2*
 H  9  7         5   -   8*     3   -   3*     H  9  9          1  17  17        1   8   7
-8  12  12       6   -   1*                    -2  12  12       2   -   5*       2   -   0*
-7   -  11*      7  15  14      H  9  9        -1   -   9*      3  14  15        3   -   7*
-6   -   8*                     -9  12  11      0   -   3*      4   -   0*       4   -   1*
-5   -  -4*     H  4  8        -7  11  12      1   -   3*      5  12  11        5   8   8
-4  10  10      -8  25  21     -5  24  25      2  14  15       6   -   1*
-3   -   1*     -7   -  -3*    -3  18  24                      7   7   7        H 12 10
-2   -   5*     -6  20  20     1   8   9      H 10  9                           -2   7   7
-1   -  -4*     -5   -   1*    3  24  22      -3  16  14       H  7 13          -1   -   1*
 0   -   7*     -4  19  22                                    -10   9   9       0   -   5*
 1   -   1*     -3   -   6*    H 13  9        H 11  9         -9   -   2*       1   -   2*
 2  13  12      -2  10  11     -8  13  13      0  14  13       -8   7   8       2   7   7
 3   -   4*     -1   -  -4*    -7   -  19*                     -7   -  -1*
 4  12  12       0  11 -13     -6  16  19      H  0 10        -6   6   6        H 13 10
                 1   -   3*    -5   -   0*     -10  13  11      -5   -   3*      -4   -   1*
 H 10  7        2  14  17     -4  22  23      -8  13  11       -4  14  14       -3   7   8
-3  11  12      3   -  -2*    -3   -   5*     -6   6  -6        -3  14 -14       -2   -  -1*
-2  17 -18      4  13  13     -2   -  13*     -4   9  14       -2  12  12       -1   7   5
-1  10  10                    -1   -  12*     2  15  15       -1   -  -1*       0   -   3*
 0   -  -2*     H  5  8        0  15  17      6   8   9        0  15  15        1   7   7
 1  14  14      -9  13  17     1   -   6*     8   7   7        1   -   2*
                -8   -   2*    2  22  22                       2  17  17
 H 11  7        -7  14  15                    H  1 10         3   -   5*
-2  28  25      -6   -   2*    H  2  9        -11   8   7      4   -   6*
-1   -  -6*     -5  14  12     -3  48  41     -10   -   2*     5   -   2*
```
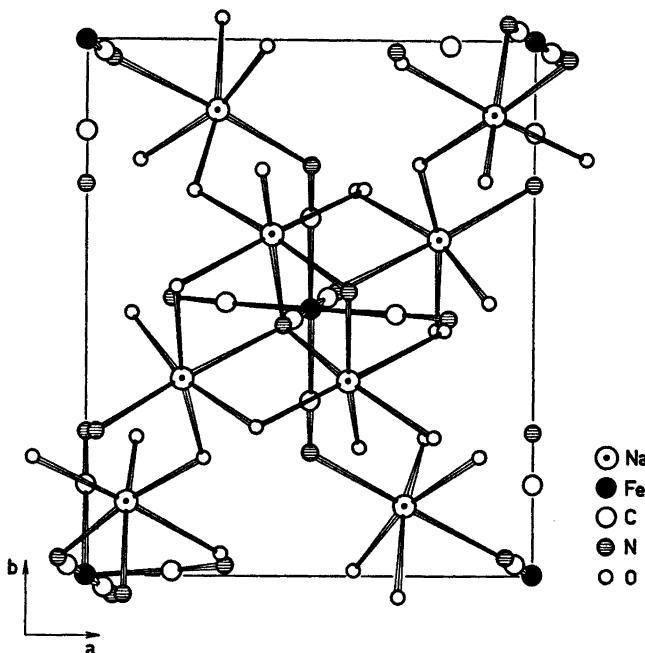
*Fig. 1.* Perspective view of $Na_4[Fe(CN)_6].10H_2O$ along the *c*-direction. Full lines indicate one unit cell. The atoms shown do not all belong to the same unit cell. Some nitrogen and oxygen atoms belonging to two neighbouring unit cells are drawn double with a small separation in the *a*-direction.

distances vary between 1.147(3) and 1.187(2) Å (mean 1.167 Å), while in $Na_4[Fe(CN)_6].10H_2O$ the C−N distances are 1.180(10), 1.165(10), and 1.174(10) Å. The Fe−C−N atoms are almost linear in both structures; the greatest deviation of a Fe−C−N angle from 180° is 2.6° in $K_4[Fe(CN)_6].3D_2O$.

A report on the structure of $H_4Fe(CN)_6$ has also been published.[13] The $[Fe(CN)_6]^{4-}$ ions are regular octahedra with Fe−C and C−N bond distances of 1.89(1) and 1.15(1) Å, respectively.

As may be seen from Table 9 the Fe−C distances in the Fe(II) compounds are shorter than the Fe−C bond distances found in Fe(III) cyanide compounds. The probability that the mean bond length differ in $Na_4[Fe(CN)_6].10H_2O$ and $K_3[Fe(CN)_6]$ is 99%. However, even if they were equal this result can only be interpreted as a proof of strong π-bonding in the Fe(II)−C bonds.

The mean values of the Mn−C and C−N bond distances found in $Na_4[Mn(CN)_6].10H_2O$, *i.e.* Mn−C=1.95(3) Å and C−N=1.16(3) Å, may be compared with those found in

$K_3[Mn(CN)_5NO].2H_2O$,[10] *i.e.* Mn−C=1.98(1) Å and C−N=1.16(1) Å (mean values) and in $K_3[Mn(CN)_6]$,[11] Mn−C=2.00(1) Å and C−N= 1.14(1) Å (mean values). Thus even here it is
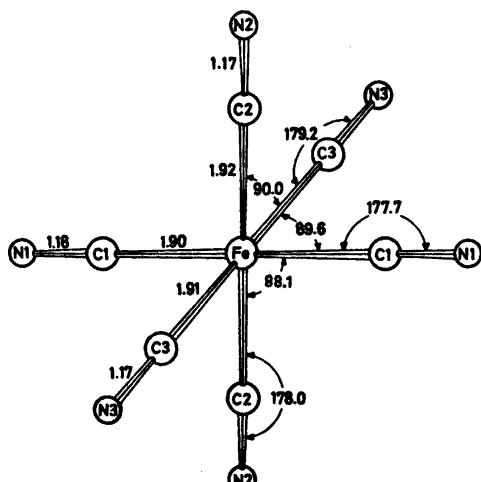


*Fig. 2.* The $[Fe(CN)_6]^{4-}$ octahedron.

*Table 9.* Comparison of bond lengths in hexacyanido complex ions.

| Central atom | Compound | Me – C distance | Mean | C – N distance | Mean |
|---|---|---|---|---|---|
| $Fe^{II}$ | $Na_4[Fe(CN)_6] \cdot 10H_2O$ | 1.902(7)<br>1.906(7)<br>1.920(8) | 1.909 | 1.180(10)<br>1.174(10)<br>1.165(10) | 1.173 |
| $Fe^{II}$ | $K_4[Fe(CN)_6] \cdot 3D_2O^a$ | 1.908(4)<br>1.956(4)<br>1.920(2)<br>1.915(2) | 1.925 | 1.184(3)<br>1.147(3)<br>1.150(2)<br>1.187(2) | 1.167 |
| $Fe^{II}$ | $H_4[Fe(CN)_6]$ | 1.88(1)<br>1.88(1)<br>1.91(1) | 1.89 | 1.14(1)<br>1.16(1)<br>1.15(1) | 1.15 |
| $Fe^{III}$ | $K_3[Fe(CN)_6]$ | 1.93(1)<br>1.95(2)<br>1.97(2) | 1.95 | 1.13(2)<br>1.13(2)<br>1.17(3) | 1.14 |
| $Mn^{II}$ | $Na_4[Mn(CN)_6] \cdot 10H_2O$ | 1.91(2)<br>1.95(1)<br>1.98(1) | 1.95 | 1.14(2)<br>1.14(2)<br>1.19(2) | 1.16 |
| $Mn^{III}$ | $K_3[Mn(CN)_6]$ | 1.98(2)<br>2.00(1)<br>2.02(1) | 2.00 | 1.15(2)<br>1.13(2)<br>1.14(2) | 1.14 |

*a* The structure of $K_4[Fe(CN)_6] \cdot 3D_2O$ is disordered [12,15] with a disorder of the so called OD type (for nomenclature, see Ref. 16). Therefore the stated standard deviations may be under-estimated.

evident that the $\pi$-bonding in Mn(II) – C is so large that the bonds are equal or even shorter in length than in the Mn(III) complex.

REFERENCES

1. Philips, C. S. G. and Williams, R. J. P. *Inorganic Chemistry*, Clarendon Press, Oxford 1966, Vol. 2, pp. 272 – 275.
2. Alexander, J. J. and Gray, H. B. *J. Amer. Chem. Soc.* 90 (1968) 4260.
3. Alexander, J. J. and Gray, H. B. *Coord. Chem. Rev.* 2 (1967) 29.
4. Vannerberg, N.-G. *Acta Chem. Scand. 24* (1970) 2335.
5. Vannerberg, N.-G. *Acta Chem. Scand. 26* (1972) 2863.
6. Tullberg, A. and Vannerberg, N.-G. *Acta Chem. Scand. 25* (1971) 343.
7. Brauer, G. *Handbuch der präparativen anorganischen Chemie*, Ferd. Enke, Stuttgart 1962, Vol. II, p. 1286.
8. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1962, Vol. III.
9. The program library of the Dept. of Inorg. Chem. Göteborg. DATA P1 and BLOCK have been written locally by O. Lindgren, DATA P2 was originally written by Coppens, Leiserowitz and Rabinowich (1965), DRF by A. Zalkin, Berkeley, California and LALS by P. Gantzel, R. Sparks and T. Trueblood.
10. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
11. Cruickshank, D. W. J. *The Equations of Structure Refinements*, Glasgow 1964.
12. Taylor, J. C., Mueller, M. H. and Hitterman, R. L. *Acta Crystallogr. A 26* (1970) 559.
13. Pierrot, M., Kern, R. and Weiss, R. *Acta Crystallogr. 20* (1966) 425.
14. Tullberg, A. and Vannerberg, N.-G. *Acta Chem. Scand. 21* (1967) 1426.
15. Pearson, W. B., Ed., *Structure Reports 11* (1947) 421, 424; *24* (1960) 300.
16. Dornberger-Schiff, K. *Lehrgang über OD-Strukturen*, Akademie-Verlag, Berlin 1966.