The OD-structure of K₃Mn(CN)₆

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The crystal structure of potassium hexacyanomanganate(III) has been solved by 3-dimensional X-ray methods. Potassium hexacyanomanganate(III) has an OD-structure consisting of ordered layers whose stacking is disordered. The OD-groupoid can be formulated as:

\[ P \; (n); \; c; \; m \]
\[ n_{1}; \; n_{2}; \; c_{3} \]

The complex ion has the symmetry \( D_{3d} \) with manganese-carbon bond lengths of 1.981 Å, 1.999 Å and 2.025 Å, \( \sigma = 0.014 \) Å.

Cyanide complexes and, in particular, hexacyanide complexes of transition metals are well-known species. Their absorption spectra have been investigated thoroughly and interpreted on the basis of a very strong crystal field due to the cyanide ions.¹ More recent investigations based on ligand field models show that metal-ligand \( \pi \)-bonding is of importance.²

A number of pentacyanonirosyl complexes have been investigated at this Department.³⁻⁶ In these compounds, the \( \pi \)-bonding between the metal and the cyanide group is probably small due to the extremely strong \( \pi \)-bonding between the metal atom and the nitrosyl group. A comparison of the pentacyano and the hexacyano complexes ought thus to provide information concerning the nature of the chemical bonding in metal cyanide complexes.

Unfortunately, there are no reliable crystal determinations of hexacyanides. Many investigations have, of course, been performed, but they show little agreement, due to the fact that all the structures so far studied have been disordered and that the resulting problems have not been tackled with the appropriate methods (cf. Table 1).⁷⁻⁻¹³ Consequently, the structure of potassium hexacyanomanganate(III) has now been determined.

Potassium hexacyanomanganate(III) was prepared according to the method of Lower and Fernelius, whereby an aqueous solution of manganese(III) orthophosphate, prepared from manganese dichloride, nitric acid, and phosphoric acid, is treated with an excess of potassium cyanide.¹⁴ Apparently well-developed crystals were obtained.

Accurate cell dimensions were determined from Guinier powder photographs using potassium chloride as an internal standard and CuKα₁ radiation \([\lambda(CuKα₁) = 1.54060 \text{ Å}]\). About thirty reflexions were indexed with the program Xalg Powder and the same program was used to refine the cell constants.¹⁵ The reflexions could be indexed both by assuming an orthorhombic and a monoclinic unit cell (Tables 2 and 3).

### Table 1. Historical summary. Dimensions in Å units.

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### Table 2. Unit cell dimensions for K₃Mn(CN)₆.

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Table 3. Observed and calculated sin^2 values for $K_2\text{Mn(CN)}_4$.

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Single crystals of potassium hexacyanomanganate(III) were rotated about the c-axis in a photographic Weissenberg camera and in a Philips Pailred diffractometer. The diffractograms had the following feature in common: all layers for which $l=2L$, where $L$ is an integer, contained sharp reflexions with reciprocal coordinates $HKL$ corresponding to axes of $13.529 \text{ Å}$, $10.501 \text{ Å}$, and $4.218 \text{ Å}$ in direct space. The relative intensities of two different reflexions were the same for all crystals. On the other hand, layers for which $l=2L+1$ contained diffuse streaks with pronounced maxima. The reciprocal coordinates of the streaks are $\xi, k, l$. One unit in the $\xi$ direction in reciprocal space is defined as corresponding to a distance of $6.765 \text{ Å}$ in direct space, i.e. this distance, which is called $\alpha_{\xi}$, is the separation between two layers which will be seen later on. The relation between the intensity maxima of these streaks vary from crystal to crystal. The crystal from which the Pailred diffraction data were collected was a small prism, $0.014 \text{ cm long}$, with a rhombic basal plane of dimensions $0.0035 \times 0.0036 \text{ cm}^2$. The c-axis was parallel to the prism axis while the orthorhombic a and b axes were parallel to the diagonals of the basal plane. This crystal showed rather sharp and well-defined maxima on the odd layer lines. The separation between the reflexions in these layer lines corresponded to an $a$-axis of $27.058 \text{ Å}$. Maxima for which $\xi=n\pm l/4$ did not have equal intensities for $\xi kl$ and $\bar{\xi} kl$ while $\xi kl$ and $\bar{\xi} kl$ reflexions for which $\xi=n/2$ were of equal intensity. The former reflexions thus show monoclinic

Table 4. Extinction rules for the OD Structure of K₃Mn(CN)₆.

| i | \( \xi k l \) | absent for \( l = 2L \) if \( \xi = H \) |
| ii | \( H k L \) | absent for \( H + L = 2n + 1 \) |
| iii | \( \xi 0 l \) | absent for \( l = 2n + 1 \) |
| iv | \( 0 k l \) | absent for \( k = 2n + 1 \) and \( l = 2n + 1 \) |

symmetry, while the latter show orthorhombic symmetry. A total of 851 sharp reflections and 250 intensity maxima were registered.

The conditions for the systematic absences may be summarized as in Table 4. The readers not familiar with the notation in this paper are recommended to study Ref. 16. It is evident that a structure denoted by \( \tilde{\phi}(xyz) \) which is related to the true structure by

\[
\tilde{\phi}(x,y,z) = \phi(x,y,z) + \phi(x,y,z + \frac{1}{2})
\]

is, according to (i) and (ii), periodic with the translation vectors \( \vec{A} = \vec{a} \), \( \vec{B} = \vec{b} \), and \( \vec{C} = \vec{c}/2 \).

This “superposition structure” shows B-face centering, whereas the true structure is not periodic in the \( \vec{a} \)-direction but periodic in the \( \vec{b} \)- and \( \vec{c} \)-directions.

According to condition (iii), for every atom in \( (xyz) \) there must be another in \( (x',y',\frac{1}{2} + z) \) and, as the \( x \)-coordinates are identical, the atoms must be situated in the same plane, and linked by a \( c \)-glide perpendicular to \( b \). Condition (iv) implies that for each atom in \( (x,y,z) \) there must be an identical atom in \( (x',y + \frac{1}{2}z + \frac{1}{2}) \) and this holds true whether the packing of layers is disordered or not, which means that the two atoms must belong to the same layer. The minimum symmetry of a single layer is thus \( P(n)c2 \) but, owing to the high symmetry of the building units, the actual symmetry is probably \( P(n)cm \).

The B-face centering of the superposition structure shows that adjacent layers are linked by the translation:

\[
\frac{\vec{c}}{4} + \vec{a}_0 \text{ or } -\frac{\vec{c}}{4} + \vec{a}_0
\]

where \( \vec{a}_0 \) is the vector between two successive layers. Thus the OD-groupoid can be formulated as:

\[
P(n); \quad c; \quad m
\{
\{n_1, \tilde{n}_1, n_2, \tilde{n}_2, a_2\}
\]

Fig. 1. A diagram of the symmetry elements in the OD-groupoid family \( P(n) c m/n_1, \tilde{n}_1, a_2 \).
An open triangle corresponds to a structural element at \( y \), a filled triangle to one at \( \tilde{y} \), a horizontally shaded triangle to one at \( \frac{1}{2} + y \) and a vertically shaded triangle to one at \( \frac{1}{2} - y \).
There are two possible structures of maximum degree of order, so-called "MDO-structures". The structure in which the layers are packed obliquely over one another, denoted MDO$_2$, would have space group $P2_1/c$, while the other, denoted MDO$_1$, has a "zig-zag" packing of layers and would have space group $Pnca$. The cell dimensions of the two structures are given in Table 2 (see figs. 1 and 2).

![Diagram of structures]

*Fig. 2. The sequence of layers in the structures of maximum degree of order MDO$_1$ and MDO$_2$. The symbols for $y$-coordinates are the same as in Fig. 1.*

The intensity material was divided in four parts:

(a) 850 sharp reflexions or family reflexions, with indices $HkL$, belonging to the periodic superposition structure.
(b) 105 intensity maxima at $2L+1$ and $\xi = n/2 \ (n=\text{integer})$ belonging to the orthorhombic MDO$_1$ structure.
(c) 120 intensity maxima at $2L+1$ and $\xi = n+(l/4) \ (n=\text{integer})$ belonging to the monoclinic MDO$_2$ structure.
(d) 10 weak intensity maxima at $2L+1$ and $\xi = n-(l/4) \ (n=\text{integer})$ belonging to a twinned monoclinic MDO$_2$ structure.

After the usual Lorentz, polarisation, and absorption corrections, the superposition structure was solved with the aid of a 3-dimensional Patterson synthesis based on the reflexions (a). From this synthesis the positions of the manganese and potassium ions were determined. A subsequent Fourier synthesis yielded the positions of all the light atoms.

The structure was refined by least squares methods to an $R$-value of 0.076. The positions of the atoms and some of the most interesting distances and angles are given in Tables 5 and 6.

Table 5. Atomic positions and temperature factors in the superposition structure. (\(MV=K\) or \(Mn\))

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Table 6. Interatomic distances and bond angles in the superposition structure of \(K_3Mn(CN)_6\).

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<td>C2</td>
<td>1.983 ± 0.010</td>
<td>N2 – N2 0.126 ± 0.032</td>
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<td>C1</td>
<td>2.010 ± 0.013</td>
<td>C1 – MV1 – C2 90.75 ± 0.38</td>
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<tr>
<td>N1</td>
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<tr>
<td>K1 – K1</td>
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<td>N1 92.66 ± 0.31</td>
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<td>N2</td>
<td>1.124 ± 0.034</td>
<td>MV1 – C1 178.10 ± 1.11</td>
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<td>C2</td>
<td>1.417 ± 0.022</td>
<td>C2 – N2 178.38 ± 1.93</td>
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For a detailed description of the structure a knowledge of the superposition structure only is not sufficient. In the superposition structure each atom appears at two different positions with a height corresponding to half the usual electron density. Atoms can thus come very close to one another causing low resolution. In this particular structure, for example, the manganese atom and one of the potassium ions totally overlap each other. It is therefore necessary to include the intensities of the diffuse streaks and especially of the maxima on these streaks in the structure analysis.

It can be shown that for the positions in reciprocal space \(\xi'kl\) and \(\xi''kl\), where \(\xi' = n/2\) and \(\xi'' = n + l/4\), for a given crystal the square of the Fourier transformed structure factor is proportional to the square of the structure factor for a single layer.\(^{16}\) As the monoclinic \(MDO_2\) unit cell contains one layer only, the family reflexions and the reflexions at \(\xi''kl\) can be combined by applying different scale factors to a set of reflexions whose structure factors are directly proportional to those of the \(MDO_2\) structure.

Table 7. Observed and calculated structure factors for the MDO₂-structure. The columns given are h, k, l, F₀, and Fₐ.

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Table 7. Continued.

Table 8. Atomic positions and vibrations in the MDO$_2$ structure.

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Standard deviations in positional and thermal parameters.

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<th>$\sigma(z)$</th>
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<td>0.0017</td>
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<td>0.0030</td>
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</table>

The probable positions in the MDO$_2$ structure were calculated from the known superposition structure. The structure was then refined with least squares methods. In the last three cycles so-called anisotropic temperature factors were used. The $R$-factor converged to 0.072. The observed and calculated structure factors, the positions and vibrations of the atoms and bond distances and angles are to be found in Tables 7, 8, and 9. The reflection maxima belonging to the orthorhombic MDO$_2$ structure were not mixed with the family reflections but refined separately regarding the space group as $Pnma$. The $R$-factor was of course considerably higher but the structure of the single layer in the MDO$_4$ region was proved to be the same as that in an MDO$_5$ region. A comparison between observed and calculated structure factors is given in Table 10.

Table 9. Bond distances and bond angles in the MDO₄ structure.

|       | 1.981 ± 0.015 Å | 180.00 ± 0.0 | 94.5 ± 0.4 | 85.5 ± 0.4 | 94.8 ± 0.4 | 85.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |
|-------|-----------------|--------------|-----------|-----------|-----------|-----------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mn1   | C3              | C1           | K1        | N1        | K2        | N2        | N3           | N2        | N1        | C1        | C3        | C1        | N1        | C2          | N3        | N1        | C1        | C2        | C1        | N1        | C2          | N3        | N1        | C1        | C2        | C1        | N1        | C2          | N3        | N1        | C1        |
| C2    | 2.989 ± 0.014   | C2           | 94.5 ± 0.4 | 85.5 ± 0.4 | 94.8 ± 0.4 | 85.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |
| C1    | 2.925 ± 0.014   | C1           | 94.8 ± 0.4 | 85.2 ± 0.4 | 94.2 ± 0.4 | 84.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |
| N2    | 3.130 ± 0.018   | N2           | 95.2 ± 0.4 | 83.4 ± 0.5 | 94.2 ± 0.4 | 84.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |
| N3    | 3.134 ± 0.014   | N3           | 95.2 ± 0.4 | 83.4 ± 0.5 | 94.2 ± 0.4 | 84.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |
| N1    | 3.164 ± 0.011   | N1           | 95.2 ± 0.4 | 83.4 ± 0.5 | 94.2 ± 0.4 | 84.2 ± 0.4 | 180.00 ± 0.0 | 86.3 ± 0.5 | 93.1 ± 0.5 | 84.8 ± 0.4 | 95.2 ± 0.4 | 83.4 ± 0.5 | 80.6 ± 0.5 | 85.2 ± 0.4 | 84.2 ± 0.4 | 93.3 ± 0.3 | 156.4 ± 0.5 | 73.3 ± 0.4 | 84.4 ± 0.4 | 122.6 ± 0.4 | 79.8 ± 0.5 | 142.4 ± 0.4 | 146.4 ± 0.4 | 78.0 ± 0.3 | 124.9 ± 0.7 | 89.1 ± 0.5 | 68.3 ± 0.5 | 85.8 ± 0.4 | 127.0 ± 0.4 | 176.8 ± 1.0 | 177.7 ± 1.6 | 176.8 ± 1.4 |

THE FORMAL CHARGE ON THE MANGANESE ATOM

There are three main features of the metal-ligand bonds which can influence the formal positive charge on the central ion:

a) The σ-bonds which decrease the charge on the manganese atom.
b) The π-bonds, $t_2g \rightarrow a^*$, which increase the charge on the manganese atom.
c) The π-bonds, $\pi \rightarrow t_{2g}$, which decrease the charge on the manganese atom.

In order to obtain a rough estimate of the formal charge, the structure was refined, as mentioned above, by using scattering factors for K⁺, Mn³⁺, C⁰, N⁰ and for K⁺, Mn³⁺, C⁰ and N¹⁻, respectively. After refinement of the structure to convergence of the R-factor, refinement was continued in successive steps using the scattering factors for Mn³⁺ (Ar 3d⁴), for Mn²⁺ (Ar 3d⁵), for Mn⁺

Table 10. Observed and calculated structure factors for the MDO\textsubscript{1} structure. The family reflexions have been excluded.

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(Ar $3d^54s^3$), and for Mn$^+$ (Ar $3d^54s^2$). As the number of reflexions is large and only one parameter, namely the scattering factor for manganese, is varied, even a small improvement of the $R$-factor can be significant. The best fit was, in both series, obtained with the scattering factor for Mn$^+(3d^54s^14p^0)$, (cf. Table 11).

Table 11. The $R$-factor as a function of the form factors used for the manganese and nitrogen atoms.

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Although, the population of electrons in the $d$-orbitals is probably greater than that corresponding to the electronic configuration $d^5$ and is certainly greater than $p^5$ in the $4p$ orbitals, it is interesting to note the good fit obtained when the Mn$^+$ form factor is used, since this formal charge is of the same order as that calculated for Co(CN)$_6^{3−}$.

DESCRIPTION OF THE STRUCTURE

The MDO$_4$ structure is built up from potassium ions and Mn(CN)$_6^{3−}$ complex anions. The potassium ions and the center of the complex ions constitute a slightly distorted cubic close-packed arrangement, which means that the bulky complex ions achieve 12 coordination, while the potassium ions are surrounded by four complex ions in such a way that they have six nitrogen atoms as nearest neighbours at the corners of a somewhat distorted octahedron. Each potassium ion then has six neighbouring carbon atoms at somewhat longer distances.

The manganese atoms are surrounded by six carbon atoms forming an octahedron which is probably orthorhombically distorted. The deviations of the angles between the manganese-carbon bonds from 180° or 90° are, in all cases, less than the corresponding standard deviations.

The manganese-carbon bond distances are, however, 1.981, 1.999, and 2.025 Å with standard deviations of 0.014 Å, which means that the probability that there is a difference between two of the bonds, is 95 %. The corresponding distances obtained from the superposition structure are 1.983 ± 0.010 Å (two distances) and 2.010 ± 0.013 Å.

The carbon-nitrogen bond lengths are 1.154, 1.131, and 1.140 Å with standard deviations 0.020, 0.018, and 0.024 Å and the angles between the carbon manganese and carbon-nitrogen bonds are 176.8°, 176.8°, and 177.7° with standard deviations of about 1°. However, the information concerning the nitrogen positions comes mostly from the family reflexions, which place two nitrogen atoms very close to each other (see above). This artificial overlap is only partly removed by the information from the intensity maxima, which

means that bond distances involving nitrogen atom positions should be handled with care. The corresponding distances and bond angles obtained from the superposition structure are 1.124 ± 0.034 and 1.134 ± 0.019 Å and 178.4 ± 1.9° and 178.1 ± 1.1°, respectively.

DISCUSSION

It is well-known that the cyanide ions create a very strong ligand field in a transition metal ion and that the complex ions are accordingly of the low spin type. Usually this high field is associated with a strong metal-ligand bond, but the manganese-carbon bond length is even longer than the sum of the atomic radii. The origin of the strong field is, however, probably due to metal atom-ligand π-bonding. As the complex is of the low spin type, the ground state is triply degenerate with $O_h$ symmetry. If the symmetry is lowered to tetragonal, i.e. $D_{4h}$, the ground state could still be doubly degenerate. First for symmetry $D_{2d}$ would the degeneracy be completely lifted. This is in accordance with the observed structure. The symmetry is most probably $D_{2d}$ but the symmetry $D_{4h}$ with two short and one longer manganese-carbon bond cannot be ruled out. The connection between a short metal-ligand bond and a long nitrosyl bond length has been demonstrated in a couple of complexes.4–6 Obviously there must even here be a relationship between the metal-ligand distance and the cyanide bond length, but, due to the disorder, the data are not of sufficient quality to reveal it.

As mentioned above, it may be worthwhile to compare the complex ion Mn(CN)$_6$NO$^-$ with Mn(CN)$_6^{3-}$. In the former structure there is considerable π-bonding between the manganese atom and the nitrosyl group, and it has been suggested that π-bonding to the cyanide groups ought to be negligible.17,18

The symmetry of the diamagnetic nitrosyl complex is $C_{4v}$. The manganese-carbon bond distances are 1.97 ± 0.02 Å (3 dist.), 2.00 ± 0.01 (1 dist.) Å, and 2.01 ± 0.01 Å (1 dist.) i.e. of the same magnitude as in the present compound. The same holds true for the cyanide bond lengths which are 1.14 ± 0.02 Å (1 dist.), 1.15 ± 0.02 Å (1 dist.), 1.16 Å (1 dist.), and 1.18 Å (2 dist.). The mean value is 1.16 Å as compared with 1.14 Å found in this structure. From bond distances alone it is not possible to conclude that the metal-carbon bonds are dissimilar in the two complexes.

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REFERENCES


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