

The Crystal Structure of Hexakis(ethylisocyanide)manganese(I) Tri-iodide, $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$

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The crystal structure of the title compound has been determined from single crystal X-ray diffractometer data collected at -105°C . $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$ crystallizes in space group $R\bar{3}$ with $a=8.665(3)$ Å, $\alpha=88.12(3)^\circ$ and $Z=1$. Full-matrix least-squares refinement of the 44 structural parameters gave $R=0.024$ for 1110 independent reflections. The configuration of ligands about manganese is approximately octahedral with Mn–C and C–N distances of 1.924(3) and 1.162(3) Å. The Mn–C–N and C–N–C angles are $176.5(2)^\circ$ and $172.4(3)^\circ$, respectively.

Crystal structure and ESCA studies on transition metal hexacyano complexes indicate^{1–7} that the π -contribution to the metal-carbon bond increases with decreasing effective nuclear charge on the central metal atom, provided that sufficient d electrons are available. M(II)–C(N) bonds are thus usually shorter than their M(III)–C(N) counterparts. The investigation is now being extended to cover formal oxidation states lower than +II by including hexaisocyno complexes. The crystal structure of $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ has been reported previously,⁸ while that of $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$ is presented in this paper. In order to elucidate the role of phenyl rings in the stabilisation of the metal-ligand π system, it is intended, where possible, to investigate both alkyl and aryl complexes. The crystal structure of $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ is now therefore under investigation.

EXPERIMENTAL

Ethyl isocyanide, prepared according to Casanova, Schuster and Werner,⁹ and anhydrous manga-

nese(II) iodide were dissolved in absolute ethanol.¹⁰ $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$, which is less soluble in ethanol than $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}$, crystallized within a few hours from the ethanolic solution as dark reddish-brown rhombohedra with faces of the form $\{100\}$.

Intensities from a crystal, $0.019 \times 0.010 \times 0.013$ cm, were measured for $2\theta \leq 60^\circ$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation and the $\omega-2\theta$ scanning technique. Since preliminary investigations indicated considerable thermal motion of the atoms and loss in intensity of a given reflection with time, the crystal was held at -105°C with the Syntex LT1 cryostat. Two reflections measured after each fiftieth reflection then exhibited a negligible drop in intensity during the collection of the data. The 2θ scan speed was varied between 2 and 8°min^{-1} and a 96-step profile was recorded for each reflection, the Lehmann-Larsen method¹¹ being used¹² to correct for background. Correction was made for Lorentz and polarization effects; correction was applied for absorption, the crystal being divided into a $6 \times 4 \times 4$ grid. Symmetry-related reflections were averaged giving 1270 independent reflections. Of these, 1110 for which $F_o^2 \geq 3\sigma(F_o^2)$, according to counting statistics, were regarded as being observed and were used in the subsequent calculations. The unit cell parameters at -105°C and their standard deviations were determined by a least-squares procedure based on accurately determined setting angles for 12 reflections.

CRYSTAL DATA

Hexakis(ethylisocyanide)manganese(I) tri-iodide, $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$; $M_r=766.1$; trigonal, space group $R\bar{3}$, $a=8.665(3)$ Å, $\alpha=88.12(3)^\circ$, $Z=1$, $D_c=1.96 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha)=41.6 \text{ cm}^{-1}$. The compound crystallizes as dark reddish-brown rhombohedra.

Table 1. Fractional coordinates and thermal parameters ($\times 10^3$). Estimated standard deviations are given in parentheses. The temperature coefficient is $\exp[-2\pi^2(a^*h^2U_{11} + \dots + b^*c^*klU_{23})]$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn	1 <i>a</i>	0.0000	0.0000	0.0000	10.8(2)	10.8	10.8	-2.6(3)	-2.6	-2.6
C(1)	6 <i>f</i>	0.2030(3)	0.0670(3)	-0.0618(3)	18(1)	14(1)	15(1)	-1(2)	-4(2)	-2(2)
N(1)	6 <i>f</i>	0.3245(3)	0.1042(3)	-0.1065(3)	18(1)	22(1)	21(1)	-4(2)	0(2)	-1(2)
C(2)	6 <i>f</i>	0.4710(3)	0.1414(3)	-0.1811(3)	17(1)	27(1)	26(1)	-10(2)	7(2)	-4(2)
C(3)	6 <i>f</i>	0.5561(3)	0.2606(4)	-0.0929(4)	20(1)	25(1)	36(2)	-13(2)	-2(2)	1(2)
I(1)	1 <i>b</i>	0.50000	0.50000	0.50000	21.8(1)	21.8	21.8	4.6(2)	4.6	4.6
I(2)	2 <i>c</i>	0.31065(2)	0.31065	0.31065	31.7(1)	31.7	31.7	-7.9(1)	-7.9	-7.9

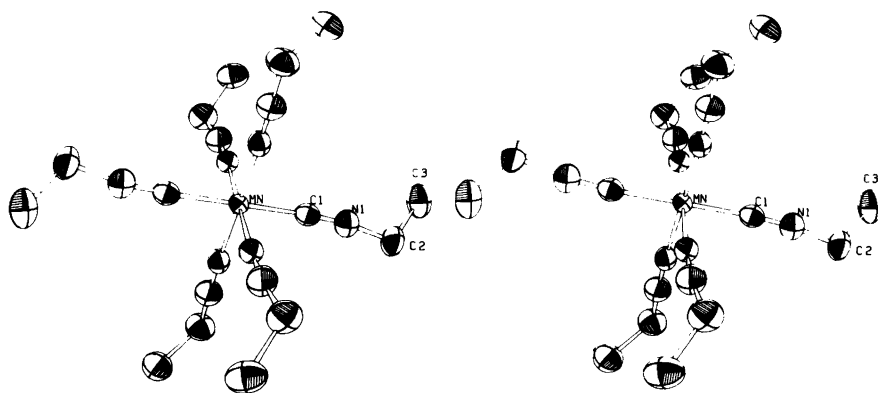


Fig. 1. Stereoscopic view of the $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]^+$ ion, orientated as in Fig. 2. The thermal ellipsoids enclose 90% probability.

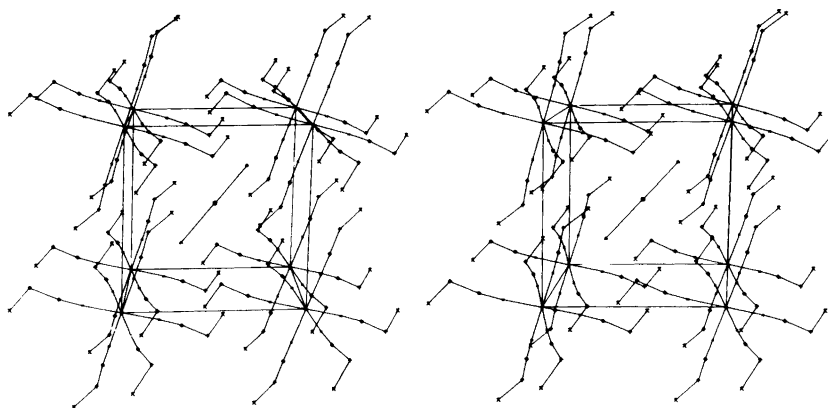


Fig. 2. Stereoscopic view of the structure.

DETERMINATION OF THE STRUCTURE

The structure was solved from Patterson and successive electron density maps.¹² Block-diagonal¹² and, ultimately, full-matrix¹² least-squares refinement of the positional and anisotropic thermal parameters yielded $R=0.024$ for 44 parameters; when the 160 unobserved reflections were included $R=0.029$. The F_o values were weighted according to¹³ $w=(a+F_o+cF_o^2)^{-1}$ with $a=24.0$ and $c=0.014$. The scattering factors were those of Doyle and Turner¹⁴ for the neutral atoms. Atomic coordinates and thermal parameters are listed in Table 1. Structure factors can be obtained from the authors on request. A final difference map showed a maximum electron density of $0.9 \text{ e } \text{Å}^{-3}$. No attempt was made to locate the hydrogen atoms.

DISCUSSION

Stereoscopic projections of the complex ion and the unit cell are shown in Figs. 1–2. Bond distances and angles within the $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]^+$ ion are given in Table 2.

The manganese atom is octahedrally coordinated by the six isocyanide ligands, the Mn–C distance being 1.924(3) Å. Both the Mn–C(1)–N(1) and

C(1)–N(1)–C(2) linkages are approximately linear and the geometry of the ethyl isocyanide ligand appears to be normal.^{15,16}

The short Mn–C bond and relatively long C–N bond indicate metal-ligand back-bonding, as predicted by a molecular orbital calculation¹⁷ on $[\text{Mn}(\text{CNCH}_3)_6]^+$ in which Mn–C was held at 1.97 Å. If the Mn–C distance in $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]^+$ is compared with those found in the hexacyanomanganate ions (Table 3), there is seen to be a steady increase with increasing formal oxidation state of manganese, from 1.924(3) Å in the present compound, through 1.95(1) Å in $\text{Na}_4[\text{Mn}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ to 2.002(8) Å in $\text{K}_3[\text{Mn}(\text{CN})_6]$. This is consistent with previous observations^{1–7} indicating an increase in the $d-\pi^*$ contribution to the metal-carbon bond with decreasing effective nuclear charge on the metal atom. An opposite trend in Mn–C distances would be expected were the bonds purely of σ -character. The Cr–C bond lengths in hexakis(phenylisocyanide)chromium(0) and the hexacyanochromate ions show a similar trend (Table 3).

In the presence of a stronger π acceptor than cyanide or isocyanide, e.g. NO^+ or CO, the transfer to the cyanide or isocyanide ligands is reduced, as is apparent from the Mn(I)–C distances of 1.97(1) Å and 1.98(1) Å in $[\text{Mn}(\text{CO})_3(\text{CNCH}_3)_2\text{Br}]$ ¹⁵ and $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$,¹⁸ respectively.

A comparison between the metal-carbon bond lengths in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ and $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$, both formally d^6 , indicates that the decrease in σ bond strength in going from Mn(I) to Cr(0) is largely compensated for by an increase in $d-\pi^*$ back-bonding. Such compensation would appear to be less effective for the d^4 ions $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{CN})_6]^{4-}$. In the pentacyanonitrosyl ions, in

Table 2. Bond lengths (Å) and angles (°) within the $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]^+$ ion. Estimated standard deviations are given in parentheses.

Mn–C(1)	1.924(3)	Mn–C(1)–N(1)	176.5(2)
C(1)–N(1)	1.162(3)	C(1)–N(1)–C(2)	172.4(3)
N(1)–C(2)	1.447(4)	N(1)–C(2)–C(3)	112.0(2)
C(2)–C(3)	1.528(4)	C(1)–Mn–C(1)	88.2(1)

Table 3. Mean M–C and C–N bond lengths in some cyano- and isocyanide complexes of manganese and chromium.

Compound	Formal oxidation state of metal	Formal ground state config.	Mean M–C (Å)	Mean C–N (Å)	Ref.
$[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$	I	d^6	1.924(3)	1.162(3)	present work
$[\text{Mn}(\text{CO})_3(\text{CNCH}_3)_2\text{Br}]$	I	d^6	1.97(1)	1.13(1)	15
$\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$	I	d^6	1.98(1)	1.16(1)	18
$\text{Na}_4[\text{Mn}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$	II	d^5	1.95(1)	1.16(1)	4
$\text{K}_3[\text{Mn}(\text{CN})_6]$	III	d^4	2.002(8)	1.142(12)	1
$[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$	0	d^6	1.938(3)	1.176(4)	8
$\text{Na}_4[\text{Cr}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$	II	d^4	2.053(4)	1.156(5)	6
$\text{K}_3[\text{Cr}(\text{CN})_6]$	III	d^3	2.077(5)	1.136(7)	3

which the $d \rightarrow \pi^*$ transfer is effectively concentrated to a single ligand, the π contribution to the metal-nitrogen bond has been shown¹⁹ to increase from Fe to V, i.e. with decreasing effective nuclear charge on the central metal atom. In the hexacyanometalates(II), such a trend is observed at the beginning of the series (Fe to V) but is reduced for chromium⁶ and negated for vanadium,⁵ presumably owing to an insufficient number of d electrons. The close similarity of the metal-carbon bond lengths in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ and $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$ thus supports the conclusion drawn previously¹⁻⁷ that, provided sufficient d electrons are available, the π contribution to the metal-carbon bond will increase with decreasing effective nuclear charge on the central metal atom.

The π contribution to the metal-carbon bond in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ would appear to be enhanced by interaction with the π -system of the phenyl rings.⁸ It is hoped that the crystal structure of $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ will provide information as to the relative magnitude of this effect.

The tri-iodide ion lies along the $\bar{3}$ axis and the I-I distance, 2.934(2) Å, agrees well with values determined previously^{16,20} for tri-iodide ions. Although there are no short I...I interactions between tri-iodide ions in $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$, the I-I distance is slightly longer than that, 2.920 Å, suggested²⁰ for a free symmetrical tri-iodide ion.

The closest contacts between the iodine atoms of the tri-iodide ion and the isocyanide ligands are 4.060(4)–4.098(3) Å.

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